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# Behavior of the Enthalpies of Dissolution and Formation in the System Silver-Indium

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The enthalpy of dissolution in the system Ag–In has been measured at 1100 K in the whole range of composition. The behavior of the enthalpy of dissolution points out the existence of the compound $Ag_3In$ in the liquid state. The enthalpy of formation in the range of the $\gamma$ phase has also been determined at 623 and 773 K. The enthalpy of formation is negative. The partial molar enthalpy of formation of silver is negative but increase with the increase of the composition, and that of indium is negative and decreases with increasing composition. The enthalpy of formation depends insignificantly on the temperature. A pronounced temperature dependence of the enthalpy of formation seemed not to be a general property of all metallic alloys as reported earlier.

The behavior of the thermodynamic functions of alloys depends on (1) the ratio of the atomic radii of the components, (2) the electronegativity and (3) the valence electron concentration ($C_{ve}$) which is given by

$$C_{ve} = v_1 + x_2 \cdot (v_2 - v_1), \qquad (1)$$

where $v_1$ is the valence of the first component in the binary alloy. $x_2$ and $v_2$ refer to the mole fraction and the valence of the second component, respectively. Based upon these factors, it was possible to derive systematic statements for the behavior of the enthalpy of mixing in liquid alloys.[1,2] The quantity $C_{ve}$ (Eq. 1), and in some cases the above given factors (2) and (3) contribute in determining the trend of the enthalpy of formation. However, solid solutions differ from liquid ones in that they include miscibility gaps and phases of different structures. This led to a need of more detailed information on common factors which are responsible for predicting the behavior of the enthalpy of formation in solid solutions. Hence, we now extend our previous studies[3–5] to include more observations on the properties of the enthalpy of formation by studying the system silver–indium which has been selected due to its somewhat large range of miscibility in the solid state, and due to the existence of a $\gamma$ phase[6] which has not been studied before.

Another point of interest is to see if the enthalpy of formation displays a pronounced temperature dependence and to decide if this temperature dependence is a general property of all metallic alloys as claimed by Wittig and Schöffl.[7]

## Experimental

**Sample.** The metals used were: indium of extra purity grade (E. Merck Co.) and 99.88 mass percent silver (Riedel de Haen Co., Germany). The preparation, treatment and testing of the samples were all the same as described before.[1] The samples were tempered for 10 h at 773 K, and 170 h at 623 K. In the measurement process of the enthalpy of dissolution, the solid samples of silver with different masses (12.970—0.160 g) were dropped in liquid samples of indium (1.534 g) being heated at 1100 K. For measurement of the enthalpy difference of the single miscible phase, the solid alloy samples with masses lying between 1.435 and 1.545 g were dropped at 623 and 773 K in a liquid phase (having the same composition as that of the solid alloy sample) which exists at 1100 K inside the calorimeter.

**Calorimetric Technique.** The calorimeter used in the present study has been described in detail elsewhere.[5] The cylindrical calorimeter of Themax steel which represents a sample container has a hollow space coated with a layer of aluminum oxide. The role of this $Al_2O_3$ layer is to prevent reaction of the sample with the calorimeter. The cover of the calorimeter, also coated with a layer of aluminum oxide, has three wells for the tube of the drop device, stirrer (made of ceramic) and the thermocouple. The calorimeter is suspended inside a metallic shield system of V2A steel. This contains two cylindrical compensating systems of Thermax steel placed below and above the calorimeter. The lower compensating system has wells of each 3.5 mm diameter for the twelve differential Pt-to-(Pt+10 mass percent Rh) thermocouples. The whole assembly is placed in a vertical tube furnace. Another vertical tube furnace is placed above the cooling system which in turn was placed at the mouth of a silica glass tube which contains the whole assembly. The role of the second tube furnace was to temper the sample at any high temperature before its final drop in the calorimeter. The calibration of the thermocouples used was based on a standard Pt-PtRh thermocouple. A digital millivoltmeter (Hewlett-Packard 2401 C) was used for a registration of the thermal potential of the thermocouples. The temperature drifts of the calorimeter caused by the lower compensating body were negligible. The derived temperatures are judged to correspond with the IPTS-68 to within 0.01 K at 500 K and 0.1 K at 1000 K. The temperature was regulated by means of a p-regulator.[8]

The calibration of the calorimeter was conducted by measuring the enthalpy of a standard tin sample.[9] The calibration factor is determined with an accuracy of 0.3%.

## Results and Discussion

**(i) Enthalpies.** Values of $[H^\circ_1(T)-H^\circ_1(623\ \mathrm{K})]$; $[H^\circ_1(T)-H^\circ_1(773\ \mathrm{K})]$ and $[H^\circ_2(T)-H^\circ_2(623\ \mathrm{K})]$; $[H^\circ_2(T)-H^\circ_2(773\ \mathrm{K})]$ are presented in Table 1. The deviation for a single measurement is 0.35%.

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Table 1. Experimentally Determined Enthalpy Differences of Silver and Indium
M(Ag)=107.868 g mol$^{-1}$; M(In)=114.82 g mol$^{-1}$

| $T$/K | $H_1^\circ(T)-H_1^\circ(623\text{ K})$ kJ mol$^{-1}$ | $H_1^\circ(T)-H_1^\circ(773\text{ K})$ kJ mol$^{-1}$ | $H_2^\circ(T)-H_2^\circ(623\text{ K})$ kJ mol$^{-1}$ | $H_2^\circ(T)-H_2^\circ(773\text{ K})$ kJ mol$^{-1}$ |
|---|---|---|---|---|
| 700 | 2.100 | — | 2.332 | — |
| 800 | 4.978 | 0.759 | 5.362 | 0.817 |
| 900 | 8.027 | 3.680 | 8.391 | 3.847 |
| 1000 | 11.815 | 6.772 | 11.420 | 6.876 |
| 1100 | 14.673 | 10.034 | 14.449 | 9.905 |
| 1200 | 18.198 | 13.467 | 17.479 | 12.935 |

Table 2. Enthalpy Differences of the AgIn Alloys in kJ mol$^{-1}$
M(Ag)=107.868 g mol$^{-1}$; M(In)=114.82 g mol$^{-1}$

| $x_{\text{In}}$ | $H_3^\circ(1100\text{ K})-H_3^\circ(623\text{ K})$ | $H_3^\circ(1100\text{ K})-H_3^\circ(773\text{ K})$ |
|---|---|---|
| 0.300 | 24.446 | 19.611 |
| 0.350 | 24.513 | 19.690 |
| 0.400 | 24.726 | 19.732 |
| 0.450 | 24.719 | — |

Table 3. Integral and Partial Molar Enthalpies of Dissolution at 1100 K in the System Ag-In in kJ mol$^{-1}$. Estimated Standard Deviations in Parenthesis
M(Ag)=107.868 g mol$^{-1}$; M(In)=114.82 g mol$^{-1}$

| $x_2$ | $-\Delta_s H^\circ$ | $-\Delta_s H_1^\circ$ | $+\Delta_s H_2^\circ$ |
|---|---|---|---|
| 0.000 | 0 | 0 | — |
| 0.100 | 2.862(20) | 1.087 | — |
| 0.200 | 4.551(20) | 3.502 | −12.614 |
| 0.300 | 5.630(18) | 6.190 | − 4.381 |
| 0.400 | 5.138(24) | 8.386 | − 0.207 |
| 0.500 | 4.142(10) | 9.611 | + 1.347 |
| 0.600 | 3.025(15) | 9.675 | + 1.432 |
| 0.700 | 1.977(11) | 8.679 | + 0.945 |
| 0.800 | 1.132(15) | 7.003 | + 0.355 |
| 0.900 | 0.525(10) | 5.329 | + 0.052 |
| 1.000 | 0 | 4.616 | 0 |

Table 2 collects values for the enthalpy differences of the alloys: [$H_3^\circ$(1100 K)$-H_3^\circ$(623 K)] and [$H_3^\circ$(1100 K)$-H_3^\circ$(773 K)] as measured in the present study. The deviation is 0.4% for a single measurement.

**(ii) Enthalpy of Dissolution.** The enthalpy of dissolution of solid silver in liquid indium at the temperature $T_1$ can be determined according to the following equations:

$$-(1-x_2)\cdot \text{Ag}(\text{s}, T_1) - x_2\cdot \text{In}(l, T_1) + \text{Ag}_{1-x_2}\text{In}_{x_2}(l, T_1) = 0, \quad (2)$$

$$\Delta_s H^\circ = -(1-x_2)\cdot H_1^\circ(T_1) - x_2\cdot H_2^\circ(T_1) + H_3^\circ(T_1), \quad (3)$$

where $\Delta_s H^\circ$ is the enthalpy of dissolution of Ag in In, and $H_3^\circ$ is the enthalpy of the alloy at the mole fraction of indium $x_2$. Table 3 summarizes the values of the integral and partial molar enthalpies of dissolution at 1100 K in the whole range of composition. A number within parenthesis is the estimated standard deviation (esd). The accuracy obtained is 0.8%. The present value is in excellent agreement with that obtained by Hultgren et al.[6]

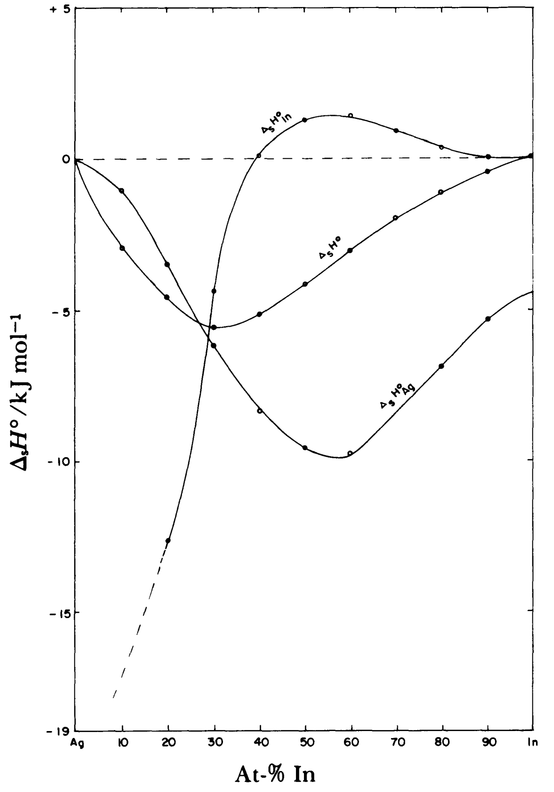

Fig. 1. The integral and partial molar enthalpies of dissolution at 1100 K in system Ag-In.

From curve-fitting calculations, the following polynomial function for $\Delta_s H^\circ$ is derived:

$$\Delta_s H^\circ = -48.448x_2+132.302x_2^2-123.876x_2^3+40.022x_2^4. \quad (4)$$

Figure 1 shows the plot of the integral and partial molar enthalpies of dissolution $\Delta_s H^\circ$, $\Delta_s H^\circ_{\text{Ag}}$, $\Delta_s H^\circ_{\text{In}}$, against the composition. The integral enthalpy of dissolution is negative and decreases with the increase of the composition to reach a minimum at $x_2$=0.3; after that the enthalpy of dissolution increases with the increase of indium mole fraction. This behavior of $\Delta_s H^\circ$ with a minimum lying at $x_2$=0.3 points out the existence of a compound with the form $Ag_3In$. This may be quantitatively explained by using the Wagner effect:[10] assuming that we have to deal with a heteropolar system with the compound $Ag_3In$, the minimum of $\Delta_s H^\circ$ should lie at the composition of the compound: $x_{In}=1-3/(1+3)=0.25$, where Ag is considered to be the donor and In the acceptor (see Ref. 11). With reference to Eq. 4, $\Delta_s H^\circ$ at $x_2$=0.3 is equal to −5.648 kJ mol$^{-1}$, while $\Delta_s H^\circ$ at $x_2$=0.25 is equal to −5.622 kJ mol$^{-1}$. The deviation between the two values (26 J mol$^{-1}$) is not much larger than the value expected from the experimental uncertaintities (14—18 J). It is also possible that the Wagner effect is overlapped by another dissolution effect so that the minimum of the enthalpy of dissolution is shifted to the composition $x_2$=0.3. This means that we have to deal with a non-ideal Wagner effect (see Ref. 11). It is also noteworthy that such behavior of the enthalpy of dissolution which suggests the existence of a compound at $x_2$=0.3 indicates that the maximum of the volume of dissolution may also lie at $x_2$=0.3.

With reference to the definition of the partial molar quantities:

$$y_1 = Y - x_2 \cdot (\partial Y / \partial x_2)_{T,p}, \tag{5}$$

$$y_2 = Y - (x_2 - 1) \cdot (\partial Y / \partial x_2)_{T,p}, \tag{6}$$

and using Eq. 4, we obtain:

$$\Delta_s H_1^\circ = -\ 132.302 x_2^2 + 247.752 x_2^3 - 120.066 x_2^4, \tag{7}$$

$$\begin{aligned}\Delta_s H_2^\circ = &-\ 48.448 + 264.604 x_2 \\ &- 503.930 x_2^2 + 407.840 x_2^3 - 120.066 x_2^4.\end{aligned} \tag{8}$$

Figure 1 shows the partial molar enthalpies of dissolution of silver and indium against the composition. The partial molar enthalpy of dissolution of silver $\Delta_s H_{Ag}^\circ$ is negative and takes a minimum at the composition 58 at-% In. This is due to the delivery of electrons from silver to indium. Such a delivery of electrons increases with the increase of indium mole fraction so that $\Delta_s H_{Ag}^\circ$ becomes more negative to reach a minimum at equilibrium being established at the maximum of the $C_{ve}$ which lies at $x_2$=0.58. The partial molar enthalpy of dissolution of indium, $\Delta_s H_{In}^\circ$ is negative in the range 0 to 40 at-% In but increases with the increase of the composition to take positive values above 40 at-% In with a maximum at $x_2$=0.58. This behavior is also understandable: The insertion of the somewhat larger indium atom in the structure causes a positive deformation work which increases with increasing composition since the lattice suffers higher tension. The maximum of $\Delta_s H_{In}^\circ$ at $x_2$=0.58 (the same composition of $\Delta_s H_{Ag}^\circ$ minimum) also represents the maximum of $C_{ve}$ at equilibrium.

**(iii) Enthalpy of Formation.** The enthalpy of formation can be calculated from the enthalpy of dissolution using the method as described before.[2] The procedure can be explained through the following equations:

$$-(1 - x_2) \cdot \mathrm{Ag}(\mathrm{s}, T_0) - x_2 \cdot \mathrm{In}(\mathrm{s}, T_0) + \mathrm{Ag}_{1-x_2}\mathrm{In}_{x_2}(\mathrm{s}, T_0) = 0. \tag{9}$$

This reaction represents the formation reaction of the alloy from Ag and In at the initial temperature $T_0$. The enthalpy of formation of the alloy AgIn is:

$$\Delta_f H^\circ = -(1 - x_2) \cdot H(T_0) - x_2 \cdot H_2^\circ(T_0) + H_3^\circ(T_0). \tag{10}$$

The indices 1, 2, and 3 indicate silver, indium, and the alloy, respectively.

Subtraction of Eq. 10 from Eq. 3, yields:

$$\begin{aligned}\Delta_s H^\circ - \Delta_f H^\circ = &-(1 - x_2) \cdot [H_1^\circ(T_1) - H_1^\circ(T_0)] \\ &- x_2 \cdot [H_2^\circ(T_1) - H_2^\circ(T_0)] + [H_3^\circ(T_1) - H_3^\circ(T_0)].\end{aligned} \tag{11}$$

The term $[H_3^\circ(T_1) - H_3^\circ(T_0)]$ which appears in Eq. 11 is the enthalpy difference of the alloy; this was measured between 623 and 1100 K and between 773 and 1100 K. The differences $[H_1^\circ(T) - H_1^\circ(T_0)]$ and $[H_2^\circ(T) - H_2^\circ(T_0)]$ are measured accurately (Table 1).

Table 4 presents values for the integral and partial molar enthalpies of formation at 623 and 773 K. A number within parenthesis is the estimated standard deviation (esd). The average error of the individual measurement was found to be 0.6% for the enthalpy of formation at 623 K and 0.36% for that at 773 K. There exists no report on the enthalpy of formation in the

Table 4. Integral and Partial Molar Enthalpies of Formation of the $\gamma$ Phase in the System Silver-Indium in kJ mol$^{-1}$. Estimated Standard Deviations in Parenthesis
M(Ag)=107.868 g mol$^{-1}$; M(In)=114.82 g mol$^{-1}$

| $x_{In}$ | $T$=773 K | | | $T$=623 K | | |
|---|---|---|---|---|---|---|
| | $-\Delta_f H^\circ$ | $-\Delta_f H_1^\circ$ | $-\Delta_f H_2^\circ$ | $-\Delta_f H^\circ$ | $-\Delta_f H_1^\circ$ | $-\Delta_f H_2^\circ$ |
| 0.300 | 15.488(129) | 15.984 | 14.260 | 15.264(0) | 15.782 | 14.068 |
| 0.350 | 15.373(0) | 15.937 | 14.368 | 15.158(23) | 15.736 | 14.169 |
| 0.400 | 15.257(141) | 15.882 | 14.470 | 14.964(142) | 15.682 | 14.264 |
| 0.450 | 15.204(125) | 15.821 | 14.566 | — | — | — |

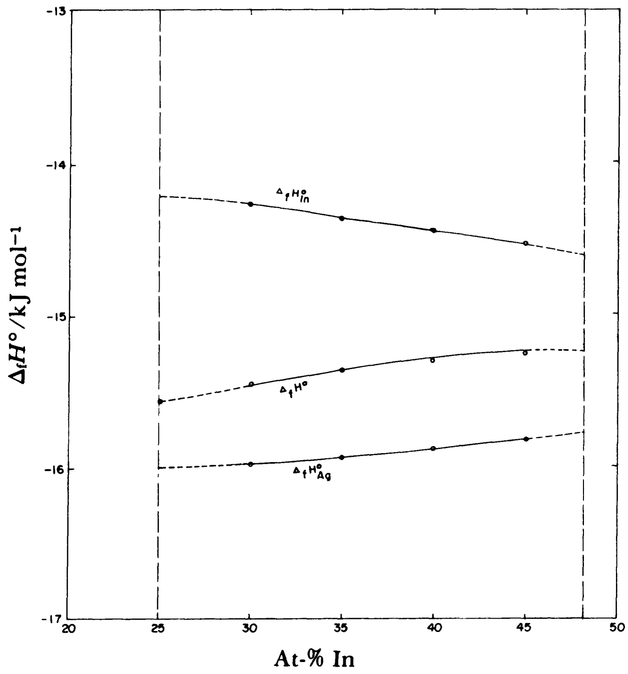

Fig. 2. The integral and partial molar enthalpies of formation at 623 K in the range of the $\gamma$ phase in the system Ag–In.

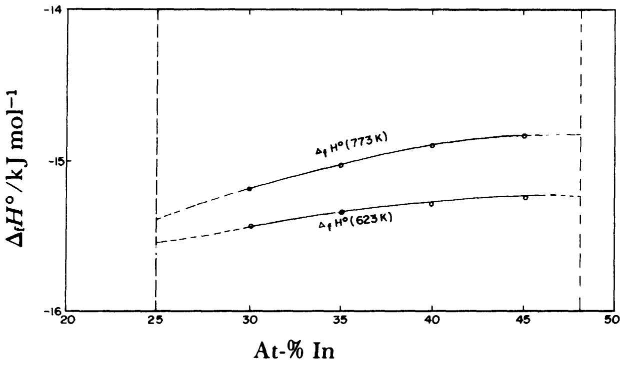

Fig. 3. The enthalpies of formation at 623 and 773 K in the range of the $\gamma$ phase in the system Ag–In.

literature, hence a comparison with the present data can not be made.

From curve-fitting calculations it was possible to derive equations for the relation of the enthalpy of formation to the mole fraction of indium:

$$\Delta_f H^\circ(623\ \mathrm{K}) = -\ 16.117 + 2.641x_2 - 1.506x_2^2 + 0.050x_2^3, \tag{12}$$

$$\Delta_f H^\circ(773\ \mathrm{K}) = -\ 15.914 + 2.607x_2 - 1.486x_2^2 + 0.049x_2^3. \tag{13}$$

These equations produce the curves of the enthalpies of formation against the temperature as shown in Fig. 3. It is clearly observable that the enthalpy of formation depends insignificantly on the temperature. This is a somewhat surprising observation since Wittig and Schöffl⁷⁾ claimed in their study on the system Al–Zn that a pronounced temperature dependence of the enthalpy of formation is a typical property of all metallic alloys. However, it appears that Wittig's conclusion was incorrect: The pronounced temperature dependence of the enthalpy of formation in the system Al–Zn was attributed to lattice defects of greater expansion of aluminum lattice in the alloy compared with the expansion in pure aluminum metal. Since such a lattice defect in the structure due to an increase in the temperature is not common to all metallic alloys, a pronounced temperature dependence of the enthalpy of formation (which is not observed on the system Ag–In) seemed not to be a general property of all metallic alloys. The relation of the enthalpy of formation to temperature depends on the type of the system and on the range of temperature and composition in which the phase can exist. This was deduced from our study on the system Sn–Sb⁵⁾ where the pronounced temperature dependence was attributed to the continuous formation of liquid from the solid solution (the $\beta'$ phase) in accordance with the phase diagram.

As illustrated in Table 4 and Figs. 2 and 3, the enthalpy of formation is negative and increases slightly with the increase of the composition due to the insertion of indium atom in the structure. The insertion of indium atom which is not much larger than silver atom in the structure leads to a small positive deformation work so that the enthalpy of formation depends slightly on the composition. The charging of the Brillouin zones is always the reason for the increase of the enthalpy of formation with the increase of the composition (see Ref. 3).

With reference to the definition of the partial molar quantities (Eqs. 5 and 6), we obtain through Eqs. 12 and 13 the following equations for $\Delta_f H_1^\circ$ and $\Delta_f H_2^\circ$:

$T = 623$ K

$$\Delta_f H_1^\circ = -\ 16.117 + 1.506x_2^2 - 0.100x_2^3, \tag{14}$$

$$\Delta_f H_2^\circ = -\ 13.476 + 3.012x_2 + 1.356x_2^2 - 0.100x_2^3 \tag{15}$$

and

$T = 773$ K

$$\Delta_f H_1^\circ = -\ 15.914 + 1.486x_2^2 - 0.098x_2^3, \tag{16}$$

$$\Delta_f H_2^\circ = -\ 13.307 - 2.972x_2 + 1.486x_2^2 - 0.098x_2^3. \tag{17}$$

Figure 2 shows that the partial molar enthalpy of silver is negative and becomes more negative at higher composition. A hypothetical illustration of this behavior is probably that a poor fraction of silver s-electrons forms a weak bond with indium ions. At higher composition, the equilibrium shifts for the benefit of the delivery of further electrons on indium.

The partial molar enthalpy of formation of indium is also negative, but increases at higher composition. The negative trend in the whole range of the $\gamma$ phase indicates the stability of the structure. However, this stability decreases at higher composition due to the insertion of the somewhat larger indium atom in the structure: the structure exhibits a higher tension resulting from a small deformation work which is associated with the insertion of the indium atom in the structure.

## References

1) F. E. Wittig, *Z. Electrochem.*, **63**, 327 (1959).

2) W. A. Badawi, *Bull. Chem. Soc. Jpn.*, **61**, 1351 (1988).

3) W. A. Badawi, *Bull. Chem. Soc. Jpn.*, **60**, 2599 (1987).

4) W. A. Badawi, *Bull. Chem. Soc. Jpn.*, **60**, 3771 (1987).

5) W. A. Badawi, *Bull. Chem. Soc. Jpn.*, **62**, 285 (1989).

6) Hultren et al., "Selected Values of the Thermodynamic Properties of Binary Alloys," Am. Soc. Metals, Ohio (1973).

7) F. E. Wittig and L. Schöffl, *Z. Metalk.*, **51**, 700 (1960).

8) F. E. Wittig, *Chemie-Ingenieur-Technik*, **32**, 1037 (1960).

9) F. E. Wittig and E. Gehring, *Z. f. Naturforschung*, **18a**, 351 (1963).

10) C. Wagner, "Thermodynamics of Alloys, Reading, Mass.," Addison-Wesley, (1952).

11) W. A. Badawi, *Bull. Chem. Soc. Jpn.*, **61**, 2261 (1988).