Measurements of Thermodynamic Quantities for Sn–Zn, In–Sb Alloys and CdCl₂–PbCl₂, PbCl₂–ZnCl₂ Mixtures by Quantitative Thermal Analysis of the Heating Process*

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The measurements of thermodynamic quantities for tin-zinc and indium-antimony binary alloys and for the cadmium chloride-lead chloride and lead chloride-zinc chloride binary mixtures were carried out by quantitative thermal analysis of the heating process. A double adiabatic wall calorimeter was used as the experimental apparatus.

The conventional cooling process method with a water calorimeter was discussed critically, and it was clarified that the cooling process method could not be employed anymore for nonmetallic materials, owing to the pronounced lack of the temperature uniformity within the specimens. It has been considered that the heating process using an adiabatic calorimeter is of great advantage for attaining the thermal equilibrium in the specimens, and a proper experimental condition was established in the present study.

The obtained results for the thermodynamic quantities agree well with the reliable published data. The free energies of mixing of the lead chloride-zinc chloride binary melts present an anomalous behavior corresponding to the observed anomalies in the other physical properties of the melts.

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I. Introduction

The thermodynamic quantities for molten binary mixtures can be obtained in a calorimetric way by using the quantitative thermal analysis developed by Oelsen(1). As the experimental method, the cooling process method has hitherto been used in which the specimen is cooled down gradually in a water calorimeter. Although it is useful for metallic materials, it cannot be employed for nonmetallic ones of which the thermal conductivities are quite low owing to the lack of the temperature uniformity within the specimens.

Recently the present authors have noticed that the heating process method using an adiabatic calorimeter might be effective not only for the metallic materials but also for the nonmetallic materials, because the temperature difference within the specimens can be reduced considerably by using an adiabatic calorimeter. In the present investigation the heating process method was developed and conducted for the two alloy systems Sn–Zn and In–Sb, and the two salt mixtures CdCl₂–PbCl₂ and PbCl₂–ZnCl₂.

II. Theory of Quantitative Thermal Analysis

The theory of quantitative thermal analysis(1) is summarized as follows. The heat content, \( J_T \), is defined as

\[
J_T = H_T - H_\theta, \tag{1}
\]

where \( H_T \) and \( H_\theta \) are the enthalpies of the specimen at \( T \) K and a specified reference temperature of \( \theta \) K, respectively. On the basis of the well-known relationship between the entropy change and the reversible heat change (the second law of the thermodynamics), we can obtain the following equation:

\[
T \int_{1/\theta}^{1/T} J_T d\frac{1}{T} + H_\theta - TS_\theta = H_T - TS_T. \tag{2}
\]

By applying eq. (2) to the pure components \( A \) and \( B \) and to a mixture of the \( x \) mole fraction of the component \( A \), we can obtain the free energy of mixing, \( \Delta G_{x,T}^{\text{mix}} \), at \( T \) K from the following equation:

\[
\Delta G_{x,T}^{\text{mix}} = T \left[ \int_{1/\theta}^{1/T} J_T d\frac{1}{T} - x \int_{1/\theta}^{1/T} J_A d\frac{1}{T} \right] - (1-x) \int_{1/\theta}^{1/T} J_B d\frac{1}{T} + \Delta H_{x,\theta}^{\text{mix}} - T\Delta S_{x,\theta}^{\text{mix}}, \tag{3}
\]
where $\Delta H_{x,0}^{\text{mix}}$ and $\Delta S_{x,0}^{\text{mix}}$ are the heat and entropy of mixing at $\theta \, \text{K}$, respectively. The heat of mixing at $T \, \text{K}$ can be calculated using the following equation:

$$
\Delta H_{x,T}^{\text{mix}} = \Delta H_{x,0}^{\text{mix}} + J_x J_{A,T} - J_{B,T} - x J_{A,T} (1-x) J_{B,T}.
$$

(4)

Thus we can derive the thermodynamic quantities solely from the heat contents of the specimen, $J_T$, when the values of $\Delta H_{x,0}^{\text{mix}}$ and $\Delta S_{x,0}^{\text{mix}}$ at the reference temperature are zero or can be known. For the binary mixtures representing a simple eutectic and having a narrow range of primary solid solutions, both of $\Delta H_{x,0}^{\text{mix}}$ and $\Delta S_{x,0}^{\text{mix}}$ are considered to be nearly zero provided that a temperature below the eutectic is adopted for the reference. Hence, the quantitative thermal analysis is considered to be a method available for determining the thermodynamic quantities for the binary mixtures representing the simple eutectic such as the Sn-Zn, CdCl$_2$-PbCl$_2$ and PbCl$_2$-ZnCl$_2$ systems. Also, this method is useful for the mixtures such as the In-Sb system forming simple compounds in solid states, when the heat and entropy of the compounds are known.

III. Features of the Cooling Process and Heating Process Methods

Quantitative thermal analysis has been conducted by some investigators$^{(1)}$~$^{(4)}$ with the cooling process method, while the present authors have recently tried the method for the Sn-Zn system$^{(5)}$. The experimental apparatus used in the present study is illustrated in Fig. 1. In the experiments, the temperatures of the specimen and the water calorimeter are recorded successively with a thermocouple (2) and a Beckman thermometer (1), immediately after the specimen in a heating furnace is dropped into a case (7). This method is very advantageous because a set of the $J_T-T$ relationship can be obtained only by one run of experiment and, moreover, the apparatus is low-priced.

For obtaining the reliable data concerning the thermodynamic quantities, an accurate measurement of the heat content is necessary, and it can be realized only when the thermal equilibrium is attained in a specimen. So, it is required that the cooling velocity and the temperature difference within the specimen are made as small as possible. It was clarified from the experimental and theoretical considerations that some factors such as the quantity and thermal conductivity of the specimen and the heat exchange between the specimen and the water calorimeter gave serious effects on the condition of the experiments, and the details are described in a separate paper$^{(5)}$. As a matter of course, the cooling velocity is reduced as the coefficient of thermal conductivity and the heat exchange coefficient decrease and as the volume of the specimen increases. In order to obtain the size effect, a considerably large quantity of the specimen (~1 kg) is used by the conventional method. Furthermore, for obtaining the small heat exchange coefficient, a devise is made on the calorimeter in order that the specimen does not touch directly with the water and the heat is exchanged through the air contained in the case (7). Thus, the cooling velocity can be reduced to a great extent though the reduction is limited$^{(5)}$.

The calculated relationships between $(\theta_x/\theta_0)$ and $(k/hr_1)$ for the case in which the spherical body of radius $r_1$ is dropped from a heating furnace into a low-temperature atmosphere at constant temperature are plotted in Fig. 2. In the figure $\theta_0$ and $\theta_x$ denotes the temperatures.
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Fig. 2 Calculated temperature distributions in a spherical body.

of the central part and a point of $r$ within the spherical body, respectively, $k$ is the coefficient of thermal conductivity of the body, and $h$ is the heat exchange coefficient between the body and the low-temperature atmosphere. As shown in Fig. 2, the temperature difference within the body decreases with increasing value of $(k/hr_1)$, and is negligibly small at the values of $(k/hr_1)$ greater than 100. For the metallic materials of which the coefficients of thermal conductivity are large, it is not so difficult to obtain the values above 100. However, it is quite difficult for the nonmetallic materials such as oxides, salts and sulphides which represent quite small values of the coefficient that are about one-hundredth to one-tenth of the metallic materials, and it should be emphasized that the cooling process method cannot be employed anymore for the nonmetallic materials.

Recently, the present authors noticed that the difficulties in the application of the cooling process method might be overcome fundamentally by using the heating process method with an adiabatic calorimeter. The operating principle of the adiabatic calorimeter is that the specimen is heated successively with the supply of a constant electric power, under which condition there is no heat exchange between the specimen and its surroundings and the heat exchange coefficient is very small (zero in an ideal case). Moreover, the quantity of the specimen can be reduced to a level of 10 to 30 g. These are the merits for obtaining the favorable temperature distribution in the specimen, and thus it can be considered that the heating process method can be employed quite effectively for the metallic materials and may also be applicable for the nonmetallic materials though care must be taken of the structure and the heating velocity of the specimen. The details of the conditions necessary to obtain the accurate data for the nonmetallic materials are described in a separate paper(6), and it was clarified that the larger surface area and the shorter path for heat transfer were desirable, and that the heating velocity of the specimen should be reduced. In the present experiments for the two salt mixtures, the assembly and the heating velocity of the specimen were chosen properly so as to satisfy the above conditions, as described in the following section.

IV. Experimental Apparatus and Procedure

A double adiabatic wall calorimeter developed by the present authors was used as the experimental apparatus. The details of the apparatus are described in a separate paper(7). The constructions of the specimen assembly and the ways of heating the specimens show considerable differences between the metallic and nonmetallic specimens.

The assembly of the specimen container employed for the Sn–Zn and In–Sb systems is illustrated in Fig. 3. The cylindrical specimen container (5) made of molybdenum (20 mm outer diameter, 30 mm height and 0.4 mm thickness) is kept in the center of the first adiabatic wall (3) made of nickel. Previously, it was confirmed that the container did not react with the specimen. The specimens weighing 30 to 35 g were melted in advance in a heating furnace and cooled gradually in order that the phase equilibrium could be easily realized in the specimen during the experiments. Moreover, the specimens are stirred from time to time using the device (1). The constant electric power of 1.25 W is provided to the nichrome heater (8) which is wound on the outer surface of the container through the isolating medium of the mica sheet (6), and the specimens are heated successively, for the Sn–Zn system from a reference temperature of 423 K to 723 K, and for the In–Sb system from a reference temperature of 373 K to 923 K. The heat content of the specimen is evaluated by subtracting that of the specimen container
Fig. 3 Construction of the specimen assembly for the alloy systems.
(1) silica stirrer, (2) holding device, (3) adiabatic wall, (4) silver foil, (5) specimen container, (6) mica sheet, (7) thermocouple (alumel-chromel), (8) nichrome heater, (9) differential thermocouple (alumel-chromel)

determined experimentally.

The conditions of the present experiments for the CdCl₂–PbCl₂ and PbCl₂–ZnCl₂ systems were determined on the basis of the theoretical considerations (6) to obtain the accurate data for the nonmetallic materials. The specimen assembly is illustrated in Fig. 4. The cylindrical specimen container is made of thin fused quartz (0.4 mm) and is vacuum-sealed. The open-type container as illustrated in Fig. 3 cannot be employed for the present salt systems because the specimens indicate considerably high vapor pressures, and moreover, the molten specimens creep up along the interface of the container. The smaller container volume is desirable for the heat transfer in the specimen, and the size of 20 mm outer diameter and 25 mm height is adopted. Although the specimen heater is wound on the outer surface of the container for the experiments of the metallic materials, the heater (3) is located at the position about half of the specimen radius. With this designing, the surface area for heat transfer is enlarged, and moreover, the path is shortened. The container is wrapped with a silver thin foil (5) so as to achieve the temperature uniformity along the vertical direction.

The preliminary experiments were conducted for the sintered alumina (6% porosity) having the same dimension as that of the present specimen assembly, in order to examine the availability of the present apparatus and also to determine the favorable heating velocity. It was clarified that the difference from the reliable data decreased to within ±2% in the case in which the heating velocity was below 0.75 K/min. The electric power of 0.33 W is selected in the present experiments. The experiments are conducted in the range from a reference temperature of 573 K to 873 K for the CdCl₂–PbCl₂ system, and from a reference temperature of 473 K to 823 K for the PbCl₂–ZnCl₂ system.

The starting chlorides of CdCl₂ and PbCl₂ are prepared with the wet methods, and zinc chloride is the chemical reagent of the special grade (Wako Company in Japan). These are refined by bubbling dried HCl gas into the melts. The specimens weighing 13 to 15 g and vacuum-sealed in the quartz containers are furnace melted in advance and cooled gradually for obtaining the phase equilibrium in the specimens during the experiments.
V. Experimental Results

1. Experimental results for the Sn–Zn and In–Sb systems

The heat contents, $J_T$ for the Sn–Zn and In–Sb systems are illustrated three-dimensionally in Figs. 5 and 6, respectively. Much information concerning the thermo-chemical properties such as specific heat and heats of fusion and solution is involved in these figures. The deflection points in the $J_T-T$ curves are corresponding to the temperatures of phase changes, and we can obtain the phase diagrams by projecting these points on the bottom $T-X$ plane. The liquidus and eutectic temperatures for the present systems agree within $\pm 2$ K with those by Hansen\(^8\). The three-dimensional figure for the In–Sb system is rather complicated compared to that for the Sn–Zn system, because the In–Sb system forms the equiatomic compound InSb in the solid state.

The obtained heats of fusion, $7.11 \pm 0.14$ kJ/mol for the tin and $7.15 \pm 0.14$ kJ/mol for the zinc agree well with the selected values\(^9\) of $7.02 \pm 0.20$ kJ/mol and $7.32 \pm 0.10$ kJ/mol, respectively, and the obtained heat of the eutectic reaction for the Sn–Zn system is $8.17 \pm 0.16$ kJ/mol at the eutectic composition of $X_{Sn} = 0.85$. Moreover, the obtained heats of fusion, $3.31 \pm 0.07$ kJ/mol for the indium, $20.54 \pm 0.41$ kJ/mol for the antimony and $24.35 \pm 0.50$ kJ/mol for the compound of InSb agree well with the selected values\(^9\)\(^10\) of $3.26 \pm 0.04$ kJ/mol, $19.86 \pm 0.63$ kJ/mol and $24.04 \pm 0.84$ kJ/mol, respectively, and the heat of the eutectic reaction for the In–Sb system is $22.60 \pm 0.45$ kJ/mol at the eutectic composition of $X_{Sb} = 0.68$. The total error in the present experiments for the alloy systems is estimated to be within $\pm 2\%$.

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. 7, the values of $T \left[ \int_{1/T}^{1/T_0} J_T \, d \left( 1/T \right) \right]$ at 723 K and $\Delta G_{mix}^{723}$ for the Sn–Zn system are plotted. The present values of
Fig. 8 $T\int_{1/9}^{1/T} J_x d\frac{1}{T}$ plots and the free energies of mixing of the liquid In–Sb alloys (923 K).

I: $293\int_{1/373}^{1/923} J_x d\frac{1}{T}$

II: $293\int_{1/373}^{1/923} J_x d\frac{1}{T} + (1 - X)\int_{1/373}^{1/923} J_x d\frac{1}{T}$

III: $\Delta H_{mix}^{373} - 923\Delta S_{mix}^{373}$, IV: $\Delta G_{mix}^{373}$ (In–Sb)

V: $\Delta G_{mix}^{373}$ (In–In$_{0.5}$Sb$_{0.5}$), VI: $\Delta G_{mix}^{373}$ (In$_{0.5}$Sb$_{0.5}$–Sb), $\times: \Delta G_{mix}^{373}$ (In–Sb), Hultgren.

$\Delta G_{mix}^{373}$ agree quite well with those selected by Hultgren et al.

The values of $T\int_{1/9}^{1/T} J_x d\frac{1}{T}$ at 923 K and $\Delta G_{mix}^{373}$ for the In–Sb system are plotted. $T\int_{1/9}^{1/T} J_x d\frac{1}{T}$ plots for the In–Sb system represent the anomalous behavior in forming a minimum at the equiatomic composition and two maxima in both sides. These arise from the fact that the values of $\Delta H_{mix}^{373}$ and $\Delta S_{mix}^{373}$ at the reference temperature of 373 K are not zero because the equiatomic compound of InSb is existing at 373 K. The terms, $(\Delta H_{mix}^{373} - 923\Delta S_{mix}^{373})$, in the right hand side of eq. (3) calculated from the published data are shown in Fig. 8 (line III). The free energy of mixing at 923 K (curve IV) is obtained through the addition of these terms to the difference between curve I and line II, and the present results agree well with the reliable data. Also, the free energies of mixing for the In–In$_{0.5}$Sb$_{0.5}$ and In$_{0.5}$Sb$_{0.5}$–Sb quasi-binary systems which are shown respectively in curves V and VI are obtained by selecting the composition of $X_{Sb}=0.5$ for the reference state. As illustrated in Fig. 9, the values of heat of mixing calculated from eq. (4) agree fairly well with the results by Kleppa (the Sn–Zn system) and the present authors (the In–Sb system) obtained directly using the calorimeter, though some scatterings are observed in the present results.

2. Experimental results for the CdCl$_2$–PbCl$_2$ and PbCl$_2$–ZnCl$_2$ systems

The heat contents, $J_T$, for the CdCl$_2$–PbCl$_2$ system are illustrated three-dimensionally in Fig. 10. The liquidus temperatures agree within $\pm 5$ K with those by Oelsen et al.

The obtained heat of fusion for the lead chloride at the melting temperature of 774$\pm 2$ K is $25.10\pm 0.84$ kJ/mol as the averaged value of the three experiments and agrees fairly well with the selected value of $24.27\pm 0.84$ kJ/mol. On the other hand, the averaged value of heat of fusion for the cadmium chloride at 839$\pm 2$ K is $43.05\pm 1.25$ kJ/mol, presenting a considerably large departure from that of $31.80\pm 0.84$ kJ/mol by Alim et al. The obtained heat of the eutectic reaction is $23.43\pm 0.84$ kJ/mol at the eutectic composition of $X_{PbCl_2}=0.64$ at 660$\pm 2$ K. The specific heats in the binary
melts are regarded as obeying Kopp-Neumann’s additive rule within the experimental error.

In Fig. 11, the heat contents, $J_T$, for the PbCl$_2$-ZnCl$_2$ system are illustrated. The liquidus temperatures agree within ±8 K with those by Umetsu et al.\(^{(16)}\) and by Ugai et al.\(^{(17)}\) The obtained heat of fusion for the zinc chloride at the temperature of 588 ± 4 K is 9.62 ± 0.42 kJ/mol as the averaged value of the three experiments agrees fairly well with that of 10.25 kJ/mol by Cubicciotti et al.\(^{(18)}\) The heat of the eutectic reaction is 10.04 ± 0.42 kJ/mol at the eutectic composition of $X_{\text{ZnCl}_2} = 0.77$ at 568 ± 3 K. The specific heats in the binary melts are regarded as obeying the additive rule.

In Fig. 12, the values of $T[\int_{1/T}^{1/T} J_x d 1/T]$ at 873 K and $\Delta G^\text{mix}_{873}$ for the CdCl$_2$-PbCl$_2$ system are plotted. The free energies of mixing for the binary melts present a behavior of bisymmetry at $X_{\text{PbCl}_2} = 0.5$ and the slightly negative deviations from ideal mixing. The extrapolated values from the data of Nakazawa et al.\(^{(19)}\) agree well within ±0.25 kJ/mol with the present results. In Fig. 13, the values of $T[\int_{1/T}^{1/T} J_x d 1/T]$ at 823 K and $\Delta G^\text{mix}_{823}$ for the PbCl$_2$-ZnCl$_2$ system are plotted. The binary melts of this system show an anomaly in that $\Delta G^\text{mix}_{823}$ is considerably less negative in the concentration range above $X_{\text{ZnCl}_2} = 0.5$, though it presents a very small deviation from ideal mixing in the low concentration range of zinc chloride. The activities of the binary melts are obtained from the tangents of $\Delta G^\text{mix}$ curves, and are illustrated in Fig. 14. Similarly, the activities for the PbCl$_2$-ZnCl$_2$ system present the anomalous behavior showing considerably large, positive deviations from ideal mixing in the low concentration range of lead chloride. The heats of mixing of the CdCl$_2$-PbCl$_2$ and PbCl$_2$-ZnCl$_2$ systems are regarded as being nearly zero within the experimental error, in accord-
In this section, several points are discussed concerning the heating process method and the obtained results.

In the present calorimeter with double adiabatic walls, the heat transfer from the specimen assembly to its surroundings increases with increasing temperature owing to the deterioration of the adiabatic control and to the increment of the heat exchange coefficient between the specimen and its surroundings. The thermal leakage gives a negative effect on the accuracy of the experiments, especially at the elevated temperatures, though it is reduced to a considerably smaller quantity than that in the conventional calorimeter with a single adiabatic wall. The thermal leakage at 923 K that is the maximum temperature in the present experiments is at most 0.84 J/min, causing about 1.5% error in the present experiments for the metallic materials. The error of the present experiments for the salt mixtures is estimated to be within ±3% and is slightly larger than that for the metallic systems, because the temperature uniformity within the specimen is not so easily attainable compared to the metallic systems. In order to obtain the favorable results for heat of mixing on the basis of eq. (4), an accurate determination of the heat contents is necessary because the value of heat of mixing is derived from the difference between their large quantities. Thus it is very difficult to obtain the accurate data for such systems as the present salt mixtures of which the heats of mixing are quite small, and moreover, the heat contents are considerably large compared to those of the metallic systems. However, concerning the free energy of mixing, the error is estimated to be at most within ±0.29 kJ/mol even if the measurements of the heat contents are conducted with an expected error of ±3%, and the scatters of the calculated values are small as shown in Figs. 12 and 13.

The quantitative thermal analysis has been employed hitherto for the binary systems representing simple eutectic alloys, and the present study for the In–Sb system is considered the first application to a system other than simple eutectic systems. The present results are favorable and it can be considered that the quantitative thermal analysis of the
heating process is also useful for the systems forming intermetallic compounds. However, it should be noted that the published data on the heat and entropy of formation for the compounds are needed and the reliability of the derived results depends on the accuracy of these data.

Finally, some anomalies observed in the present results for the salt systems are discussed briefly. On the basis of the experimental result by Cubicciotti et al.\textsuperscript{(18)} that the solid zinc chloride presents the glassy state when quenched rapidly from the molten state, it can be supposed that the glassy state also might exist in the solid cadmium chloride which presents a similar crystal structure to that of the zinc chloride. All of the published data concerning the heat of fusion for the cadmium chloride were obtained using drop calorimeters (quench method). Hence, it can be considered that the published data may be underestimated by the quantity of the heat of the transformation from the glassy to the crystalline state if the glassy state occurs during rapid cooling. The present result for the heat of fusion showing a higher value by the quantity of about 11.25 kJ/mol than the published data is considered to be acceptable.

As shown in Fig. 11, the zinc chloride presents an anomaly in that the heat content increases abruptly in the temperature range above 523 K. It can be considered that the anomaly is caused by the change of the crystal structure of the solid zinc chloride, judging from the anomalous volume changes\textsuperscript{(21)} observed in this temperature range. Furthermore, the PbCl\textsubscript{2}–ZnCl\textsubscript{2} system presents an anomaly in that the activities of lead chloride and zinc chloride deviate quite positively from Raoult's law. This corresponds to the observed anomalies in the other physical properties of the melts such as density\textsuperscript{(16)}, electrical resistivity\textsuperscript{(22)} and viscosity\textsuperscript{(22)}.

VII. Summary

Measurements of the thermodynamic quantities for Sn–Zn and In–Sb binary alloys and for CdCl\textsubscript{2}–PbCl\textsubscript{2} and PbCl\textsubscript{2}–ZnCl\textsubscript{2} binary mixtures were carried out by a quantitative thermal analysis of the heating process, which is the newly developed method by the present investigators. The conventional cooling process method with a water calorimeter was discussed critically, and it was clarified that the cooling process method could no longer be employed for the nonmetallic materials, owing to the lack of the temperature uniformity within the specimen. On the other hand, it was considered that the heating process method with an adiabatic calorimeter had some advantages for realizing the thermal equilibrium in the specimen, and a proper experimental condition was established in the present study.

The obtained free energies of mixing for the liquid alloy systems Sn–Zn and In–Sb agree well with the reliable published data, presenting the maximum differences of 80 J/mol and 240 J/mol, respectively. The liquid CdCl\textsubscript{2}–PbCl\textsubscript{2} system represents a simple behavior showing a maximum free energy of mixing of $-6500\pm200$ J/mol at $X_{\text{PbCl}_2}=0.50$. The liquid PbCl\textsubscript{2}–ZnCl\textsubscript{2} system shows a maximum free energy of mixing of $-4600\pm140$ J/mol at $X_{\text{PbCl}_2}=0.45$, and exhibits an anomalous behavior in that a very small deviation from ideal mixing occurs in the concentration range of lead chloride above $X_{\text{PbCl}_2}=0.50$ and a fairly large, positive deviation below $X_{\text{PbCl}_2}=0.45$.

The accuracy of the thermodynamic quantities obtained from the present heating process method depends basically on the accuracy in determining the heat contents, and it is considered that the present method is not inferior to the conventional methods for activity determinations such as vapor pressure and electromotive force measurements provided that the heat contents can be measured with an accuracy of $\pm2\sim\pm3\%$ as in the present experiments. Although the conventional cooling process method is applicable only to alloy systems, it can be expected that the present heating process method will be employed extensively for determining the thermodynamic quantities of various binary mixtures including the systems of nonmetallic materials.

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