Thermochimica Acta, 232 (1994) 303–315
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01391-F

Thermodynamic investigations of liquid Te-saturated PbSe–PbTe solid solutions

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(Received 5 March 1993; accepted 6 June 1993)

Abstract

The activity of PbTe in liquid Te-saturated PbSe–PbTe solid solutions in the temperature range from 730 to 830 K was measured by an electrochemical technique using LiCl–KCl + 5 wt.% $PbCl_2$ as the molten salt electrolyte. The activity of PbSe was calculated by Gibbs–Duhem integration using the α-function. From the e.m.f. values of the cell measured at different temperatures, the partial, integral and excess molar thermodynamic quantities were calculated. All the excess partial molar thermodynamic quantities at infinite dilution were accurately estimated by Chiotti's method. Continuous variation of activity and of the activity coefficient of both the components with composition, indicates that the PbSe–PbTe system is completely miscible and consists of a single-phase field throughout the entire range of composition in the range 730–830 K.

INTRODUCTION

Chalcogenides of group IVa elements are important semiconductors and have gained prominence for their applications in various electronic devices, such as photodiodes, photoresistors, thermoelectric generators, lasers and infrared detectors. Although these binary chalcogenides possess useful semiconducting properties, they offer limited and fixed values of electronic parameters, namely the energy gap, the electrical, thermal and photoconductivities, and the thermoelectric figure of merit. These limitations can be overcome and electronic materials can be designed and tailor-made to suit specific property requirements by alloying. Pseudo-binary alloy systems between group IVa chalcogenides offer wide selective ranges and have thus attracted considerable attention. In this paper, one such system PbSe–PbTe, is described.

In order to adjust the desired semiconducting characteristics by varying the alloy composition, it is important to have accurate knowledge of the phase diagram and thermodynamic properties of the system.

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Although the phase diagram of the PbSe–PbTe system has been studied by a number of investigators [1–4], the thermodynamic data are scarce and insufficient to predict the behaviour of solid solutions. Urusov [5] and Sokolov et al. [6] have studied this system by vapour pressure measurements. Shamsuddin and Misra [7] have reported some thermodynamic properties of the PbSe–PbTe system. The present investigation was undertaken because of the sparse thermodynamic data and because the solution thermodynamics of the PbSe–PbTe system are not known. In this paper, the activity of PbTe in liquid Te-saturated PbSe–PbTe solid solutions was determined by an electrochemical technique using molten salt electrolyte. Various partial, integral and excess thermodynamic quantities have been calculated.

EXPERIMENTAL

Materials

High purity (99.99%) lead, selenium and tellurium, obtained from the Bhabha Atomic Research Centre, Bombay, were used in this investigation. The following analytical reagent grade salts were used for preparation of the electrolyte; lead chloride (Web., Germany), lithium chloride (Riedel, Germany) and potassium chloride (Qualigens, India).

Preparation of solid solutions

A series of solid solutions in the PbSe–PbTe system with PbTe added in 10 mol% increments was prepared by pyrosynthesis of the constituents. The high-purity component elements (Pb, Se and Te) were weighed to an accuracy of $\pm 1 \times 10^{-5}$ g in stoichiometric proportions and sealed in silica capsules under a vacuum of better than 1.3×10^{-3} Pa. The capsules were heated at a rate of 3 K min^{-1} to 50 K above the liquidus, held at this temperature for 24 h, and then quenched in cold water. XRD analyses of the quenched samples established that the product was a single phase.

Electrochemical measurements

The activity of PbTe in the liquid Te-saturated PbSe–PbTe system was determined by measuring the e.m.f. of the following electrochemical cell

$$\mathrm{PbTe(s) + Te(l)} \mid \mathrm{LiCl{-}KCl + 5\ wt.\%\ PbCl_2} \mid \mathrm{PbTe_xSe_{1-x}(s) + Te(l)}$$

The cell assembly used in the present investigation, shown in Fig. 1(A) and (B), is made of Borosil glass and has five lower limbs, each of 8 mm

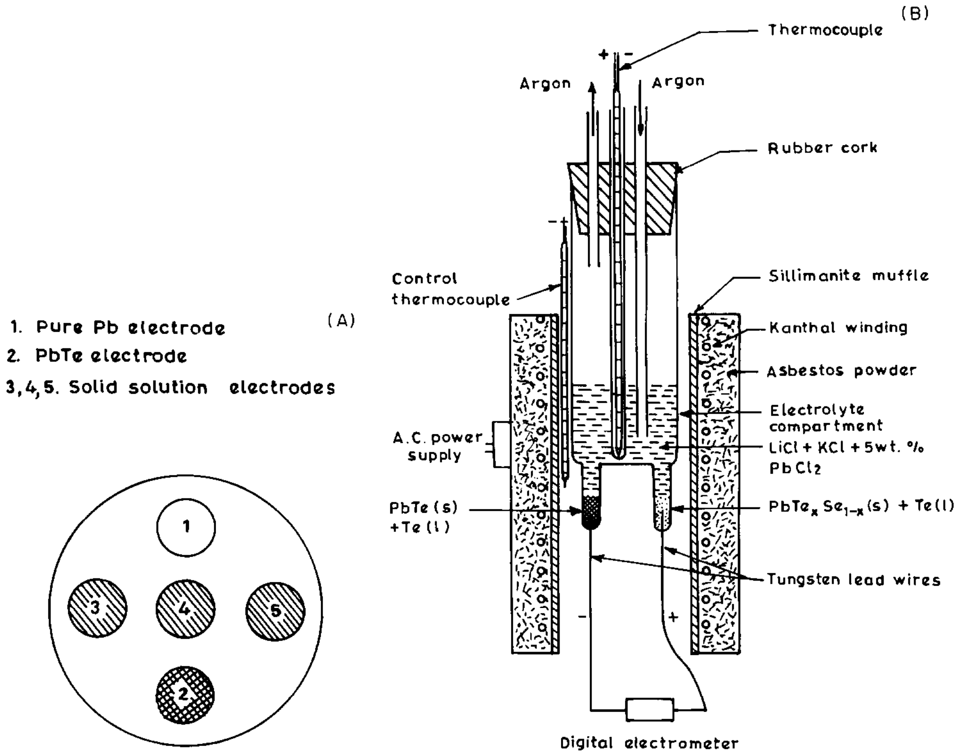

Fig. 1. (A) Cross sectional view of the galvanic cell with five lower limbs. (B) Schematic diagram of the galvanic cell with two limbs.

internal diameter, below a tubular electrolyte compartment of 50 mm internal diameter. Figure 1(A) shows the cross-sectional view of the cell and Fig. 1(B) shows the elevation of a cell with two lower limbs. At the bottom of each limb is sealed an identical electrode lead wire made of tungsten (0.4 mm diameter and 200 mm length).

The experiment began by forming electrodes in the different limbs. In one limb, the compound PbTe was formed, and in the other limbs, electrodes of the appropriate solid solutions $PbTe_xSe_{1-x}$ were formed by heating the powder mixture of the compound and the desired solutions with 10 at.% excess of Te at 750 K for about 1 h under pure, dried argon. Thus each compound and solid solution electrode was saturated with liquid tellurium. Further details of the cell assembly and experimental techniques have been described elsewhere [7–9].

The cell attained equilibrium after 24 h and thereafter the e.m.f. values remained stable for more than 30 h. The general criteria for reversibility were applied to ensure the correct reversible cell e.m.f., i.e. time-independent e.m.f. at a constant temperature; reproducibility of e.m.f. values whether approached from the high or low temperature side; and recoverability of the same e.m.f. after passage of a small amount of impressed current through the cell in either direction. Reversibility of the cell indicates the absence of any side or exchange reaction. After attaining a constant e.m.f. at one temperature, the temperature was changed and sufficient time was allowed for re-establishment of equilibrium. The e.m.f. values were measured in both heating and cooling cycles. Each composition was remeasured to check the reproducibility of results.

RESULTS AND DISCUSSION

Activity of the components

The virtual cell reaction of the galvanic cell may be represented as

$$\mathrm{PbTe(pure)} \rightarrow \mathrm{PbTe\ (in\ PbSe{-}PbTe)} \tag{1}$$

The activity of PbTe (a_{PbTe}) in the system PbSe–PbTe was calculated from the relation

$$\ln a_{\mathrm{PbTe}} = -nFE/RT \tag{2}$$

where n is the number of electrons transferred during reaction (1), E is the e.m.f. of the cell, F is the Faraday constant and R is the universal gas constant. The reversible cell e.m.f. values measured in the temperature range 730–830 K are listed in Table 1. The variation of e.m.f. with

TABLE 1

Galvanic cell e.m.f. (mV) at different temperatures

x_{PbTe}	Temperature in K			$E = A + BT$	
	730	793	830	$-A$	$+B$
0.1	42.40 ± 1.05	54.90 ± 1.10	64.61 ± 1.15	118.25	0.2196
0.2	28.38 ± 1.00	36.71 ± 1.05	42.58 ± 1.05	74.67	0.1410
0.3	21.00 ± 1.00	25.80 ± 1.00	30.50 ± 1.00	47.17	0.0930
0.4	16.50 ± 0.95	21.59 ± 0.95	23.98 ± 1.00	38.48	0.0754
0.5	14.00 ± 0.95	16.80 ± 0.95	19.40 ± 1.00	24.82	0.0530
0.6	10.55 ± 0.80	12.91 ± 0.80	15.00 ± 0.95	21.49	0.0437
0.7	9.02 ± 0.50	10.60 ± 0.50	11.21 ± 0.55	7.17	0.0222
0.8	6.12 ± 0.40	7.08 ± 0.45	7.76 ± 0.45	5.78	0.0163
0.9	3.60 ± 0.30	3.70 ± 0.30	3.80 ± 0.30	−2.17	0.0020

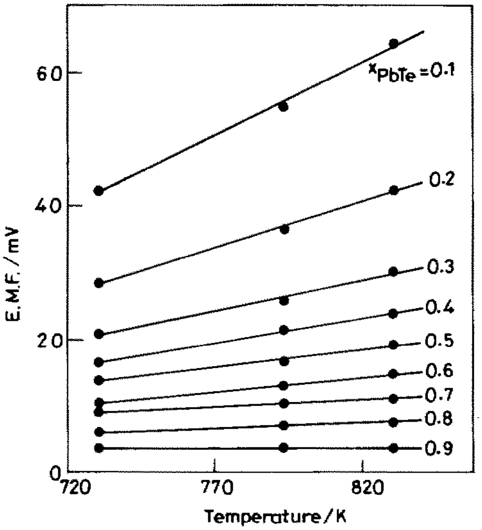

Fig. 2. E.m.f. vs. temperature plot of the galvanic cell.

temperature for nine compositions (shown in Fig. 2) was calculated by the least-squares method and is summarized in Table 1 in the form of a linear equation $E = A + BT$. The error limits shown in the table are maximum deviations from average values based on two independent runs.

From the e.m.f. values measured at different temperatures, the activities of PbTe in liquid Te-saturated PbSe–PbTe solid solutions were calculated and are summarized in Table 2. The corresponding values of the activity coefficient of PbTe (γ_{PbTe}) at different temperatures as calculated using the relation

$$\gamma_{PbTe} = a_{PbTe}/x_{PbTe} \tag{3}$$

TABLE 2

Activity and activity coefficient of PbTe in liquid Te-saturated PbSe–PbTe solid solutions

x_{PbTe}	a_{PbTe}			γ_{PbTe}		
	730 K	793 K	830 K	730 K	793 K	830 K
0.0	–	–	–	2.683	2.140	1.829
0.1	0.2596 ± 0.0087	0.2004 ± 0.0065	0.1641 ± 0.0053	2.596 ± 0.087	2.004 ± 0.064	1.641 ± 0.052
0.2	0.4055 ± 0.0127	0.3414 ± 0.0105	0.3039 ± 0.0089	2.028 ± 0.065	1.707 ± 0.053	1.520 ± 0.045
0.3	0.5128 ± 0.0163	0.4698 ± 0.0138	0.4261 ± 0.0119	1.709 ± 0.054	1.566 ± 0.046	1.420 ± 0.040
0.4	0.5917 ± 0.0178	0.5315 ± 0.0148	0.5113 ± 0.0143	1.479 ± 0.045	1.329 ± 0.037	1.278 ± 0.036
0.5	0.6407 ± 0.0194	0.6115 ± 0.0170	0.5812 ± 0.0162	1.281 ± 0.039	1.223 ± 0.034	1.162 ± 0.033
0.6	0.7150 ± 0.0182	0.6853 ± 0.0161	0.6573 ± 0.0175	1.192 ± 0.030	1.142 ± 0.027	1.096 ± 0.029
0.7	0.7506 ± 0.0119	0.7332 ± 0.0107	0.7308 ± 0.0112	1.072 ± 0.017	1.047 ± 0.002	1.044 ± 0.016
0.8	0.8231 ± 0.0105	0.8128 ± 0.0107	0.8049 ± 0.0101	1.029 ± 0.013	1.016 ± 0.013	1.006 ± 0.012
0.9	0.8918 ± 0.0085	0.8973 ± 0.0078	0.8992 ± 0.0075	0.991 ± 0.009	0.997 ± 0.008	0.999 ± 0.008

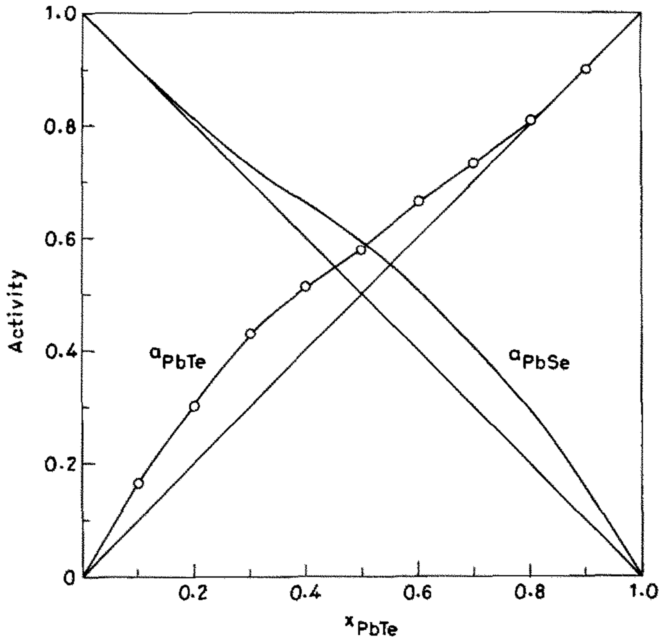

Fig. 3. Activity–composition relations in Te-saturated PbSe–PbTe solid solutions at 830 K.

are presented in Table 2. The activity and activity coefficient both decrease with increasing temperature. Figures 3 and 4 present, respectively, the variation of the activity and activity coefficient of PbTe with the alloy composition at a typical temperature of 830 K. The plots exhibit positive

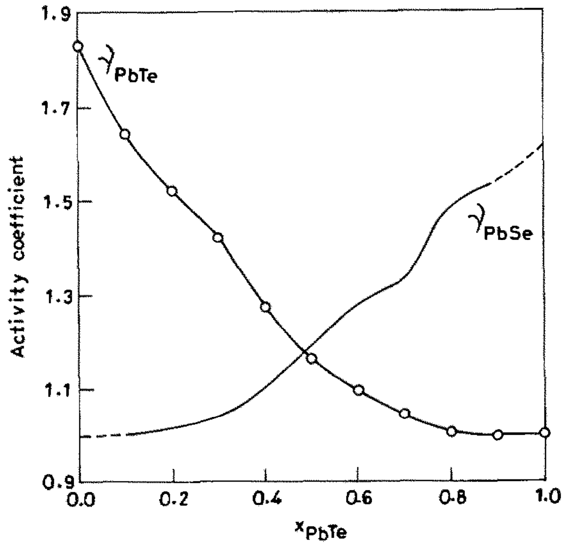

Fig. 4. Activity coefficient–composition relations in Te-saturated PbSe–PbTe solid solutions at 830 K.

TABLE 3

Activity and activity coefficient of PbSe in liquid Te-saturated PbSe–PbTe solid solutions

x_{PbSe}	a_{PbSe}			γ_{PbSe}		
	730 K	793 K	830 K	730 K	793 K	830 K
0.0	–	–	–	2.421	2.036	1.621
0.1	0.2305	0.1931	0.1542	2.305	1.931	1.542
0.2	0.3740	0.3491	0.2972	1.870	1.745	1.486
0.3	0.5061	0.4790	0.4001	1.687	1.597	1.334
0.4	0.5637	0.5448	0.5110	1.409	1.362	1.278
0.5	0.6472	0.6260	0.5950	1.294	1.252	1.190
0.6	0.7136	0.6913	0.6611	1.189	1.152	1.102
0.7	0.7545	0.7493	0.7293	1.078	1.070	1.042
0.8	0.8319	0.8310	0.8145	1.040	1.039	1.018
0.9	0.8964	0.9027	0.9020	0.996	1.003	1.002

deviation from Raoult's law up to 83 mol% PbTe, beyond which the PbSe–PbTe system obeys Raoult's law. The continuous variation of activity and activity coefficient with composition confirms that the system is completely miscible in the solid state and consists of a single-phase field throughout the entire range of composition. This agrees with the results of Grimes [2] and Steininger [4].

The activity of PbSe in Te-saturated PbSe–PbTe solid solutions has been calculated using the following form of Gibbs–Duhem integration [10]

$$\ln \gamma_{PbSe} = -\alpha_{PbTe} x_{PbTe} x_{PbSe} - \int_{x_{PbSe}=1}^{x_{PbSe}=x_{PbSe}} \alpha_{PbTe} \, dx_{PbSe} \tag{4}$$

where $\alpha_{PbTe} = \ln \gamma_{PbTe}/(1 - x_{PbTe})^2$.

The values of the activity and activity coefficient of PbSe in Te-saturated PbSe–PbTe solid solutions thus obtained are presented in Table 3. The values (at a typical temperature of 830 K) are also plotted in Figs. 3 and 4. These figures show positive deviation from Raoult's law up to 90 mol% PbSe, beyond which the system obeys Raoult's law.

Partial, integral and excess molar thermodynamic properties

From the e.m.f. values measured at any temperature (Table 1), the partial molar free energy of mixing of PbTe ($\Delta\bar{G}^{M}_{PbTe}$) in liquid Te-saturated PbSe–PbTe solid solutions was calculated using the relation

$$\Delta\bar{G}^{M}_{PbTe} = RT \ln a_{PbTe} = -nFE \tag{5}$$

The values of the partial molar enthalpy ($\Delta\bar{H}^{\mathrm{M}}_{\mathrm{PbTe}}$) and entropy ($\Delta\bar{S}^{\mathrm{M}}_{\mathrm{PbTe}}$) of PbTe in the liquid Te-saturated PbSe–PbTe system were obtained, respectively, from the intercept and slope of $\Delta\bar{G}^{\mathrm{M}}_{\mathrm{PbTe}}$ versus T plots. In the calculation of $\Delta\bar{H}^{\mathrm{M}}_{\mathrm{PbTe}}$ and $\Delta\bar{S}^{\mathrm{M}}_{\mathrm{PbTe}}$, the heat capacity contribution to formation of solid solutions in the narrow temperature range from 730 to 830 K was neglected. The excess partial molar thermodynamic quantities were computed as follows

$$\Delta\bar{G}^{\mathrm{XS}}_{\mathrm{PbTe}} = \Delta\bar{G}^{\mathrm{M}}_{\mathrm{PbTe}} - \Delta\bar{G}^{\mathrm{M}}_{\mathrm{id}} = RT\ln\gamma_{\mathrm{PbTe}} \tag{6}$$

$$\Delta\bar{H}^{\mathrm{XS}}_{\mathrm{PbTe}} = \Delta\bar{H}^{\mathrm{M}}_{\mathrm{PbTe}},\ \text{because}\ \Delta\bar{H}^{\mathrm{M}}_{\mathrm{id}} = 0 \tag{7}$$

and

$$\Delta\bar{S}^{\mathrm{XS}}_{\mathrm{PbTe}} = \Delta\bar{S}^{\mathrm{M}}_{\mathrm{PbTe}} - \Delta\bar{S}^{\mathrm{M}}_{\mathrm{id}} = -\partial(\Delta\bar{G}^{\mathrm{XS}}_{\mathrm{PbTe}})/\partial T \tag{8}$$

The partial molar thermodynamic quantities thus computed are summarized in Table 4, and are plotted as a function of composition (x_{PbTe}) at 830 K in Fig. 5. For comparison, the corresponding values of $\Delta\bar{G}^{\mathrm{M}}_{\mathrm{id}}$ and $T\Delta\bar{S}^{\mathrm{M}}_{\mathrm{id}}$ are also presented in the figure.

The analogous thermodynamic parameters for the second component (PbSe) have also been calculated from the estimated values of a_{PbSe} and γ_{PbSe} (based on Gibbs–Duhem integration) and are listed in Table 5.

The excess partial thermodynamic quantities ($\Delta\bar{Q}^{\mathrm{XS}}$) of the components at infinite dilution can be estimated by the method discussed by Chiotti [11]. This method, based on $x_i\Delta\bar{Q}^{\mathrm{XS}}_i$ versus x_i plots, is advantageous for determining excess partial molar quantities at infinite dilution because the plots have zero intercepts at $x_i = 0$ as well as at $x_i = 1$. Hence, any excess partial molar thermodynamic quantity at infinite dilution ($\Delta\bar{Q}^{\mathrm{XS(0)}}_i$) can be estimated accurately from the slope of $x_i\Delta\bar{Q}^{\mathrm{XS}}_i$ versus x_i plots at $x_i \rightarrow 0$. For the estimation of $\Delta\bar{G}^{\mathrm{XS(0)}}_{\mathrm{PbTe}}$ and $\Delta\bar{G}^{\mathrm{XS(0)}}_{\mathrm{PbSe}}$ at different temperatures, $x_{\mathrm{PbTe}}\Delta\bar{G}^{\mathrm{XS}}_{\mathrm{PbTe}}$ and $x_{\mathrm{PbSe}}\Delta\bar{G}^{\mathrm{XS}}_{\mathrm{PbSe}}$ are plotted as functions of x_{PbTe} and x_{PbSe}, respectively, in

TABLE 4

Partial and excess molar thermodynamic quantities of PbTe in liquid Te-saturated PbSe–PbTe solid solutions

x_{PbTe}	$\Delta\bar{G}^{\mathrm{M}}_{\mathrm{PbTe}}/(\mathrm{kJ\ mol^{-1}})$			$\Delta\bar{G}^{\mathrm{XS}}_{\mathrm{PbTe}}/(\mathrm{kJ\ mol^{-1}})$			$\Delta\bar{H}^{\mathrm{M}}_{\mathrm{PbTe}}/\mathrm{kJ\ mol^{-1}}$	$\Delta\bar{S}^{\mathrm{M}}_{\mathrm{PbTe}}/\mathrm{J\ K^{-1}\ mol^{-1}}$	$\Delta\bar{S}^{\mathrm{M}}_{\mathrm{PbTe}}/\mathrm{J\ K^{-1}\ mol^{-1}}$
	730 K	793 K	830 K	730 K	793 K	830 K			
0.0	–	–	–	5.989	5.015	4.167	25.000	–	25.53
0.1	−8.185	−10.597	−12.471	5.789	4.583	3.418	22.816	42.37	23.22
0.2	−5.478	−7.085	−8.219	4.290	3.526	2.887	14.412	27.21	13.83
0.3	−4.053	−4.980	−5.887	3.254	2.957	2.421	9.108	17.95	7.94
0.4	−3.185	−4.167	−4.629	2.376	1.874	1.694	7.428	14.56	6.94
0.5	−2.702	−3.243	−3.745	1.505	1.327	1.038	4.810	10.25	4.47
0.6	−2.036	−2.491	−2.895	1.064	0.877	0.630	4.149	8.44	4.19
0.7	−1.741	−2.046	−2.164	0.424	0.305	0.297	1.385	4.30	1.34
0.8	−1.181	−1.366	−1.498	0.173	0.105	0.042	1.118	3.15	1.29
0.9	−0.695	−0.714	−0.733	−0.056	−0.019	−0.006	−0.423	0.37	−0.50

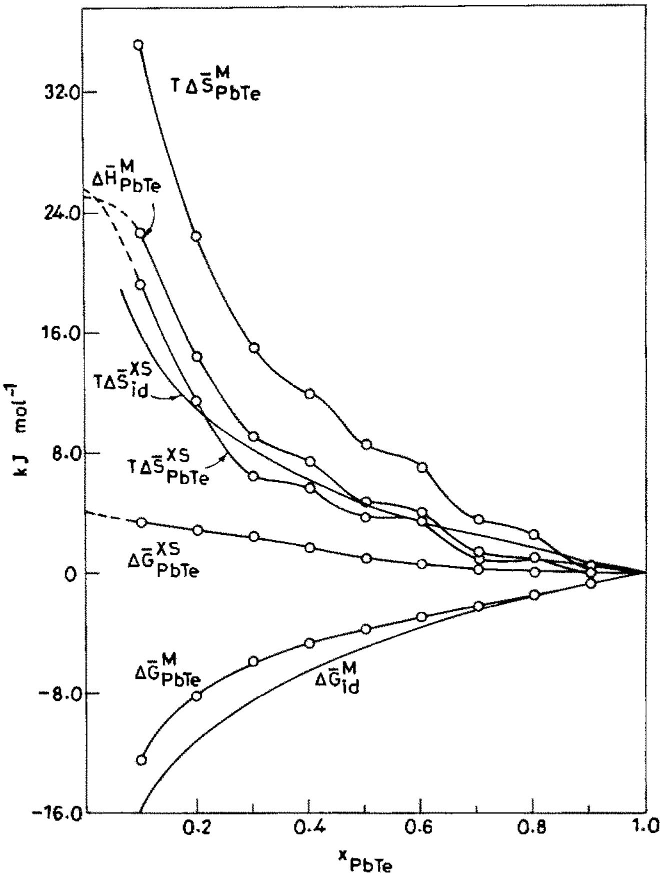

Fig. 5. Partial and excess molar thermodynamic quantities of PbTe in liquid Te-saturated PbSe–PbTe solid solutions at 830 K.

TABLE 5

Partial and excess molar thermodynamic quantities of PbSe in liquid Te-saturated PbSe–PbTe solid solutions

x_{PbSe}	$\Delta\bar{G}^{M}_{PbSe}$/kJ mol^{-1}			$\Delta\bar{G}^{XS}_{PbSe}$/kJ mol^{-1}			$\Delta\bar{H}^{M}_{PbSe}$/ kJ mol^{-1}	$\Delta\bar{S}^{M}_{PbSe}$/ J K^{-1} mol^{-1}	$\Delta\bar{S}^{XS}_{PbSe}$/ J K^{-1} mol^{-1}
	730 K	793 K	830 K	730 K	793 K	830 K			
0.0	–	–	–	5.367	4.688	3.334	23.567	–	23.22
0.1	−8.906	−10.842	−12.900	5.068	4.338	2.989	19.672	38.96	19.81
0.2	−5.969	−6.938	−8.372	3.799	3.673	2.734	11.030	23.11	9.73
0.3	−4.133	−4.853	−6.321	3.174	3.084	1.987	11.183	20.76	10.76
0.4	−3.479	−4.004	−4.633	2.082	2.037	1.690	4.744	11.20	3.85
0.5	−2.641	−3.088	−3.583	1.566	1.482	1.200	4.090	9.17	3.41
0.6	−2.220	−2.339	−2.856	0.880	1.029	0.669	2.142	5.88	1.63
0.7	−1.710	−1.903	−2.178	0.455	0.448	0.283	1.605	4.51	1.55
0.8	−1.190	−1.220	−1.416	0.164	0.251	0.124	0.348	2.07	0.21
0.9	−0.664	−0.675	−0.693	0.025	0.020	0.034	−0.460	0.28	−0.59

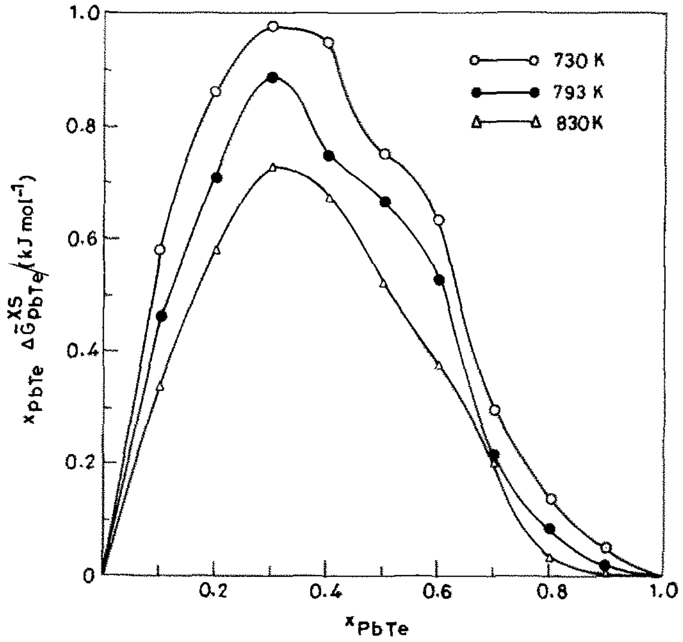

Fig. 6. Chiotti plots of $x_{\mathrm{PbTe}}\Delta\bar{G}^{\mathrm{XS}}_{\mathrm{PbTe}}$ vs. x_{PbTe} at different temperatures for estimation of $\Delta\bar{G}^{\mathrm{XS}}_{\mathrm{PbTe}}$ at infinite dilution.

Figs. 6 and 7. The values of γ_{PbTe} (and γ_{PbSe}) at infinite dilution, $\gamma^{(0)}_{\mathrm{PbTe}}$ (and $\gamma^{(0)}_{\mathrm{PbSe}}$) have been calculated from the values of $\Delta\bar{G}^{\mathrm{XS(0)}}_{\mathrm{PbTe}}$ (and $\Delta\bar{G}^{\mathrm{XS(0)}}_{\mathrm{PbSe}}$) using the relationship

$$\ln \gamma^{(0)}_{\mathrm{PbTe}} = \Delta\bar{G}^{\mathrm{XS(0)}}_{\mathrm{PbTe}}/RT \tag{9}$$

For the estimation of temperature-independent excess partial molar quantities, namely $\Delta\bar{H}^{\mathrm{M}}_{\mathrm{PbTe}}$, $\Delta\bar{H}^{\mathrm{M}}_{\mathrm{PbSe}}$, $\Delta\bar{S}^{\mathrm{XS}}_{\mathrm{PbTe}}$ and $\Delta\bar{S}^{\mathrm{XS}}_{\mathrm{PbSe}}$ at infinite dilution, these quantities are presented in suitable form in Fig. 8. All the terminal values for PbTe, namely $\Delta\bar{G}^{\mathrm{XS(0)}}_{\mathrm{PbTe}}$, $\Delta\bar{H}^{\mathrm{M(0)}}_{\mathrm{PbTe}}$, $\Delta\bar{S}^{\mathrm{XS(0)}}_{\mathrm{PbTe}}$ and $\gamma^{(0)}_{\mathrm{PbTe}}$, and for PbSe, namely $\Delta\bar{G}^{\mathrm{XS(0)}}_{\mathrm{PbSe}}$, $\Delta\bar{H}^{\mathrm{M(0)}}_{\mathrm{PbSe}}$, $\Delta\bar{S}^{\mathrm{XS(0)}}_{\mathrm{PbSe}}$ and $\gamma^{(0)}_{\mathrm{PbSe}}$, obtained from the relevant figures and calculations are incorporated in the relevant tables (Tables 2–5). The limiting values for the component PbTe are also shown in Figs. 4 and 5.

The integral molar thermodynamic quantities ΔQ of the system were calculated from the partial molar thermodynamic quantities of both binary components

$$\Delta Q_{\mathrm{PbTe}_x\mathrm{Se}_{1-x}} = x_{\mathrm{PbTe}}\,\Delta\bar{Q}_{\mathrm{PbTe}} + x_{\mathrm{PbSe}}\,\Delta\bar{Q}_{\mathrm{PbSe}} \tag{10}$$

The integral molar quantities thus obtained (at different temperatures) are summarized in Table 6 and are also presented in Fig. 9, in suitable form, as a function of composition at 830 K. For comparison, values of $\Delta G^{\mathrm{M}}_{\mathrm{id}}$ and $T\,\Delta S^{\mathrm{M}}_{\mathrm{id}}$ are also included in the figure. From Table 6, it is clear that the

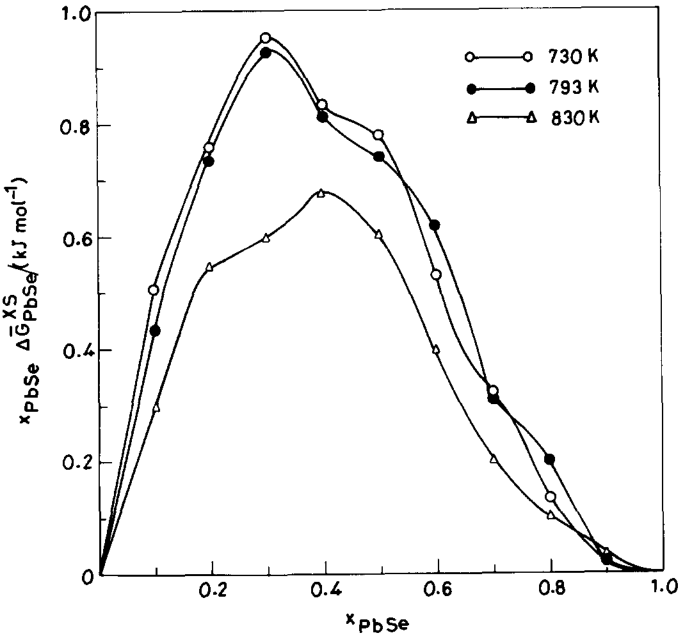

Fig. 7. Chiotti plots of $x_{PbSe}\Delta\bar{G}^{XS}_{PbSe}$ vs. x_{PbSe} at different temperatures for estimation of $\Delta\bar{G}^{XS}_{PbSe}$ at infinite dilution.

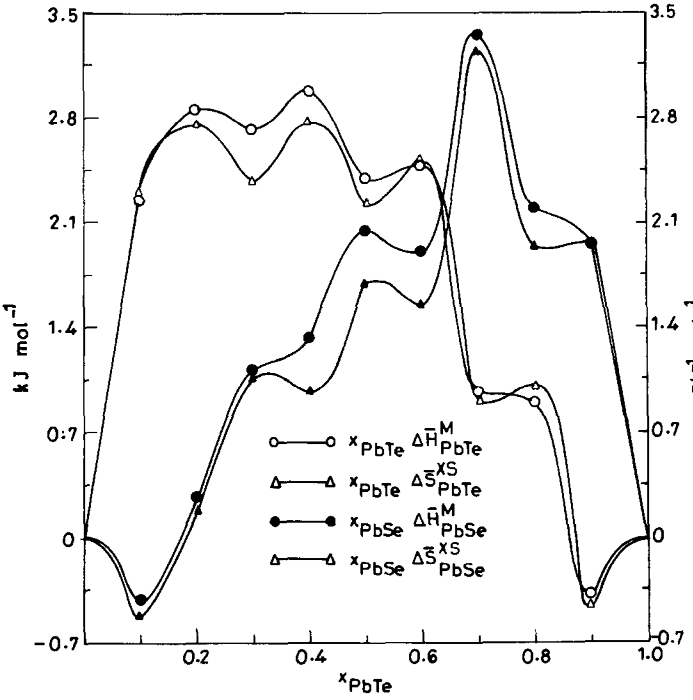

Fig. 8. Chiotti plots of $\Delta\bar{H}^{M}_{PbTe}$, $\Delta\bar{H}^{M}_{PbSe}$, $\Delta\bar{S}^{XS}_{PbTe}$ and $\Delta\bar{S}^{XS}_{PbSe}$ vs. composition to estimate their values at infinite dilution.

TABLE 6

Integral and excess molar thermodynamic quantities of liquid Te-saturated PbSe-PbTe solid solutions

x_{PbTe}	ΔG^M/kJ mol^{-1}			ΔG^{XS}/kJ mol^{-1}			ΔH^M/ kJ mol^{-1}	ΔS^M/ J K^{-1} mol^{-1}	ΔS^{XS}/ J K^{-1} mol^{-1}
	730 K	793 K	830 K	730 K	793 K	830 K			
0.1	−1.416	−1.667	−1.871	0.601	0.476	0.372	1.870	4.49	1.79
0.2	−2.048	−2.393	−2.777	0.989	0.906	0.677	3.160	7.10	2.94
0.3	−2.413	−2.826	−3.291	1.295	1.201	0.924	3.857	8.54	3.47
0.4	−2.606	−3.070	−3.565	1.478	1.367	1.079	4.255	9.35	3.75
0.5	−2.672	−3.166	−3.664	1.536	1.405	1.119	4.439	9.70	3.95
0.6	−2.613	−3.096	−3.590	1.471	1.341	1.054	4.387	9.55	3.95
0.7	−2.459	−2.888	−3.411	1.249	1.139	0.804	4.318	9.22	4.17
0.8	−2.139	−2.480	−2.873	0.898	0.819	0.580	3.090	7.12	2.97
0.9	−1.516	−1.727	−1.950	0.456	0.417	0.294	1.590	4.23	1.51

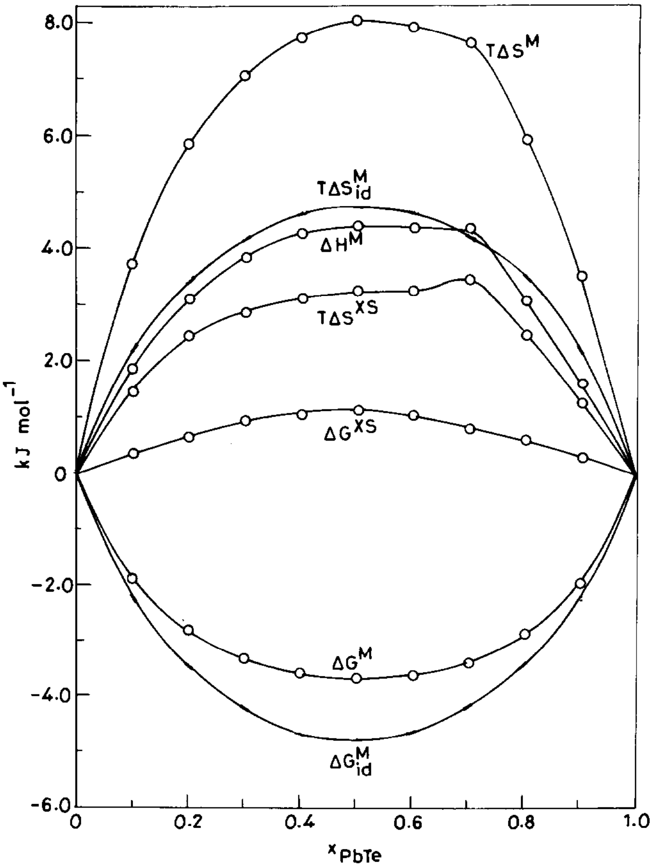

Fig. 9. Integral and excess molar thermodynamic quantities of liquid Te-saturated PbSe-PbTe solid solutions at 830 K.

negative values of the integral molar free energy of formation of PbSe–PbTe solid solutions increase with increasing temperature at each composition. This indicates that the feasibility of forming psuedo-binary solid solutions in the system increases with increasing temperature. The thermodynamic stability of the $PbTe_xSe_{1-x}$ increases with increasing temperature.

CONCLUSIONS

The activities of PbTe and PbSe in liquid Te-saturated PbSe–PbTe solid solutions in the temperature range 730–830 K exhibit positive deviation from Raoult's law and decrease with increasing temperature.

The continuous variation of the activity and activity coefficient of both the components, namely PbTe and PbSe, with composition indicates that the PbSe–PbTe system is completely miscible and consists of a single-phase field throughout the entire range of composition in the temperature range from 730 to 830 K. The detailed analysis of the α-function indicates that the PbSe–PbTe system does not follow a regular solution model. The thermodynamic stability of the system was seen to increase with increasing temperature.

ACKNOWLEDGEMENTS

The authors thank the Head of the Department of Metallurgical Engineering, Institute of Technology, Banaras Hindu University, for providing the necessary laboratory facilities. Financial assistance from the Ministry of Human Resource Development, Government of India, New Delhi (in the form of a sponsored research project) is gratefully acknowledged.

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