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Thermodynamic investigations of liquid-Te-saturated CdTe–ZnTe solid solutions

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Abstract

The activity of ZnTe in liquid-Te-saturated CdTe–ZnTe solid solutions in the range 743–848 K was measured by an electrochemical technique using LiCl–KCl + 5 wt% $ZnCl_2$ as the molten salt electrolyte. The activity of CdTe 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 have been calculated. All the excess partial molar thermodynamic parameters at infinite dilution have been accurately estimated by Chiotti's method. The thermodynamic properties of the system have been analysed in terms of Darken's stability and excess stability parameters. The continuous variation of the activity and activity coefficients of both the components, and the smooth, gradual variation of the values of stability and excess stability with composition indicate that the CdTe–ZnTe system is completely miscible and consists of a single-phase field throughout the entire range of composition in the range 743–848 K.

Keywords: Activity coefficient; EMF; Model; Solid solution; Thermodynamics; XRD

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1. Introduction

The development of crystal-growing techniques from metals has created a need for accurate thermodynamic data and a knowledge of the phase equilibria in semiconductor alloy systems [1–4] due to their potentially promising electrical and optical

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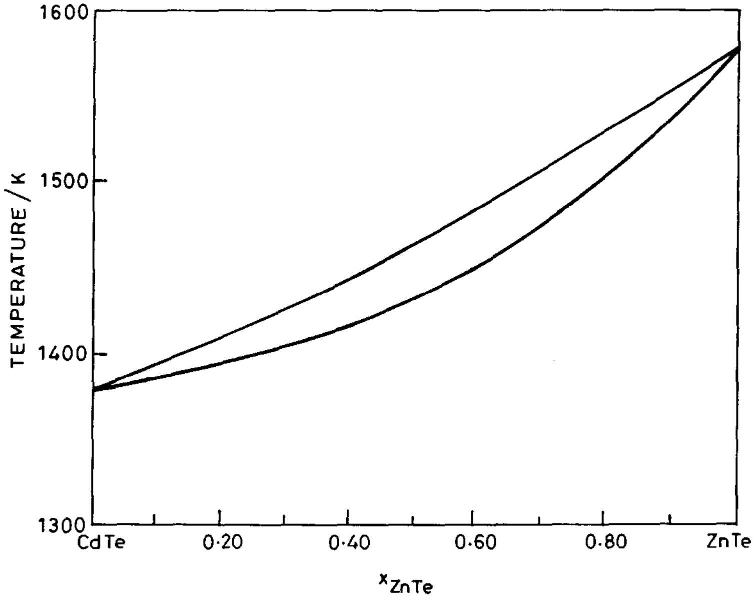

Fig. 1. Phase diagram of the CdTe–ZnTe system [12].

properties. There is much interest, in particular, in systems forming pseudo-binary solid solutions because the binary chalcogenides offer limited, fixed electronic parameter values, namely, the energy gap, the electrical 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 IIB chalcogenides offer widely selective ranges and have thus attracted considerable attention. The thermodynamic properties of the binary systems Zn–Te [5,6], Cd–Te [7,8] and Zn–Cd [9–11] have been studied by many investigators. However, thermodynamic data on the ternary system Zn–Cd–Te are scarce. The pseudo-binary CdTe–ZnTe system, forming a series of solid solutions [12,13] of the cubic zinc blende structure, follows Vegard's law [14,15]. Extensive studies have been made on the phase diagram of the system [12,16–18]; the phase diagram established by Steininger et al. [12] is shown in Fig. 1. Thermodynamic investigations on CdTe–ZnTe have been conducted by Zabdyr [19] and Katayama et al. [20] using an electrochemical technique. Zabdyr [19] has reported ideal behaviour of the system, whereas Katayama et al. [20] have observed positive deviation from ideality. Because of this discrepancy, the present investigation was undertaken to ascertain the thermodynamic behaviour of the CdTe–ZnTe system and to obtain accurate thermodynamic data by the electrochemical technique using LiCl–KCl + 5 wt.% $ZnCl_2$ as the molten salt electrolyte.

2. Experimental

2.1. Materials

High purity (99.999% pure) zinc and cadmium obtained from Johnson Matthey, UK, and tellurium obtained from Bhabha Atomic Research Centre, Bombay were used in this investigation. The following analytical reagent grade salts were used for preparation of the electrolyte: zinc chloride (Loba-Chemie, India), lithium chloride (Sisco, India) and potassium chloride (Qualigens, India).

2.2. Preparation of solid solutions

A series of solid solutions in the CdTe–ZnTe system, with a 10 mol% interval of ZnTe, was prepared by pyrosynthesis of the constituent elements. The high purity elements (zinc, cadmium and tellurium) were weighed to an accuracy of $\pm 1 \times 10^{-5}$ g in stoichiometric proportions and sealed in thick-walled silica capsules under a vacuum of better than 10^{-5} mbar. The capsules were heated at a rate of 2.5 K min^{-1} and held at 1300 K for about 40 h and then for 5 h at 1420 K. The samples were thoroughly shaken periodically and finally quenched in cold water.

2.3. Sample characterization

X-ray diffraction profiles of all the samples were recorded with a Philips PW1710 diffractometer using Cu K_{α_1} radiation to check the formation of single phases in the samples. All the samples were found to be single-phase solid solutions, by observation of the sharp peaks in the XRD patterns.

2.4. Electrochemical measurements

The activity of ZnTe in the liquid-Te-saturated CdTe–ZnTe system was determined by measuring the open circuit e.m.f. of the electrochemical cell

$$\text{ZnTe(s)} + \text{Te(l)}|\text{LiCl–KCl} + 5\ \text{wt\%}\ \text{ZnCl}_2|\text{Zn}_x\text{Cd}_{1-x}\text{Te(s)} + \text{Te(l)} \qquad (1)$$

The cell assembly used in the present investigation was made of Borosil glass having five lower limbs (each of 8 mm internal diameter) below a tubular electrolyte compartment (50 mm internal diameter). At the bottom of each limb were sealed identical electrode wires of tungsten (0.4 mm diameter and 200 mm length). The experiment was started by forming proper electrodes in the different limbs. In one limb the compound ZnTe, and in the other limbs, electrodes of appropriate solid solutions of $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ were formed by heating the powder mixture of the compound and the desired solid solutions with 10 at% excess of Te at 750 K for about 1 h under pure, dried argon. Thus, the electrodes of the compound and solid solutions were saturated with liquid tellurium. Further details of the cell assembly and experimental technique have been described elsewhere [21,22].

The temperature of the cell was controlled to an accuracy better than ±0.5 K by a digital temperature controller. Both the temperature and the cell e.m.f. were measured by a digital electrometer (Model 617, Keithley, USA) at an input impedance exceeding 2×10^{12} Ω. The cell attained equilibrium after 24 h and thereafter the e.m.f. values remained stable for 30 h. The general criteria for reversibility, i.e. the time-independent e.m.f. at constant temperature, the reproducibility of e.m.f. values whether approached from the higher or lower temperature side, and the recoverability of the same e.m.f. after passage of a small amount of current through the cell in either direction, were applied to ensure the correct reversible cell e.m.f. The reversibility of the galvanic cell (1) indicates the absence of any side or exchange reactions. 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 repeated to check the reproducibility of the results.

3. Results and discussion

3.1. Activity of components

The virtual cell reaction of the galvanic cell (1) may be represented as

$$\text{ZnTe (pure)} \rightarrow \text{ZnTe (in CdTe–ZnTe)} \tag{2}$$

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

$$a_{\text{ZnTe}} = \exp(-nFE/RT) \tag{3}$$

where n is the number of electrons transferred during reaction (2), E is the open circuit e.m.f. of the galvanic cell (1), F is the Faraday constant and R is the universal gas constant. The reversible cell e.m.f. values of the galvanic cell (1) measured in the temperature range 743–848 K are listed in Table 1. The variation of e.m.f. with temperature for nine compositions, shown in Fig. 2, was obtained by a least-square method and is also summarized in Table 1 in the form of the linear equation, $E = A + BT$. The error limits shown in the figure and table are the maximum deviations from average values based on two independent runs. From the e.m.f. values measured at different temperatures, the activities of ZnTe (a_{ZnTe}) in the Te-saturated $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ solid solutions were calculated and are listed in Table 2. The corresponding values of the activity coefficient of ZnTe (γ_{ZnTe}) were calculated using the relationship

$$\gamma_{\text{ZnTe}} = a_{\text{ZnTe}}/x_{\text{ZnTe}} \tag{4}$$

and are presented in Table 3 in the form of the linear equation, $\ln \gamma_{\text{ZnTe}} = A/T + B$. The activity and activity coefficient are both seen to decrease with increasing temperature. The variations of the activity and activity coefficient of ZnTe with the alloy composition (ZnTe) at a typical temperature of 848 K are shown in Figs. 3 and 4, respectively. The activity plot exhibits positive deviation from Raoult's law.

Table 1
Galvanic cell (1) e.m.f. values (in mV) at different temperatures

	Temperature in K				$E = A + BT$	
x_{ZnTe}	743	778	808	848	$-A$	B
0.1	38.49 ±1.00	42.63 ±1.05	46.87 ±1.11	53.79 ±1.25	70.31	0.1498
0.2	23.48 ±0.89	26.80 ±0.92	30.17 ±0.97	35.32 ±0.97	60.99	0.1132
0.3	17.45 ±0.65	19.46 ±0.72	22.43 ±0.78	25.71 ±0.90	42.80	0.0806
0.4	13.64 ±0.51	15.45 ±0.54	17.49 ±0.60	20.32 ±0.68	34.11	0.0640
0.5	10.66 ±0.46	12.94 ±0.48	14.48 ±0.51	16.55 ±0.62	30.55	0.0556
0.6	8.99 ±0.40	10.53 ±0.41	11.68 ±0.44	12.82 ±0.47	21.13	0.0373
0.7	6.61 ±0.36	7.88 ±0.39	9.13 ±0.42	10.54 ±0.44	17.93	0.0364
0.8	4.80 ±0.30	5.82 ±0.35	6.47 ±0.40	7.26 ±0.40	12.06	0.0229
0.9	2.68 ±0.24	2.98 ±0.27	3.28 ±0.28	3.83 ±0.30	5.55	0.0110

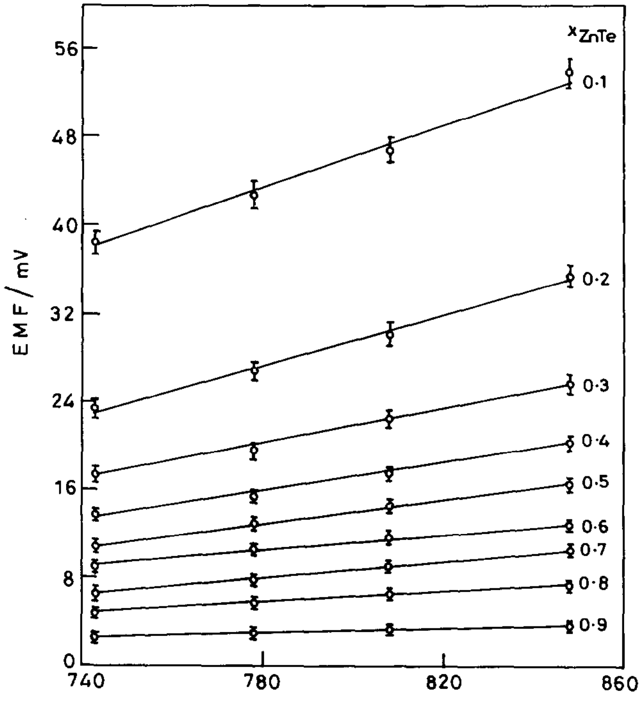

Fig. 2. EMF vs. temperature plot of galvanic cell (1).

Table 2
Activities of ZnTe and CdTe in liquid-Te-saturated CdTe–ZnTe solid solutions at different temperatures

x_{ZnTe}	a_{ZnTe}				a_{CdTe}			
	743 K	778 K	808 K	848 K	743 K	778 K	808 K	848 K
0.1	0.3004	0.2802	0.2601	0.2293	0.9133	0.9133	0.9130	0.9088
0.2	0.4802	0.4495	0.4203	0.3802	0.8434	0.8399	0.8379	0.8350
0.3	0.5797	0.5595	0.5256	0.4746	0.7931	0.7822	0.7791	0.7764
0.4	0.6529	0.6306	0.6050	0.5733	0.7446	0.7347	0.7223	0.7020
0.5	0.7167	0.6797	0.6600	0.6356	0.6904	0.6903	0.6728	0.6453
0.6	0.7552	0.7304	0.7150	0.7040	0.6474	0.6327	0.6098	0.5694
0.7	0.8133	0.7905	0.7693	0.7493	0.5642	0.5461	0.5305	0.5047
0.8	0.8607	0.8406	0.8304	0.8197	0.4756	0.4515	0.4210	0.3837
0.9	0.9197	0.9150	0.9100	0.9005	0.3187	0.2729	0.2445	0.2180

Table 3
Activity coefficients of ZnTe and CdTe in liquid-Te-saturated CdTe–ZnTe solid solutions at different temperatures

x_{ZnTe}	γ_{ZnTe}				$\ln \gamma_{\mathrm{ZnTe}} = A/T + B$	
	743 K	778 K	808 K	848 K	A	$-B$
0.0	3.853	3.388	3.054	2.754	2025	1.381
0.1	3.004	2.800	2.600	2.293	1613	1.057
0.2	2.400	2.250	2.100	1.900	1400	0.999
0.3	1.933	1.867	1.750	1.582	1208	0.949
0.4	1.632	1.575	1.513	1.433	778	0.604
0.5	1.433	1.360	1.320	1.271	714	0.553
0.6	1.259	1.217	1.192	1.173	490	0.511
0.7	1.162	1.129	1.100	1.071	422	0.343
0.8	1.075	1.050	1.038	1.025	280	0.308
0.9	1.022	1.017	1.011	1.001	128	0.150
x_{CdTe}	γ_{CdTe}				$\ln \gamma_{\mathrm{CdTe}} = A/T + B$	
	743 K	778 K	808 K	848 K	A	$-B$
0.0	4.172	3.502	3.143	2.754	2472	1.909
0.1	3.187	2.730	2.445	2.180	2282	1.921
0.2	2.378	2.258	2.105	1.919	1301	0.872
0.3	1.881	1.820	1.769	1.683	768	0.541
0.4	1.618	1.582	1.525	1.424	663	0.257
0.5	1.381	1.381	1.346	1.291	414	0.257
0.6	1.241	1.225	1.204	1.170	353	0.255
0.7	1.133	1.117	1.113	1.109	124	0.045
0.8	1.054	1.050	1.047	1.044	59	0.027
0.9	1.015	1.015	1.014	1.010	28	0.022

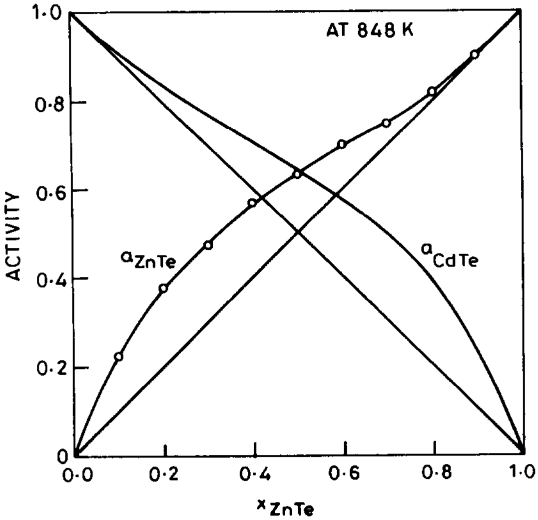

Fig. 3. Activity–composition relations in Te-saturated CdTe–ZnTe solid solutions at 848 K.

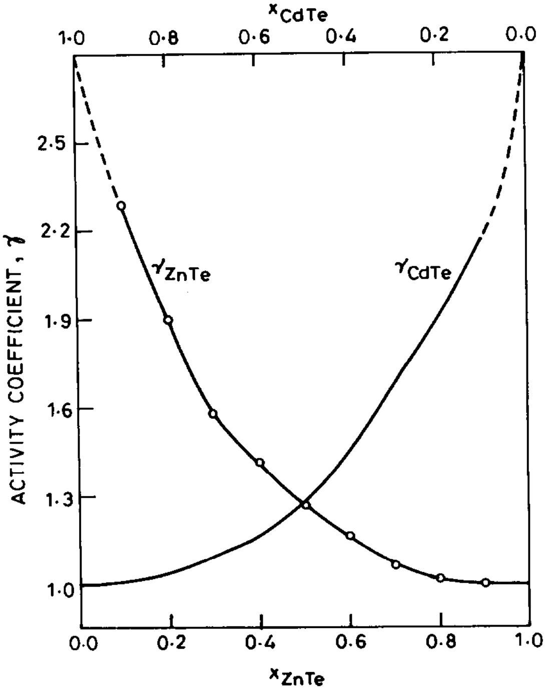

Fig. 4. Activity coefficient–composition relations in Te-saturated CdTe–ZnTe solid solutions at 848 K.

This is in agreement with the result of Katayama et al. [20]. The continuous variation of activity and activity coefficient with composition indicates that the CdTe–ZnTe system is completely miscible and consists of a single-phase field throughout the entire range of composition in the temperature range 743–848 K. This is in conformity with the results of Steininger [13], Tai [14], and Woolley and Ray [15].

The activity of CdTe in the liquid-Te-saturated CdTe–ZnTe solid solutions has been calculated using the following form of Gibbs–Duhem integration [23]

$$\ln \gamma_{\mathrm{CdTe}} = -\alpha_{\mathrm{ZnTe}}\, x_{\mathrm{ZnTe}}\, x_{\mathrm{CdTe}} - \int_{x_{\mathrm{CdTe}}=1}^{x_{\mathrm{CdTe}}=x_{\mathrm{CdTe}}} \alpha_{\mathrm{ZnTe}}\, \mathrm{d}x_{\mathrm{CdTe}} \qquad (5)$$

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

The values of the activities and activity coefficients of CdTe in liquid-Te-saturated CdTe–ZnTe solid solutions thus obtained are presented in Tables 2 and 3 and are also shown in the Figs. 3 and 4, at a typical temperature of 848 K, respectively. The activity values of CdTe show positive deviation from Raoult's law up to 90 mol% of CdTe, beyond which the system obeys Raoult's law. The small positive deviation from ideality in CdTe–ZnTe solid solutions is consistent with the small positive deviation of the liquidus and solidus curves in the phase diagram characterized by concavity towards the composition axis.

3.2. *Partial, excess and integral molar thermodynamic properties*

From the e.m.f. values measured at any temperature (Table 1), the partial molar free energies of mixing of ZnTe ($\Delta\bar{G}^{\mathrm{M}}_{\mathrm{ZnTe}}$) in liquid-Te-saturated CdTe–ZnTe solid solutions were calculated using the relationship

$$\Delta\bar{G}^{\mathrm{M}}_{\mathrm{ZnTe}} = RT \ln a_{\mathrm{ZnTe}} = -nFE \qquad (6)$$

The values of partial molar enthalpy ($\Delta\bar{H}^{\mathrm{M}}_{\mathrm{ZnTe}}$) and entropy ($\Delta\bar{S}^{\mathrm{M}}_{\mathrm{ZnTe}}$) of ZnTe in the CdTe–ZnTe system were obtained, respectively, from the intercept and slope of $\Delta\bar{G}^{\mathrm{M}}_{\mathrm{ZnTe}}$ versus T plots (using the least-squares method). The heat capacity contributions to the formation of solid solutions in the narrow span of temperatures 743–848 K were neglected in the calculations of $\Delta\bar{H}^{\mathrm{M}}_{\mathrm{ZnTe}}$ and $\Delta\bar{S}^{\mathrm{M}}_{\mathrm{ZnTe}}$. The excess partial molar thermodynamic quantities, namely $\Delta\bar{G}^{\mathrm{XS}}_{\mathrm{ZnTe}}$, $\Delta\bar{H}^{\mathrm{XS}}_{\mathrm{ZnTe}}$ and $\Delta\bar{S}^{\mathrm{XS}}_{\mathrm{ZnTe}}$ were calculated using the relationships

$$\Delta\bar{G}^{\mathrm{XS}}_{\mathrm{ZnTe}} = \Delta\bar{G}^{\mathrm{M}}_{\mathrm{ZnTe}} - \Delta\bar{G}^{\mathrm{id}}_{\mathrm{ZnTe}} = RT \ln \gamma_{\mathrm{ZnTe}} \qquad (7)$$

$$\Delta\bar{H}^{\mathrm{XS}}_{\mathrm{ZnTe}} = \Delta\bar{H}^{\mathrm{M}}_{\mathrm{ZnTe}} \quad \text{as } \Delta\bar{H}^{\mathrm{id}}_{\mathrm{ZnTe}} = 0 \qquad (8)$$

and

$$\Delta\bar{S}^{\mathrm{XS}}_{\mathrm{ZnTe}} = \Delta\bar{S}^{\mathrm{M}}_{\mathrm{ZnTe}} - \Delta\bar{S}^{\mathrm{id}}_{\mathrm{ZnTe}} = -\partial(\Delta\bar{G}^{\mathrm{XS}}_{\mathrm{ZnTe}})/\partial T \qquad (9)$$

The temperature-independent partial thermodynamic quantities, namely $\Delta\bar{H}^{\mathrm{M}}_{\mathrm{ZnTe}}$, $\Delta\bar{S}^{\mathrm{M}}_{\mathrm{ZnTe}}$ and $\Delta\bar{S}^{\mathrm{XS}}_{\mathrm{ZnTe}}$, and $\Delta\bar{G}^{\mathrm{M}}_{\mathrm{ZnTe}}$ and $\Delta\bar{G}^{\mathrm{XS}}_{\mathrm{ZnTe}}$ at different temperatures are summarized in Table 4. All the thermodynamic quantities in the form of $\Delta\bar{G}^{\mathrm{M}}_{\mathrm{ZnTe}}$, $\Delta\bar{G}^{\mathrm{XS}}_{\mathrm{ZnTe}}$,

Table 4
Partial and excess molar thermodynamic quantities of ZnTe in liquid-Te-saturated ZnTe–CdTe solid solutions

x_{ZnTe}	$-\Delta\bar{G}^{M}_{ZnTe}$ in kJ mol^{-1}				$\Delta\bar{G}^{xs}_{ZnTe}$ in kJ mol^{-1}				$\Delta\bar{H}^{M}_{ZnTe}$ in kJ mol^{-1}	$\Delta\bar{S}^{M}_{ZnTe}$ in J K^{-1} mol^{-1}	$\Delta\bar{S}^{xs}_{ZnTe}$ in J K^{-1} mol^{-1}
	743 K	778 K	808 K	848 K	743 K	778 K	808 K	848 K			
0.0	-	-	-	-	8.333	7.895	7.500	7.143	13.809	-	9.44
0.1	7.429	8.234	9.049	10.382	6.795	6.660	6.419	5.851	13.588	28.16	9.01
0.2	4.534	5.165	5.827	6.821	5.408	5.246	4.984	4.526	11.785	21.88	8.49
0.3	3.364	3.750	4.329	4.963	4.072	4.039	3.760	3.234	10.274	18.19	8.18
0.4	2.633	2.988	3.376	3.922	3.027	2.938	2.780	2.538	6.578	12.35	4.73
0.5	2.058	2.494	2.791	3.195	2.224	1.989	1.865	1.692	5.894	10.74	4.98
0.6	1.735	2.036	2.254	2.474	1.421	1.269	1.178	1.127	4.088	7.05	2.82
0.7	1.277	1.525	1.756	2.028	0.927	0.783	0.640	0.486	3.842	7.20	2.55
0.8	0.932	1.127	1.252	1.399	0.447	0.316	0.247	0.174	2.325	4.41	2.27
0.9	0.515	0.575	0.634	0.739	0.134	0.107	0.074	0.004	1.075	2.13	1.25

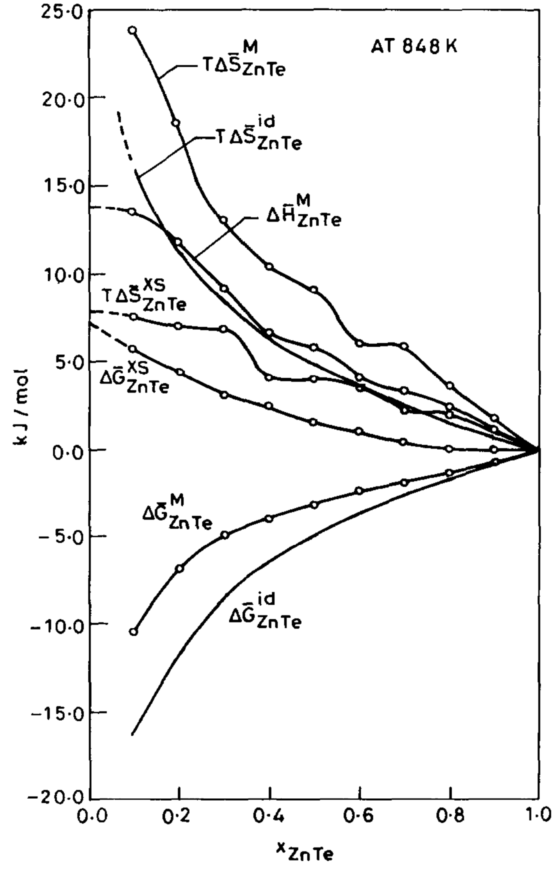

Fig. 5. Partial and excess thermodynamic quantities of ZnTe in liquid-Te-saturated CdTe–ZnTe solid solutions at 848 K.

$\Delta\bar{H}^{M}_{ZnTe}$, $T\Delta\bar{S}^{M}_{ZnTe}$ and $T\Delta\bar{S}^{XS}_{ZnTe}$ as a function of composition x_{ZnTe} are plotted in Fig. 5 at 848 K. For comparison, the corresponding values of $\Delta\bar{G}^{id}_{ZnTe}$ and $T\Delta\bar{S}^{id}_{ZnTe}$ are also incorporated in the figure.

The analogous thermodynamic parameters for the second component, i.e. CdTe, namely $\Delta\bar{G}^{M}_{CdTe}$, $\Delta\bar{H}^{M}_{CdTe}$, $\Delta\bar{S}^{M}_{CdTe}$, $\Delta\bar{G}^{XS}_{CdTe}$ and $\Delta\bar{S}^{XS}_{CdTe}$, have also been calculated from the estimated values of a_{CdTe} and γ_{CdTe} (based on the Gibbs–Duhem integration) and are listed in Table 5. The integral molar quantities (ΔQ^{M}: ΔG^{M}, ΔH^{M}, ΔS^{M}, ΔG^{XS} and ΔS^{XS}) of the CdTe–ZnTe solid solutions were obtained from the partial and excess molar quantities of the components, ZnTe and CdTe, using the equation

$$\Delta Q_{Zn_xCd_{1-x}Te} = x_{ZnTe}\Delta Q_{ZnTe} + x_{CdTe}\Delta Q_{CdTe} \qquad (10)$$

The integral molar quantities thus obtained (at different temperatures) are summarized in Table 6 and are also presented in Fig. 6 in a suitable form as a

Table 5
Partial and excess molar thermodynamic quantities of CdTe in liquid-Te-saturated CdTe–ZnTe solid solutions

x_{CdTe}	$-\Delta\bar{G}^{M}_{CdTe}$ in kJ mol^{-1}				$\Delta\bar{G}^{KS}_{CdTe}$ in kJ mol^{-1}				$\Delta\bar{H}^{M}_{CdTe}$ in kJ mol^{-1}	$\Delta\bar{S}^{M}_{CdTe}$ in J K^{-1} mol^{-1}	$\Delta\bar{S}^{xs}_{CdTe}$ in J K^{-1} mol^{-1}
	743 K	778 K	808 K	848 K	743 K	778 K	808 K	848 K			
0.0	–	–	–	–	8.824	8.108	7.692	7.143	20.494	–	15.95
0.1	7.065	8.399	9.464	10.741	7.160	6.496	6.005	5.494	18.881	34.99	15.85
0.2	4.591	5.144	5.813	6.753	5.352	5.267	4.999	4.594	10.933	20.79	7.40
0.3	3.535	3.914	4.258	4.821	3.902	3.875	3.830	3.668	6.561	12.22	4.63
0.4	2.686	2.961	3.323	3.970	2.974	2.966	2.833	2.490	5.561	12.29	2.18
0.5	2.289	2.398	2.663	3.089	1.994	2.086	1.994	1.798	3.564	7.77	2.19
0.6	1.822	1.994	2.185	2.495	1.334	1.310	1.248	1.107	2.984	6.43	2.01
0.7	1.432	1.589	1.677	1.784	0.771	0.718	0.719	0.731	1.007	3.31	0.35
0.8	1.052	1.128	1.188	1.272	0.326	0.316	0.311	0.302	0.482	2.08	0.20
0.9	0.561	0.586	0.612	0.675	0.090	0.095	0.096	0.068	0.248	1.07	0.12

Table 6
Integral and excess molar thermodynamic quantities of liquid-Te-saturated CdTe–ZnTe solid solutions

x_{ZnTe}	$-\Delta G^{M}$ in kJ mol^{-1}				ΔG^{ks} in kJ mol^{-1}				ΔH^{M} in kJ mol^{-1}	ΔS^{M} in J K^{-1} mol^{-1}	ΔS^{ks} in J K^{-1} mol^{-1}
	743 K	778 K	808 K	848 K	743 K	778 K	808 K	848 K			
0.1	1.248	1.352	1.456	1.646	0.763	0.753	0.726	0.648	1.584	3.78	1.09
0.2	1.750	1.937	2.117	2.383	1.342	1.302	1.244	1.149	2.740	6.04	1.86
0.3	2.013	2.238	2.474	2.827	1.762	1.713	1.632	1.482	3.789	7.78	2.69
0.4	2.148	2.393	2.662	3.067	2.011	1.963	1.862	1.679	4.419	8.79	3.20
0.5	2.174	2.447	2.728	3.143	2.109	2.038	1.932	1.745	4.730	9.26	3.49
0.6	2.116	2.407	2.683	3.074	2.043	1.950	1.842	1.673	4.690	9.14	3.54
0.7	1.955	2.242	2.508	2.867	1.821	1.712	1.598	1.440	4.531	8.71	3.65
0.8	1.664	1.932	2.164	2.470	1.428	1.307	1.201	1.059	2.021	7.68	3.52
0.9	1.170	1.358	1.517	1.739	0.838	0.748	0.668	0.553	2.855	5.41	2.71

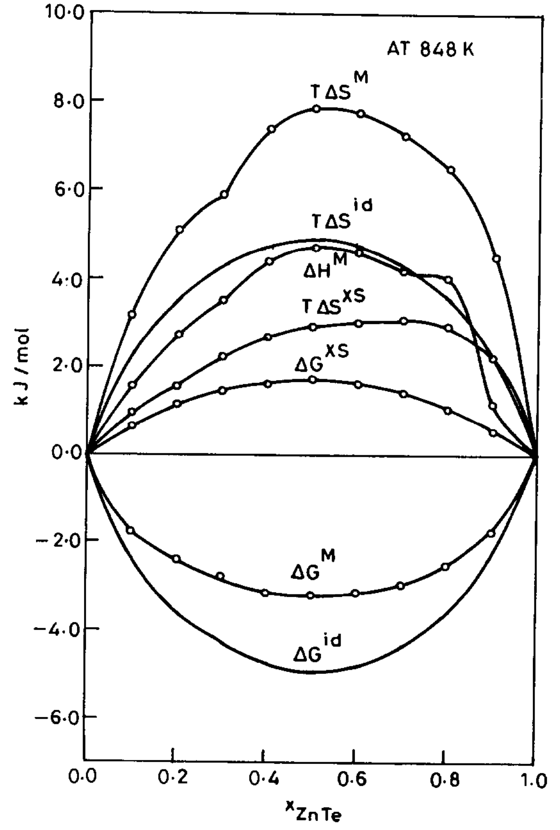

Fig. 6. Integral and excess molar thermodynamic quantities of liquid-Te-saturated CdTe–ZnTe solid solutions at 848 K.

function of composition (x_{ZnTe}) at 848 K. The quantities vary roughly parabolically. For comparison, values of ΔG^{id} and $T\Delta S^{\mathrm{id}}$ are also plotted in Fig. 6. From Table 6, it is clear that the negative values of the integral molar free energy of mixing of the solid solutions increase with increasing temperature at each composition. This indicates that the feasibility of formation of pseudo-binary solid solutions in the system CdTe–ZnTe increases with increasing temperature.

The excess partial thermodynamic quantities ($\Delta\bar{Q}^{-\mathrm{XS}}$) at infinite dilution have been estimated by the method proposed by Chiotti [24]. The method, based on $x_i\Delta\bar{Q}^{\mathrm{XS}}$ vs. x_i plots, has an advantage in determining excess partial molar quantities at infinite dilution because such plots have zero intercepts at $x_i = 0$ as well as at $x_i = 1$. Hence any excess partial thermodynamic quantity at infinite dilution ($\Delta\bar{Q}^{\mathrm{XS(0)}}$) can be estimated accurately from the slope of $x_i\Delta\bar{Q}^{\mathrm{XS}}$ vs. x_i plots at $x_i \rightarrow 0$. All the terminal values for ZnTe, namely $\Delta\bar{G}^{\mathrm{XS(0)}}_{\mathrm{ZnTe}}$, $\Delta\bar{H}^{\mathrm{M(0)}}_{\mathrm{ZnTe}}$, $\Delta\bar{S}^{\mathrm{XS(0)}}_{\mathrm{ZnTe}}$ and $\gamma^{(0)}_{\mathrm{ZnTe}}$, and for CdTe, namely $\Delta\bar{G}^{\mathrm{XS(0)}}_{\mathrm{CdTe}}$, $\Delta\bar{H}^{\mathrm{M(0)}}_{\mathrm{CdTe}}$, $\Delta\bar{S}^{\mathrm{XS(0)}}_{\mathrm{CdTe}}$ and $\gamma^{(0)}_{\mathrm{CdTe}}$ obtained by this method are incorporated in the respective tables (Tables 3–5).

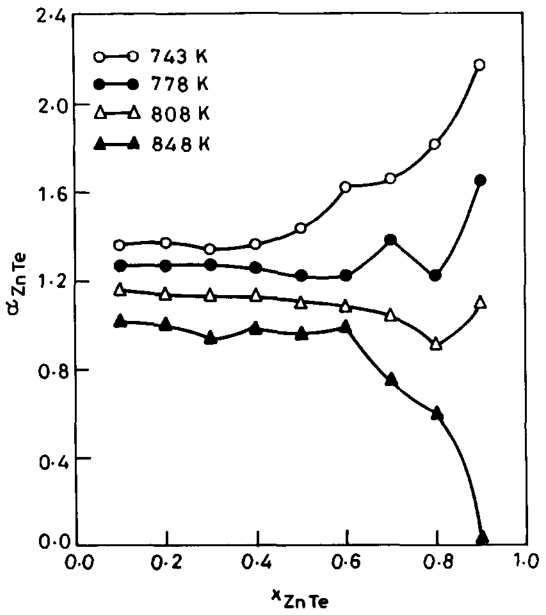

Fig. 7. Plot of α_{ZnTe} vs. x_{ZnTe} at different temperatures.

3.3. Solution model

The variation of α_{ZnTe} with composition (x_{ZnTe}) at different temperatures is shown in Fig. 7. From the figure, it is obvious that the α function is dependent on composition as well as on temperature; hence, the CdTe–ZnTe system does not follow the regular solution model. Furthermore, the α function does not satisfy Darken's quadratic formalism [25] as the data cannot be presented according to the equation

$$\ln(\gamma_{ZnTe}/\gamma^{(0)}_{ZnTe}) = \alpha_{CdTe}(x^2_{ZnTe} - 2x_{ZnTe}) \tag{11}$$

Hence, the thermodynamic behaviour of the system has been analysed in terms of Darken's stability and excess stability functions. Darken [25] has defined the stability and excess stability of a binary solution as the second derivatives of its molar free energy and excess molar free energy, respectively, with respect to the mole fraction of either constituent

$$\text{Stability} \equiv \frac{d^2\Delta G^M}{dx^2_{ZnTe}} = -2RT\frac{d(\ln a_{ZnTe})}{d(1-x_{ZnTe})^2} \tag{12}$$

$$\text{Excess stability} \equiv \frac{d^2\Delta G^{xs}}{dx^2_{ZnTe}} = -2RT\frac{d(\ln \gamma_{ZnTe})}{d(1-x_{ZnTe})^2} \tag{13}$$

Thus the values of stability and excess stability of the pseudo-binary CdTe–ZnTe system may be calculated respectively by multiplying the slopes of the ln a_{ZnTe} vs. $(1-x_{ZnTe})^2$ and ln γ_{ZnTe} vs. $(1-x_{ZnTe})^2$ plots with $-2RT$.

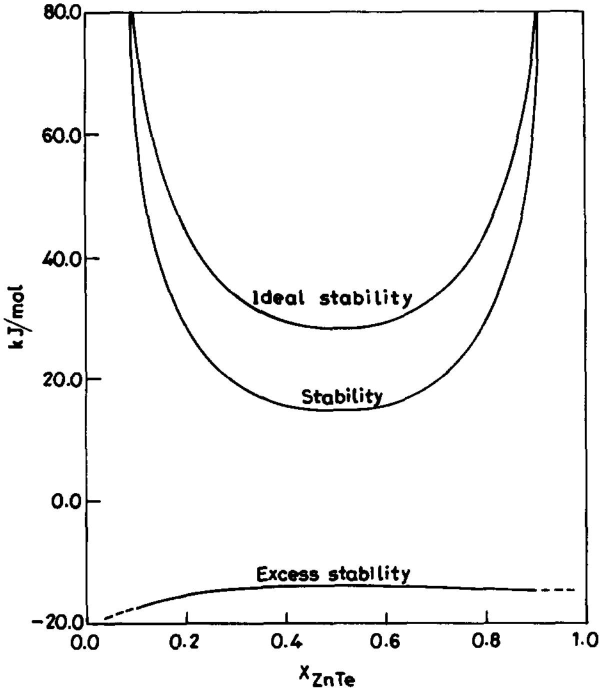

Fig. 8. Stability and excess stability functions of CdTe–ZnTe solid solutions at 848 K.

The variation of ln γ_{ZnTe} with composition in the system may be represented by the polynomial equation

$$\ln \gamma_{ZnTe} = -0.0094 + 1.0385\ (1 - x_{ZnTe})^2 - 0.2436\ (1 - x_{ZnTe})^4 + 0.2993\ (1 - x_{ZnTe})^6 \tag{14}$$

Hence the values of the excess stability have been calculated by multiplying the first derivative of Eq. (14) with respect to $(1 - x_{ZnTe})^2$ by $-2RT$. The values of Darken's stability have been calculated by adding the values of excess stability to the ideal stability, defined as

$$\text{Ideal stability} = RT/x_{ZnTe}(1 - x_{ZnTe}) \tag{15}$$

The values of stability and excess stability together with the ideal stability parameters of the solid solutions at a typical temperature of 848 K thus obtained are presented in Fig. 8. It is clear that the system is less stable compared to the ideal one. Calculations at different temperatures indicate that the stability of solid solutions increases with an increase in temperature at each composition. The smooth variation of stability and excess stability with composition further indicates that the system is completely miscible in the solid state in the temperature range 743–848 K.

4. Conclusions

Activities of ZnTe and CdTe in liquid-Te-saturated CdTe–ZnTe solid solutions in the temperature range 743–848 K exhibit positive deviation from Raoult's law and decrease with increasing temperature. The detailed analysis of the α function indicates that the CdTe–ZnTe system does not follow the regular solution model. The continuous variation of the activity and activity coefficient of both the components, ZnTe and CdTe, with composition, and the smooth variation of the values of stability and excess stability indicate that the CdTe–ZnTe system is completely miscible in the solid state and consists of a single-phase field throughout the entire range of composition in the temperature range 743–848 K. The thermodynamic stability of the system increases with an increase in temperature.

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