

## Liquid-state electrochemical study of the system indium–tin

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### Abstract

EMF measurements with liquid electrolyte were carried out in the 636–820 K range for In–Sn alloys with  $0.200 \leq X_{\text{Sn}} \leq 0.950$ . From literature data and experimental results  $E=f(X_{\text{Sn}}, T)$ , a sub-regular description is proposed for the Gibbs function of the liquid phase. © 1998 Elsevier Science B.V.

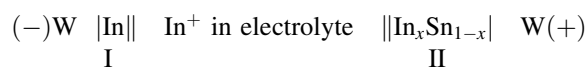
**Keywords:** EMF; Indium–tin alloys; Thermodynamics

### 1. Introduction

A preliminary potentiometric study of the Ag–In–Sn liquid system [1] revealed some discrepancy between indium chemical potential measurements available in the binary In–Sn [2] and ternary values. The electromotive force (EMF) difference observed between both works for an alloy with composition  $\text{In}_{0.5}\text{Sn}_{0.5}$  is  $\Delta E \approx 10$  mV for an absolute value of ca. 50 mV. Furthermore, a recent thermodynamic assessment of Ref. [3] shows a disagreement of ca. 20% between optimized and experimental activities of Ref. [2] in the  $0.3 \leq x_{\text{Sn}} \leq 0.7$  composition range.

The purpose of this work is to measure and describe the Gibbs energy in the liquid state, as a function of concentration and temperature in order to obtain a better agreement with the other available thermodynamic quantities.

The indium chemical potential in liquid In–Sn alloys was investigated using the galvanic cells method with liquid electrolyte:



The electrodes induce the following equilibria:

- electrode I  $(\text{In}) \rightleftharpoons \text{In}^+ + e^-$
- electrode II  $\text{In}^+ + e^- \rightleftharpoons ((\text{In}))$

where (In) represents pure liquid indium and ((In)) indium in liquid alloy.

The electromotive force between electrodes is tied in with the activity of indium by the relation  $\mu_{\text{In}} \equiv -FE = RT \ln a_{\text{In}}$ , where  $T$  is the absolute temperature in Kelvin and  $F$  the Faraday constant ( $96485.309 \text{ C mol}^{-1}$ ) [4].

From the temperature dependence  $E=f(T)$ , the partial molar enthalpy and partial molar entropy of mixing of the element indium can be deduced.

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## 2. Experimental details

### 2.1. Alloys

Samples of nine alloys, weighed from pure indium (5N) and pure tin (5N), were prepared in a  $0.20 \leq x_{\text{Sn}} \leq 0.95$  composition range. The pure elements were introduced in pyrex tubes which were sealed under vacuum ( $10^{-6}$  hPa). Cylindrical ingots (5 mm diameter, 10 mm length) were obtained on melting the alloys at 770 K. The total weights of the samples were  $\approx 1.6$  g. Full ingots were used for the measurements. Differences between the weights of pure elements and ingots were  $< 0.05\%$ .

### 2.2. Electrolyte

A eutectic mixture of lithium and potassium chlorides (46.0 weight% LiCl,  $T_{\text{eut}}=625$  K) is dried under vacuum for 24 h at room temperature and 48 h at 423 K. Salt mixtures were then melted at 900 K in a quartz vessel and maintained under a dry HCl gas flow for 1 h before being sealed in pyrex bulbs.  $\text{In}^+$  cations are formed directly by contact inside the cell between pure indium and molten salt mixtures.

### 2.3. Galvanic cell

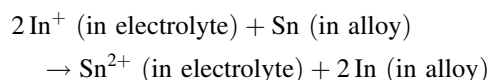
An isothermal cell with an approximate volume of 100 ml, whose schematic drawing is given in Ref. [5], was used. Special points of such a cell are:

- tungsten wires used as leads between electrodes are hermetically sealed with pyrex and allowed to maintain a good vacuum during the experiment; and
- total time of transportation of electrolyte into the vessel never exceeds 10 s. The melting of the purified electrolyte is made after 24 h vacuum ( $10^{-6}$  hPa).

### 2.4. Measurements

The cell assembly was heated in a resistance furnace with capacity of handling temperatures up to 1300 K and maintaining temperature uniformity to within  $\pm 0.2^\circ\text{C}$ . Cell temperatures were measured with a calibrated thermocouple type S (Pt–10% Rh, Pt) and

EMF values were obtained with a digital multimeter (Keithley model 193) of high input impedance with a precision of  $\pm 0.2 \mu\text{V}$ . Measurements were carried out through four runs in heating and cooling between minimum and maximum temperature and led to a total time of experimentation of 2 months for each cell. The reproducibility obtained for alloys with  $x_{\text{Sn}} \leq 0.700$  never exceeds  $\pm 0.18$  mV. This uncertainty becomes  $\pm 0.40$  mV for alloys with  $0.700 < x_{\text{Sn}} < 0.900$  and  $\pm 2.4$  mV when  $x_{\text{Sn}} = 0.900$ . Thus, the uncertainty increases with increasing tin content. An explanation may be given by considering a slight presence of a side reaction:



For that reason, we only include the results of the two first runs for the alloy  $x_{\text{Sn}} = 0.950$  and restricted the maximum experimental temperature to 780 K for alloys with  $0.700 \leq x_{\text{Sn}} < 0.900$ .

## 3. Results

A summary of equations  $E=f(T)$  obtained from experimental measurements by least-squares fitting is given in Table 1; the temperature range, number of data and statistical quantities are presented for each alloy. The potentiometric measurements, represented in Fig. 1 together with the available literature results show a complete disagreement with the reported values of the authors of [2], who used a mixture of LiBr and KBr as electrolyte. The difficulty in obtaining a good purification of bromides mixture may explain the observed difference. The comparison with the values of Ref. [6] seems to show an identical curve for the composition  $N_{\text{Sn}} = 0.90$ .

From the equations  $E=a+bT$ , the partial Gibbs energy ( $\overline{\Delta G}_{\text{In}}$ ), partial enthalpy ( $\overline{\Delta H}_{\text{In}}$ ) and partial entropy ( $\overline{\Delta S}_{\text{In}}$ ) of indium are given in Table 2 for the average temperature, 700 K, together with the corresponding integral quantities.

## 4. Discussion

In the thermodynamic assessment of [3], some disagreement can be seen between the experimental

Table 1  
Coefficients of the equations  $E=a+bT$  calculated from experimental investigation

$X_{\text{Sn}}$	$a/\text{mV}$	$b \times 10^2/\text{mV K}^{-1}$	$n$	$\bar{T}/\text{K}$	$\bar{E}/\text{mV}$	$s_0^2 \times 10^2/(\text{mV})^2$	$\sum(T_i - \bar{T})^2/\text{K}^2$	$T_{\text{min}}/\text{K}$	$T_{\text{max}}/\text{K}$
0.1996	$1.19 \pm 0.16$	$1.788 \pm 0.021$	114	731.2	14.26	0.42	360351	638	820
0.3040	$1.72 \pm 0.15$	$3.014 \pm 0.020$	115	731.9	23.78	0.37	368127	638	820
0.3998	$1.92 \pm 0.13$	$4.443 \pm 0.015$	113	728.3	34.28	0.21	346607	638	820
0.5003	$3.85 \pm 0.32$	$5.943 \pm 0.044$	106	726.4	47.021	1.47	301277	638	820
0.6002	$5.38 \pm 0.23$	$7.875 \pm 0.033$	145	702.7	60.72	0.69	255369	636	780
0.6999	$5.39 \pm 0.26$	$10.476 \pm 0.037$	140	700.4	78.77	0.82	233880	636	780
0.7994	$6.59 \pm 0.57$	$13.970 \pm 0.081$	145	703.2	104.82	4.38	260969	636	780
0.8993	$7.66 \pm 0.56$	$19.756 \pm 0.080$	137	702.5	146.45	4.09	250988	636	780
0.9499	$4.55 \pm 4.77$	$25.628 \pm 0.680$	74	701.8	184.40	145	126390	641	771

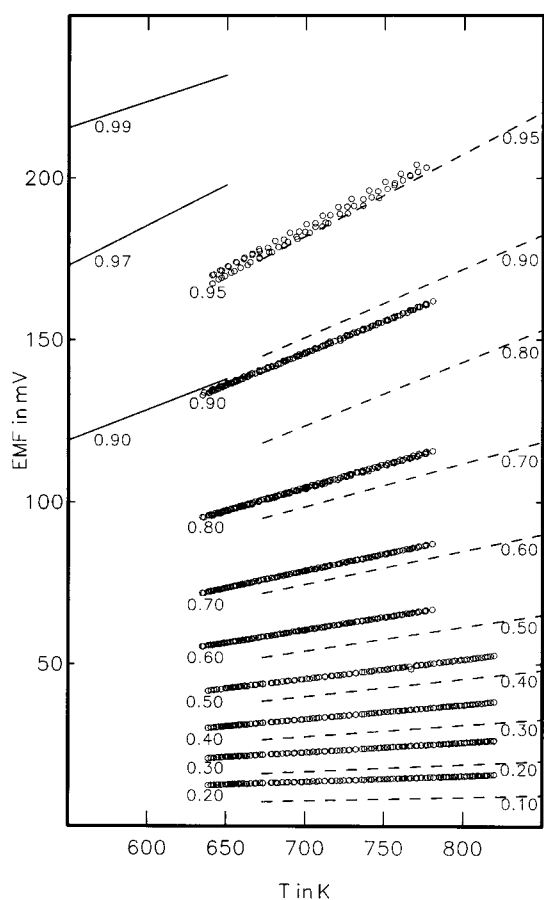


Fig. 1. Electromotive force (mV) vs. temperature (K) for different In-Sn liquid alloys: (O) this work; (—) [6]; and (---) [2].

[2] and calculated activities. As these authors used only the chemical potential data of indium [2], we propose a re-optimized coefficient set for the liquid

phase in order to obtain a more accurate Gibbs function.

According to the Scientific Group Thermodata Europe (SGTE), the temperature dependence of the molar Gibbs energy of the pure stable elements, referred to the standard state, is given by the following expression:

$$G_i^0 - H_i^{\text{SER}} = A + BT + CT \ln T + DT^2 + ET^{-1} + FT^3 + IT^7 + JT^{-9} \quad (1)$$

$H_i^{\text{SER}}$  is the enthalpy of the pure element  $i$  at 298.15 K and  $10^5$  Pa in its stable state.

The coefficients of this equation, available from [7] for indium and tin are given in Table 3.

The Gibbs energy of the liquid is presented as the sum of three parts:

$$G^{\text{liq}} - H^{\text{SER}} = G^{\text{ref}} + G^{\text{id,liq}} + G^{\text{ex,liq}} \quad (2)$$

where:

$$G^{\text{ref}} = [G_{\text{In}}^{0,\text{liq}}(T) - H_{\text{In}}^{\text{SER}}(298.15)] \cdot x_{\text{In}} + [G_{\text{Sn}}^{0,\text{liq}}(T) - H_{\text{Sn}}^{\text{SER}}(298.15)]x_{\text{Sn}} \quad (3)$$

$$G^{\text{id,liq}} = RT[x_{\text{In}} \cdot \ln(x_{\text{In}}) + x_{\text{Sn}} \ln(x_{\text{Sn}})] \quad (4)$$

$$G^{\text{ex,liq}} = x_{\text{In}}x_{\text{Sn}}[L_0 + L_1(x_{\text{In}} - x_{\text{Sn}}) + L_2(x_{\text{In}} - x_{\text{Sn}})^2 + \dots] \quad (5)$$

with the following description of the variables:

- $G^{\text{liq}}$ : Gibbs energy of one mole of atoms of liquid phase;
- $H_{\text{In,Sn}}^{\text{SER}}(298.15 \text{ K})$ : Enthalpy of the pure element In or Sn in its stable state at the reference temperature;

Table 2

Partial and integral data for In–Sn liquid alloys derived from EMF measurements at 700 K

$X_{\text{Sn}}$	$\overline{\Delta G}_{\text{In}}^{\text{L}}/$ (J mol <sup>-1</sup> ) (expt)	$\overline{\Delta H}_{\text{In}}^{\text{L}}/$ (J mol <sup>-1</sup> )	$\overline{\Delta S}_{\text{In}}^{\text{L}}/$ (J mol <sup>-1</sup> )	$\overline{\Delta G}_{\text{In}}^{\text{C}}/$ (J mol <sup>-1</sup> ) (calc)	$\overline{\Delta G}_{\text{Sn}}^{\text{L}}/$ (J mol <sup>-1</sup> )	$\Delta_{\text{mix}}G/$ (J mol <sup>-1</sup> )	$\Delta_{\text{mix}}H/$ (J mol <sup>-1</sup> )	$\Delta_{\text{mix}}S/$ (J mol <sup>-1</sup> K <sup>-1</sup> )
0.1996	-1322	-114.9	1.725	-1360	-10116	-3108	-212	4.14
0.3040	-2201	-165.6	2.908	-2250	-7440	-3828	-270	5.08
0.3998	-3186	-185.4	4.287	-3200	-5682	-4193	-296	5.57
0.5003	-4385	-371.2	5.734	-4373	-4247	-4310	-296	5.74
0.6002	-5838	-519.3	7.598	-5784	-3094	-4170	-273	5.57
0.6999	-7595	-520.1	10.108	-7569	-2138	-3768	-227	5.06
0.7994	-10070	-635.4	13.479	-10025	-1326	-3071	-167	4.15
0.8993	-14082	-739.2	19.062	-14138	-623	-1984	-90	2.70
0.9499	-17748	-439.1	24.727	-18248	-300	-1199	-46	1.65

Table 3

Phase stabilities of In and Sn [7]

Phase	Temperature range/K	$G_i^0 - H_i^{\text{SER}} = A_i + B_i T + C_i T \ln T + \sum_j D_{ij} T^j$
In (liq)	298.15 < T < 429.75	$G_{\text{In}}^{0,\text{LIQ}} - H_{\text{In}}^{\text{SER}} = -3696.798 + 84.701255T - 21.8386T \ln T - 0.00572566T^2 - (2.120321 \times 10^{-6})T^3 - 22906T^{-1} - (5.59 \times 10^{-20})T^7$
	429.75 < T < 3800	$G_{\text{In}}^{0,\text{LIQ}} - H_{\text{In}}^{\text{SER}} = -3749.81 + 116.835784T - 27.4562T \ln T + 0.00054607T^2 - (0.08367 \times 10^{-6})T^3 - 211708T^{-1}$
Sn (liq)	100 < T < 250	$G_{\text{Sn}}^{0,\text{LIQ}} - H_{\text{Sn}}^{\text{SER}} = -855.425 + 108.677684T - 25.858T \ln T + 0.00051185T^2 - (3.192767 \times 10^{-6})T^3 + 18440T^{-1} + (1.47031 \times 10^{-18})T^7$
	250 < T < 505.08	$G_{\text{Sn}}^{0,\text{LIQ}} - H_{\text{Sn}}^{\text{SER}} = 1247.957 + 51.355548T - 15.961T \ln T - 0.0188702T^2 + (3.121167 \times 10^{-6})T^3 - 61960T^{-1} + (1.47031 \times 10^{-18})T^7$
	505.08 < T < 800	$G_{\text{Sn}}^{0,\text{LIQ}} - H_{\text{Sn}}^{\text{SER}} = 9496.31 - 9.809114T - 8.2590486T \ln T - 0.016814429T^2 + (2.623131 \times 10^{-6})T^3 - 1081244T^{-1}$
	800 < T < 3000	$G_{\text{Sn}}^{0,\text{LIQ}} - H_{\text{Sn}}^{\text{SER}} = -1285.372 + 125.182498T - 28.4512T \ln T$

- $x_{\text{In}}, x_{\text{Sn}}$ : mole fractions of In and Sn in the phase;
- $G_{\text{In},\text{Sn}}^{0,\text{liq}}(T)$ : Gibbs energy of pure In or Sn at temperature  $T$  in the liquid state;
- $L_{\nu}$ : Parameters depending on temperature which can be expressed as:

$$L_{\nu} = a_{\nu} + b_{\nu}T + c_{\nu}T \ln T + \dots \quad (6)$$

where  $a_{\nu}, b_{\nu}, c_{\nu}$  are adjustable coefficients.

The coefficients were fitted to the experimental data using a least-squares method (BINGSS) described in [8,9]. The data sources used in the final data set consist of  $\Delta_{\text{mix}}H$  data of [10–14] and  $\mu_{\text{In}}$  values obtained in Ref. [6] and in this work. As explained above, the chemical potential data of Ref. [2] were not included in the optimization.

As shown in Fig. 1, the slope of the curve  $E=f(T)$  for an alloy of composition  $X_{\text{Sn}}=0.99$  [6] is weaker

than for the other alloys. Some experimental problems may be suspected such as side reactions with electrolyte. Indeed, Lazarev and Pogoreliy [6] used a NaCl–ZnCl<sub>2</sub> mixture in which case the following reaction may occur  $2\text{In} + \text{Zn}^{2+} \rightarrow 2\text{In}^+ + \text{Zn}$  and induce perturbation on both the reference and the working electrodes. For that reason results concerning this composition were removed from the optimization.

The weight of the chemical potential data has been multiplied by a factor of 1.5 in order to give the same importance to the two kinds of thermodynamic quantities ( $\Delta_{\text{mix}}H$  and  $\mu_{\text{In}}$ ). A total of 89 data were used in the final optimization. Optimized parameters are given in Table 4.

The calculated heats of mixing at 700 K (Fig. 2) are slightly more negative than the calculated curve [3] and in better agreement with the reported values [11,12,14] than with other experimental results

Table 4

Optimised coefficients according to the analytical description of the phases. Functions are expressed in  $\text{J mol}^{-1}$

Phase	$\nu$	$a_\nu$	$b_\nu$
Liquid	0	-783.19	-0.59353
	1	-149.39	

[10,13]. Nevertheless, the scatter between the experimental data being  $<20 \text{ J mol}^{-1}$ , we can conclude that both calculations are very similar for the heats of mixing of melts. As shown in Table 5, the calculated partial heat of solution of indium in tin at infinite dilution is in excellent agreement with all the experimental results within the experimental error range except those reported by Pool and Lundin [15].

In Fig. 3 are plotted:

– the experimental In chemical potential  $\mu_{\text{In}}$  presented in Refs. [2,6] and in this work. For each alloy, three values are given according to the minimum, maximum and average temperatures of the studied range of temperature. In order to compare the different results, the  $\mu_{\text{In}}$  data were all plotted at the same temperature 700 K by shifting each value by the calculated difference term

Table 5

Partial molar heat of solution of indium in tin at infinite dilution

Reference	$T/\text{K}$	$\overline{\Delta H_{\text{In}}^\infty}/(\text{J mol}^{-1})$
[10]	723	-594
[16]	513	-586±126
[16]	573	-628±126
[16]	623	-628±209
[17]	700	-945±160
[15]	750	-1016±125
[14]	521	-711±14
[18]	587	-519±90
This work experimental	700	-531±190
This work optimized	any $T$	-647

$\mu_{\text{In}}^{700} - \mu_{\text{In}}^{T_{\text{exp}}}$ . A large scatter appears for alloys with composition  $X_{\text{Sn}}=0.99$  [6] which confirms the existence of problems in the temperature dependence of the measured quantity, as explained above.

– the calculated  $\mu_{\text{In}}$  and  $\mu_{\text{Sn}}$  at 700 K and the calculated  $\mu_{\text{In}}$  curve at the same temperature according to the description in Ref. [3]. The agreement between experimental information obtained in this work and both calculations is fair.

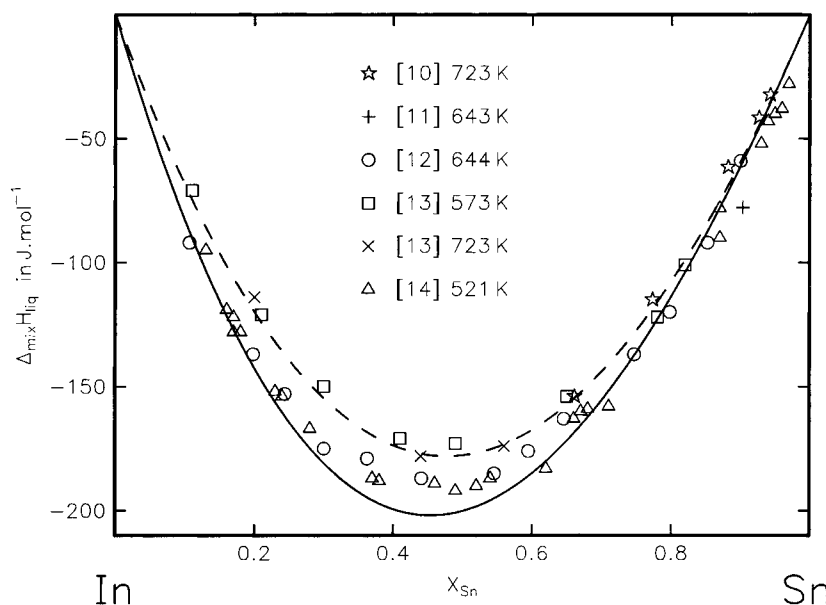


Fig. 2. Calculated and experimental heats of mixing of In-Sn liquid alloys at 700 K: (—) this work; and (- - -) [3].

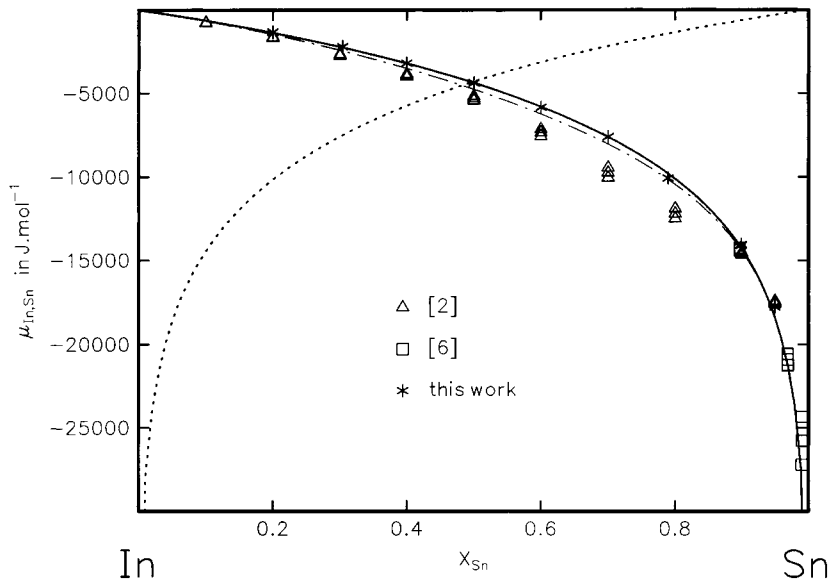


Fig. 3. Calculated partial Gibbs energy of indium and tin liquid alloys at 700 K. Experimental values are shifted by the calculated term  $\mu_{\text{In}}^{700} - \mu_{\text{In}}^{T_{\text{exp}}}$ : (—) and (· · ·) this work; and (- · -) [3].

## 5. Summary

New In chemical potential measurements have been obtained from galvanic cell method using liquid electrolyte. From temperature dependence of the electromotive force, heat and entropy of mixing have been determined in the 636–820 K range. From these results and the whole available liquid experimental data, a refinement of the Gibbs function of liquid is proposed.

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