Thermodynamic Measurements in Liquid Tin-Tellurium Alloys

M. Le BOUTEILLER, A. M. MARTRE, R. FARHI, AND C. PETOT

Electromotive force measurements on galvanic cells have been performed in order to obtain the tin activity in liquid tin-tellurium alloys in the composition range $x_{Te} = 0.756$ to 0.978 and between 673 and 913 K. The partial enthalpy and entropy of solution of tin in tellurium were deduced from these results. The position of the liquidus in the vicinity of the eutectic was specified by emf measurements and by differential thermal analysis. The existence of strong interactions in the liquid state and the existence of the compound SnTe in the solid state strongly suggest that short range order subsists in liquid alloys. A simple interaction model has allowed us to interpret correctly the experimental results in the investigated concentration range.

1. INTRODUCTION

THE present work was carried out as a continuation of the investigation of systems showing strong interactions in the liquid state.

Thermodynamic data for molten Sn, Te alloys are limited. Although several authors have reported measurements of the heats of solution,[1-5] only Predel et al[6] have published values concerning the activities at 1281 K.

2. EXPERIMENTAL

Tin activity in liquid Sn, Te alloys was determined by electromotive force measurements involving the following cell:

$$Sn(l) \mid Sn^{+2} \mid Sn, Te(l).$$
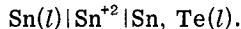
The partial thermodynamic properties of tin were found from the relations:

$$\Delta \overline{G}_{Sn} = RT \ln a_{Sn} = -2EF; \quad \Delta \overline{S}_{Sn} = 2F\left(\frac{\partial E}{\partial T}\right);$$

$$\Delta \overline{H}_{Sn} = -2F\left(\frac{\partial E/T}{\partial 1/T}\right).$$

The apparatus and experimental techniques were identical with those used in previous studies and full details may be found in an earlier publication,[7] so that a brief account will suffice here. The Pyrex galvanic cell used in this work is shown in Fig. 1. It consisted of three tin reference electrodes and five tin-tellurium alloy electrodes of different composition. The purity of tin and tellurium used in the experiment was better than 99.980 and 99.999 mass pct respectively. The liquid electrolyte was made of the eutectic mixture of potassium and lithium chlorides containing about two mass pct of stannous chloride. The electrical junctions were tungsten wires. After transfer of the liquid electrolyte into the cell which contained the electrodes, the assembly was evacuated, then filled with argon and sealed. Temperatures were controlled to ±1 K and measured

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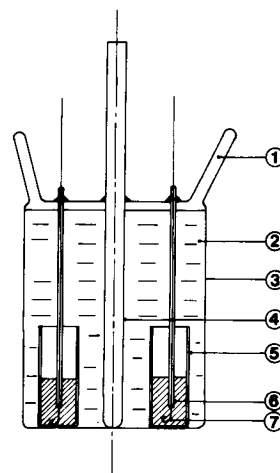Manuscript submitted August 9, 1976.

Fig. 1—Cell assembly: 1) introduction hole for alloys and electrolyte; 2) electrolyte; 3) Pyrex cell; 4) Pyrex sheath for thermocouple; 5) Pyrex crucible; 6) alloy or reference cell, Sn(l); and 7) tungsten leads.

with a chromel-alumel thermocouple placed in the middle of the cell (Fig. 1). The alloys were homogenized by maintaining the temperature of the cell approximately 40 K above the melting point of the more refractory alloy for about 12 h.

The reversibility of the cells was checked during the recording of the emf. Indeed, in seeking the null point at which the recorder potential balanced the potential of the cell, a small current from the recorder passed in either direction through the cell without disrupting the null point. The measurements were carried out at constant temperature at approximately 10 to 20 K intervals. For each isotherm the stability is verified for 30 to 45 min. Moreover the temperature range is investigated many times to verify the reproducibility of the obtained results.

3. RESULTS

3.1. Thermodynamic Properties

Fig. 2 shows the variation $E = f(T)$ for 16 alloy compositions in the range 673 to 913 K. The emf values are measured with a Tacussel electronic millivoltmeter to ±0.2 mV; this value corresponds to the observed discrepancy between the reference electrodes for the unfavorable runs corresponding to the

most tellurium-rich compositions. We have summarized our results in Table I, which shows the analytical functions of the curves $E = f(T)$. Equations are derived from the experimental data by means of a least squares adjustment. By investigating the entire temperature range by very small intervals we have established for some alloy compositions near the eutectic ($0.819 < x_{Te} < 0.947$) that the temperature coefficient of the electromotive force changes
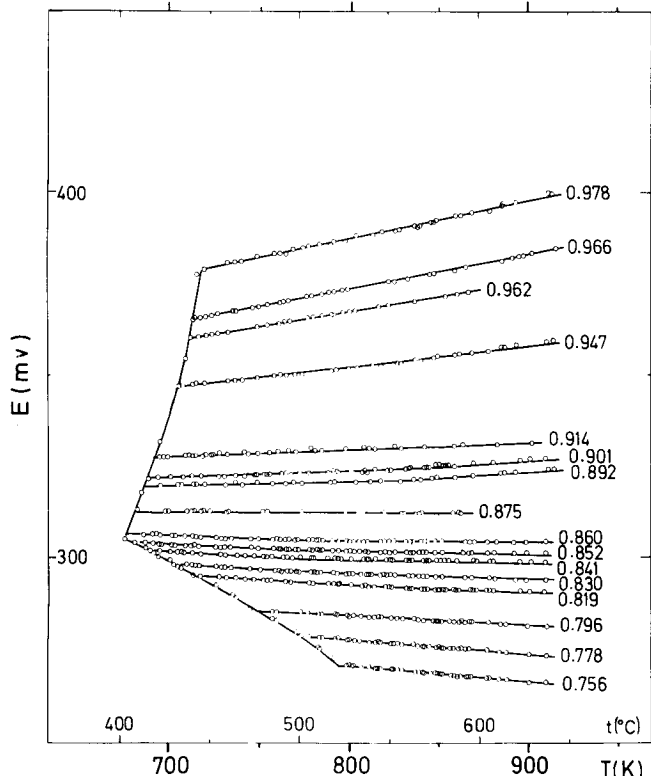
above approximately 773 K. We have represented the variations $E = f(T)$ for these alloys by two linear functions which correctly fit the experimental results. The maximum and average values of $\Delta E = \sigma t^*$ are respectively 1.67 and 0.55 mV (σ standard deviation, t^* Student's coefficient). Obviously such a representation which presents a slope discontinuity for a well determined temperature has no physical meaning. We have deduced from these results $\Delta \bar{H}_{Sn}$ and $\Delta \bar{S}_{Sn}$ values which are given in Table I. The $\Delta \bar{H}_{Sn}$ and $\Delta \bar{S}_{Sn}$ values are plotted as a function of the composition in Fig. 3. These quantities are shown by differ-
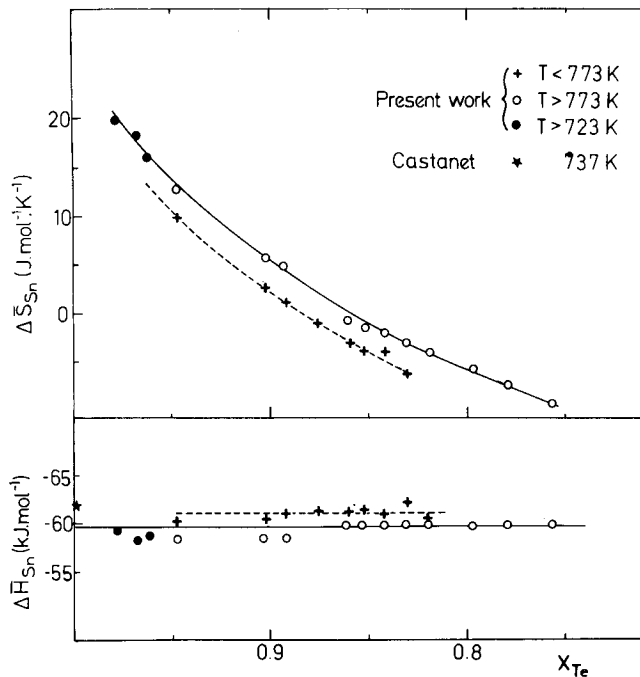

Fig. 2—Temperature dependence of the emf E.

Fig. 3—Partial enthalpy and entropy of solution of tin vs composition.

Table I

x_{Te}	Temperature Range, T(K)	Cell Potential, $E = A + BT$ (mV)	$\Delta \bar{H}_{Sn}$ (J mol^{-1})	$\Delta \bar{S}_{Sn}$ (J mol^{-1} K^{-1})
0.756		$309.70 - 0.04905\,T$	-59777 ± 397	-9.468 ± 0.473
0.778		$309.02 - 0.03962\,T$	-59647 ± 372	-7.648 ± 0.443
0.796		$307.42 - 0.02917\,T$	-59337 ± 305	-5.632 ± 0.364
0.819	$T < 773$	$311.89 - 0.02369\,T$	-60199 ± 2134	-4.572 ± 2.833
0.819	$T > 773$	$309.70 - 0.02130\,T$	-59777 ± 289	-4.109 ± 0.343
0.830		$320.31 - 0.03125\,T$	-61827 ± 414	-6.033 ± 0.556
0.830	id.	$309.48 - 0.01734\,T$	-59735 ± 255	-3.347 ± 0.310
0.841		$314.76 - 0.01857\,T$	-60756 ± 703	-3.586 ± 0.950
0.841	id.	$309.43 - 0.01192\,T$	-59727 ± 247	-2.301 ± 0.293
0.852		$318.08 - 0.02061\,T$	-61396 ± 201	-3.979 ± 0.275
0.852	id.	$309.20 - 0.00920\,T$	-59681 ± 180	-1.776 ± 0.217
0.860		$316.67 - 0.01537\,T$	-61124 ± 201	-2.967 ± 0.276
0.860	id.	$308.85 - 0.00530\,T$	-59614 ± 197	-1.025 ± 0.234
0.875		$317.22 - 0.00612\,T$	-61229 ± 205	-1.180 ± 0.275
0.892	$683 < T < 829$	$316.10 + 0.00559\,T$	-61011 ± 264	$+1.079 \pm 0.351$
0.892	$T > 773$	$300.56 + 0.02502\,T$	-58015 ± 728	$+4.832 \pm 0.862$
0.901	$T < 773$	$312.93 + 0.01308\,T$	-60400 ± 715	$+2.523 \pm 0.966$
0.901	$T > 773$	$300.41 + 0.02912\,T$	-57986 ± 632	$+5.620 \pm 0.761$
0.914		$314.74 + 0.01838\,T$	-60752 ± 636	$+3.548 \pm 0.849$
0.947	$693 < T < 829$	$311.67 + 0.05032\,T$	-60158 ± 431	$+9.711 \pm 0.561$
0.947	$T > 773$	$299.57 + 0.06542\,T$	-57823 ± 611	$+12.627 \pm 0.724$
0.962		$303.40 + 0.07991\,T$	-58563 ± 331	$+15.425 \pm 0.427$
0.966		$299.27 + 0.09282\,T$	-57764 ± 226	$+17.916 \pm 0.285$
0.978		$305.85 + 0.10160\,T$	-59036 ± 510	$+19.610 \pm 0.623$

ent symbols when they depend on the temperature range investigated. The tin activity values as a function of composition at 737 K are plotted in Fig. 4.

3.2. Phase Diagram

The values of the eutectic composition and temperature reported by Hansen *et al*[8] are respectively x_{Te} = 0.84 and T_E = 678 K. More recently Shunk[9] proposed an eutectic temperature of 674.3 K. Fig. 2 shows the typical break when the alloy x_{Te} = 0.84 passes into the two phases region (liquid + solid) for a temperature of 691 K. Moreover, the points reported on Fig. 2 which define the liquidus show that the eutectic composition is not less than x_{Te} = 0.85. Due to the scattering of the points showing the start of solidification of the hypereutectic alloys, we have used differential thermal analysis (DTA) in order to verify the results obtained from the emf measurements.

The DTA apparatus is shown in Fig. 5. The tin-tellurium alloy and the alumina powder reference are contained in Pyrex cells, whose base allows the introduction of a thermocouple. The cells are con-

tained in a stainless steel support allowing a better distribution of the heat. In order to avoid metal oxidization and tellurium vaporization, the cell containing the alloy is evacuated and then sealed. The DTA cell is then placed in a furnace whose heating rate is fixed at 2 K min^{-1}. The alloys are homogenized by maintaining their temperature for a sufficiently long time 50 K above their melting point and then cooled. The values of the eutectic and liquidus temperatures can be determined to $\pm 1/4$ K by this method. They are reported in Table II, together with the values obtained from emf measurements. Our objective being essentially to verify the liquidus points of the hypereutectic range, most measurements by DTA concern this corresponding composition range.

This set of experimental data is reported in Fig. 6, which shows that there is good agreement between the two methods for the hypereutectic alloy. The agreement is less good for the hypoeutectic alloys, but in this case, according to the work of Massart *et al*,[10] the emf method is more reliable because the liquidus slope dT/dx_{Sn} is greater. Finally we propose for the eutectic composition and temperature respectively, the values x_{Te} = 0.86 $\pm$ 0.01 and T_E = (676 $\pm$ 1) K.
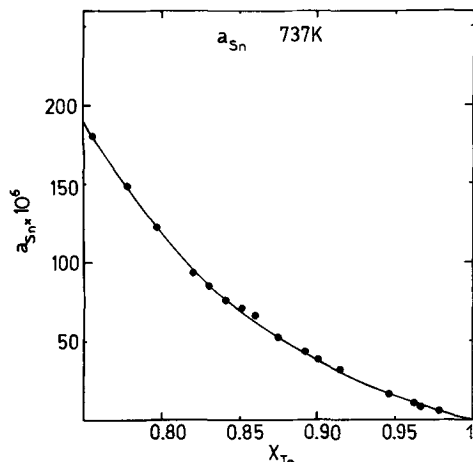

Fig. 4—Tin activities at 737 K.

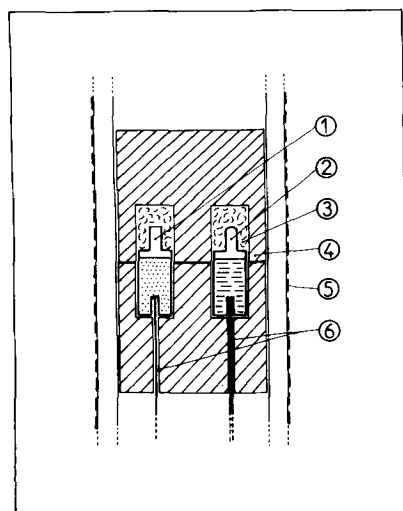Fig. 5—DTA cell assembly: 1) reference; 2) sample; 3) silica wool; 4) stainless-steel block; 5) resistance heater; and 6) thermocouple.

Table II

| Emf Measurements | | DTA Results | | |
| Temperature of the Liquidus | | Temperature of the Liquidus | | Eutectic Temperature |
x_{Te}	T(K)	x_{Te}	T(K)	T(K)
0.756	801	0.750	795	674
0.778	775	0.800	734.5	675
0.796	751	0.865	676	675
0.819	716	0.871	678	676
0.830	705	0.877	677	675.5
0.841	691	0.880	683	675
0.852	683	0.898	690.5	676
0.860	676	0.920	699	676
0.875	681	0.953	710	677
0.892	687	0.968	715	677.5
0.901	689	1.000	723	677
0.914	692			
0.947	706			
0.962	712			
0.966	714			
0.978	718			
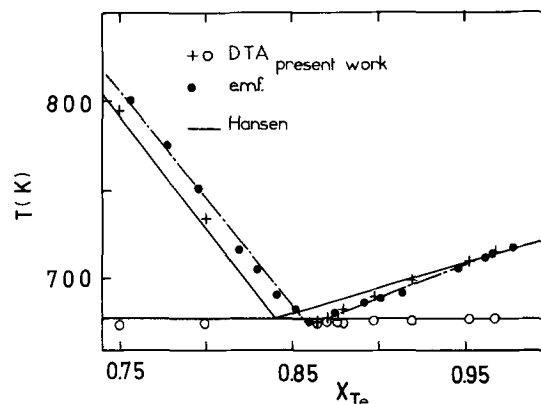
Fig. 6—Liquidus and eutectic temperatures from emf measurements and DTA.

4. DISCUSSION

The thermodynamic data for liquid alloy systems showing intermetallic compounds, considered in conjunction with the behavior of properties such as resistivity, density and X-ray measurements, have been interpreted as indicating varying degrees of short range order. For these systems there is a destruction of the long range order of the solid during the melting process, but they keep a high degree of local order, postmelting phenomena being then associated with the gradual weakening of the strong bonds.

Large exothermic heats of mixing varying considerably around the composition of the stoichiometric compound SnTe[2] and low activities in the liquid Sn, Te alloys show that there are very strong interactions in the liquid. We have then considered that a short range order subsists in the liquid alloys; that is, tin and tellurium atoms belonging to strong Sn-Te bonds could be in equilibrium with weaker bonds according to the reaction Sn + Te $\rightleftharpoons$ Sn Te. It should be observed that from a thermodynamic point of view similar approaches to liquid solutions have been made previously by some authors.[11-14]

To interpret his results concerning the electrical conductivities and the Seebeck effect of molten Sn, Te alloys, Dancy[15] proposed that between the stoichiometric composition and pure tellurium, there was a gradual transition from a melt in which the atoms are arranging approximately as in the compound SnTe, to a melt in which the chain structure of tellurium is dominant. The addition of tin to tellurium lowers the free electron density through the formation of bound states, and the process continues until the stoichiometric composition corresponding to the compound SnTe is reached.

Obviously the strong bonds would not be isolated but could make atom groups similar to those existing in the solid state with a situation in which strong bonds are temporarily formed and quickly broken up as a result of thermal agitation. In a first approach, we have assumed that the associated solution is ideal; though this assumption does not explain the tendency towards the regrouping of the strong Sn-Te bonds, the results obtained will show that the behavior of the liquid can be reasonably described by this simple model, at least in the experimental range investigated. Two tests have shown the validity of this simple model.

First we have attempted to determine the liquidus temperatures of the liquid alloys which are in equilibrium with the compound SnTe. Expressing the equality of tin and tellurium chemical potentials in the phases in equilibrium, and if the compound has a very narrow range of deviation from stoichiometry, one obtains for the liquidus equation:

$$\frac{RT}{2} \ln (a_1 a_2) = \Delta H^f - T \Delta S^f + \Delta H_1^m \left(\frac{T - T_1^m}{2T_1^m} \right) + \Delta H_2^m \left(\frac{T - T_2^m}{2T_2^m} \right) \qquad [1]$$

where a_1 and a_2 are the activities referenced to pure

liquid standard state on the liquidus curve of the liquid components Sn and Te respectively at temperature T and whose atom fractions are x_1 and x_2. ΔH^f and ΔS^f are respectively the heat and entropy of formation of the compound SnTe from solid tin and solid tellurium; ΔH_1^m, ΔH_2^m, T_1^m and T_2^m are respectively the enthalpies and temperatures of melting of the pure components Sn and Te. Moreover we consider the ideal partially associated solution which contains atoms Sn* and Te* in equilibrium with strong Sn-Te bonds according to Sn* + Te* $\rightleftharpoons$ Sn Te. The equilibrium constant takes the form $K = x_{SnTe} / x_{Sn*} x_{Te*}$ or, for simplicity, $K = x_{AB} / x_A x_B$, where x_A, x_B and x_{AB} are the mole fractions of the various species in the ternary solution. If n_1 and n_2 are the number of moles of tin and tellurium in the binary solution, n_A, n_B and n_{AB} the number of moles in the ternary solution one obtains for the atom fractions:

$$x_1 = \frac{n_A + n_{AB}}{n_1 + n_2}, \quad x_A = \frac{n_A}{n_1 + n_2 - n_{AB}},$$

$$x_{AB} = \frac{n_{AB}}{n_1 + n_2 - n_{AB}},$$

with $n_1 = n_A + n_{AB}$, $n_2 = n_B + n_{AB}$ by virtue of the mass conservation.

Consequently one can show that:

$$x_A = x_1 - x_2 x_{AB} \qquad x_B = x_2 - x_1 x_{AB}.$$

It has been shown by Prigogine and Defay[14] that macroscopic potential μ_1 and μ_2 of components of the binary solution are equal to chemical potential of the uncombined species in the ternary solution. Consequently one can write $\mu_1 = \mu_A$ and $\mu_2 = \mu_B$. If we write like Jordan,[11] $x_{AB} = (1 - P)/(1 + P)$, we have $P = \sqrt{1 - (4x_1 x_2 / 1 + K^{-1})}$. The liquidus Eq. [1] can be then written:

$$\frac{RT}{2} \ln \left[K^{-1} \left(\frac{1 - P}{1 + P} \right) \right] = \Delta H^f - T \Delta S^f + \Delta H_1^m \left(\frac{T - T_1^m}{2T_1^m} \right)$$
$$+ \Delta H_2^m \left(\frac{T - T_2^m}{2T_2^m} \right). \qquad [2]$$

Remark: If only the heat of fusion of the compound AB is known it is necessary to express the activities of the components of the supercooled liquid.[16] One can then write for the liquidus equation:

$$\frac{RT}{2} \ln \frac{1 - P^*}{1 + P^*} \frac{1 + P}{1 - P} = \Delta H_{AB}^m \left(1 - \frac{T}{T_{AB}^m} \right)$$

with $P^* = \sqrt{1 - (1/1 + K^{-1})}$; ΔH_{AB}^m and T_{AB}^m are respectively the enthalpy and the temperature of melting of the compound AB.

From our experimental results it is possible to derive the values of the equilibrium constant for each considered alloy and for various temperatures since:

$$x_A = a_1 = \exp \left(-\frac{2EF}{RT} \right), \quad x_{AB} = \frac{x_1 - x_A}{x_2}$$

and

$$x_B = 1 - x_A - x_{AB}.$$

From our assumptions K must be independent of

composition. In reality, our results show that K increases slowly with the alloy concentration in tellurium. The results obtained are reported vs $1/T$ in Fig. 7; they can be expressed by the following equation:

$$R \ln K = -17.087 + \frac{62,032}{T} \text{ J mol}^{-1}.$$

Taking into account the experimental value of ΔH^f proposed by Castanet et al^2 ($\Delta H^f \simeq -31.05$ KJ mol^{-1} in the investigated range of temperature), the entropy of formation of the compound SnTe was calculated from our emf results and from the phase diagram data. Indeed, according to Eq. [1] the Gibbs free energy of formation of the compound SnTe can be deduced from the activities of tin and tellurium in the liquid alloys in equilibrium with this compound.

In the investigated ranges of composition and temperature the activity coefficient of tin, deduced from our experimental results, can be correctly represented by equations of the form:

$$\ln \gamma_1 = \alpha x_2^2 + \beta.$$

So, it is then possible to obtain, by Gibbs-Duhem integration, the activity coefficient of tellurium in the particularly simple following form:

$$\ln \gamma_2 = \alpha x_1^2.$$

For the studied alloys, in the concentration range $0.70 < x_{Te} < 0.85$, one can then calculate the ΔG^f and ΔS^f by application of Eq. [1]. The values of ΔG^f so obtained are in good agreement with those previously published.[17] The average value of ΔS^f was deduced from these results which are summarized in Table III.

$$\Delta S^f \simeq -0.552 \text{ J mol}^{-1} \cdot \text{K}^{-1}.$$

Consequently the equation of the liquidus takes the form:

$$\frac{RT}{2} \left[\ln \frac{1 - \sqrt{1 - (4x_1x_2/1 + K^{-1})}}{1 + \sqrt{1 - (4x_1x_2/1 + K^{-1})}} + \ln K^{-1} \right]$$

$$= -43,329 + 19.623\,T. \qquad [3]$$

The values of ΔH_1^m, ΔH_2^m, T_1^m, and T_2^m are the selected values from Hultgren et $al.$[17]

As can be seen in Fig. 8, at compositions richer in tellurium than $x_{Te} = 0.50$, there is a remarkable agreement between the liquidus deduced from Eq. [3] and that obtained by ourselves and by Hansen[8] for $0.50 < x_{Te} < 0.75$. The discrepancy in the lower composition range ($x_{Te} < 0.5$) is probably due to a model defect which does not consider the weak interactions between free atoms Sn*, Te*, and the atomic groups Sn-Te.

In a second test we have compared the value of the formation enthalpy of strong Sn-Te bonds to the partial heat of solution of tin in liquid Sn, Te alloys. The enthalpy of mixing of n_1 moles of tin and n_2 moles of tellurium can be written $n_1 \Delta\overline{H}_1 + n_2 \Delta\overline{H}_2$. On the other hand, if we suppose that the mixing of n_1 moles of tin and n_2 moles of tellurium implies the formation of n_{AB} bonds belonging to the ideal ternary solution consisting of three species A, B and AB, the enthalpy
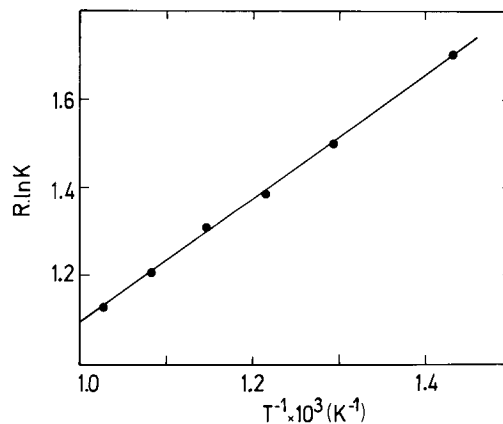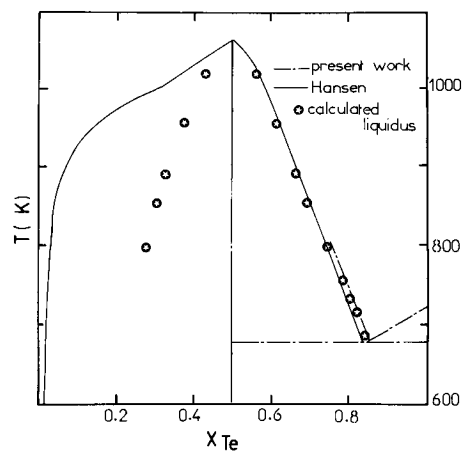

Fig. 7—Plot of calculated equilibrium constant vs $1/T$.

Fig. 8—Calculated liquidus from Eq. [3].

Table III

T(K)	691	716	751	775	801
α	−2.7540	−2.3112	−2.3710	−2.4569	−2.5300
β	−6.3076	−6.2707	−5.7467	−5.3739	−5.0160
ΔG^f(KJ mol^{-1})	−30.748	−30.677	−30.639	−30.577	−30.547
ΔS^f(J mol^{-1} K^{-1})	−0.443	−0.527	−0.552	−0.615	−0.632

of mixing can be also written $n_{AB}\,\Delta H^*$ (ΔH^* represents the enthalpy of formation of the AB bond). Therefore:

$$n_{AB}\,\Delta H^* = n_1\,\Delta\overline{H}_1 + n_2\,\Delta\overline{H}_2 \,.$$

Utilizing the definition for the mole fraction of the species 1, 2 and AB

$$n_1 = x_1\,(n_1 + n_2)$$

$$n_2 = x_2\,(n_1 + n_2)$$

$$n_{AB}\,(1 + x_{AB}) = (n_1 + n_2)\,x_{AB},$$

one obtains finally the following relation:

$$\Delta H^* = \frac{1 + x_{AB}}{x_{AB}}\,(x_1\,\Delta\overline{H}_1 + x_2\,\Delta\overline{H}_2). \qquad [4]$$

This quantity represents the enthalpy of formation ΔH^*_{Sn-Te} of a Sn-Te bond. In the special case of Sn, Te alloys at compositions richer than $x_{Te} = 0.50$

calorimetric measurements[2] have shown that the partial heat of solution of tellurium is zero in the whole liquid phase whereas $\Delta \bar{H}_{Sn}$ is constant. This has been verified from our emf measurements. Moreover the values of K show that $n_1/n_{AB} \simeq 1$. One must then verify that $\Delta \bar{H}_1 \simeq \Delta H^*_{Sn-Te}$. For this purpose we have used the results reported in Fig. 7 to determine $\Delta H^*_{Sn-Te} = -62,032$ J mol^{-1}. On the other hand we have deduced from our experimental results the value $\Delta \bar{H}_{Sn} = \Delta \bar{H}_1 = -60,250$ J mol^{-1}; Castanet *et al*[2] proposed $\Delta \bar{H}_{Sn} = -61,900$ J mol^{-1} for $T = 737$ K. The agreement here is also very good.

Consequently this simple model of ideal partially associated solutions, which assumes the presence of strong Sn-Te bonds seems to correctly represent the thermodynamic behavior of tin-tellurium alloys in the composition range $x_{Te} > 0.50$ without fitting parameters. These results compared with those deduced from electrical measurements seem to confirm that the proposed assumption is valid. Nevertheless other experiments are needed to prove more directly the existence of such associations.

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