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# Investigations of the thermodynamic properties of Te-saturated ZnSe–ZnTe solid solutions

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## Abstract

The activity of ZnTe in Te-saturated ZnSe–ZnTe solid solutions was measured in the temperature range 710–845 K by an electrochemical technique using LiCl–KCl + 5 wt.% ZnCl<sub>2</sub> as the molten salt electrolyte. The activity of ZnSe has been calculated by Gibbs–Duhem integration using the  $\alpha$  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 quantities at infinite dilution have been accurately estimated by Chiotti's method. The composition dependence of the  $\alpha$  function confirms that the system does not follow a regular solution model. The results have been analysed in terms of Darken's stability and excess stability parameters. Detailed analyses of the results confirm that the system is completely miscible in the solid state and consists of a single-phase field throughout the entire range of composition.

*Keywords:* Thermodynamics; Partial molar free energy; Solid solutions

## 1. Introduction

Chalcogenides are compounds of metals with sulphur, selenium and tellurium. The chalcogenides of group IIB elements are important materials in semiconductor technology. In recent years they have gained prominence for their applications in various electronic, optoelectronic and photoelectric devices such as photovoltaic, X-ray and  $\gamma$ -ray detectors, thin film transistors, optical modulators, photoresistors, laser windows, fibre optics and solar cells. Although binary compounds based on the chalcogenide systems possess useful semiconducting characteristics, they offer limited and fixed values of electronic as well as optical parameters, i.e. energy gap, electrical, thermal and photoconductivities, dielectric and elastic constants, refractive index etc. These limitations can be overcome and electronic materials can be designed and tailor made to suit specific property requirements by alloying. Pseudobinary alloy systems between group IIB chalcogenides offering wide selective ranges have thus attracted considerable attention. In this respect the pseudobinary chalcogenide system ZnSe–ZnTe has received prominent attention by a number of investigators [1–6] owing to its increasing applications in optoelectronic devices such as visible region light-emitting diodes and electroluminescence.

During the past few years extensive research has been directed towards the development of device applications by studying electronic and optical properties of ZnSe–ZnTe solid solutions. While the electronic and optical properties of the system are well documented, the thermodynamic properties have not been investigated so far. In order to adjust the desired semiconducting characteristics by varying the alloy composition, it is important to have accurate knowledge of the thermodynamic data of the system throughout the entire range of composition.

The thermodynamic properties of the binary components of the system, i.e. ZnTe [7] and ZnSe [8], have been systematically investigated. In a recent paper [9] the partial molar thermodynamic properties of Zn in the Te-saturated ZnSe–ZnTe system have been reported. In view of the lack of knowledge of solution thermodynamics of the system ZnSe–ZnTe, the present investigation was undertaken with the prime objective of determining reliable thermodynamic data throughout the entire composition range of the system. In the present paper the activity of ZnTe in Te-saturated ZnSe–ZnTe solid solutions has been determined by an electrochemical technique using molten salt electrolyte. Various partial, integral and excess thermodynamic quantities have been calculated. The results have been

discussed in the light of Darken's stability and excess stability parameters.

## 2. Experimental details

### 2.1. Materials

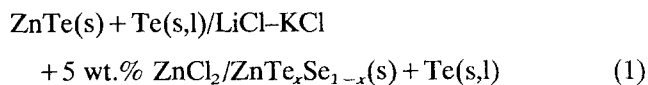
High purity (99.999% pure) selenium and tellurium obtained from Johnson Matthey (UK) and zinc powder obtained from Aldrich (USA) were used in this investigation. The following analytical reagent grade salts were used for preparation of the electrolyte: lithium chloride (Sisco, India), potassium chloride (Qualigens, India) and zinc chloride (Loba Chemie, India).

### 2.2. Preparation of compound and solid solutions

The compound ZnTe and a series of solid solutions in the system ZnSe–ZnTe at 10 mol.% intervals of ZnTe were prepared by pyrosynthesis of the component elements. About 10 g powder of high purity constituent elements (Zn, Se and Te) were weighed with an accuracy of  $\pm 10 \mu\text{g}$  in stoichiometric proportions and were homogenized and sealed in thick wall silica capsules under a vacuum of  $1.3 \times 10^{-3} \text{ Pa}$  ( $1 \times 10^{-5} \text{ mmHg}$ ). The capsules were heated at a rate of  $2.5 \text{ K min}^{-1}$  to 1350 K and held at this temperature for about 40 h and then at 1400 K for about 5 h and finally quenched in cold water. This method prevents any possibility of weight loss during the melting process and hence ensures the exact stoichiometric composition of the solid solutions.

### 2.3. Electrochemical measurements

The activity of ZnTe in solid or liquid Te-saturated ZnSe–ZnTe solid solutions was determined by measuring the open-circuit e.m.f. of the following electrochemical cell:

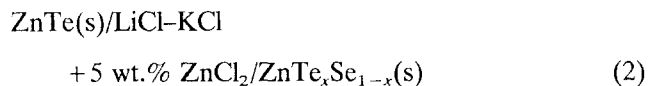


A eutectic mixture of LiCl–KCl containing 5 wt.% ZnCl<sub>2</sub> was used as the electrolyte.

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 of 50 mm internal diameter. At the bottom of each limb an identical electrode lead wire of tungsten (0.4 mm diameter and 200 mm length) was sealed. The design of the cell assembly and experimental technique were similar to those described earlier [10,11].

The experiment was started by forming the proper electrodes in different limbs. In one limb the compound

ZnTe and in the other limbs the electrodes of appropriate solid solutions (ZnTe<sub>x</sub>Se<sub>1-x</sub>) were formed by heating the powder mixture of the compound and the desired solid solutions with 10 at.% excess tellurium at 700 K for about 1 h under dried and pure argon (oxygen content less than 2 ppm). Thus each electrode of compound and solid solutions was saturated (enriched) with tellurium. In this context it is relevant to note that preliminary experiments with the cell



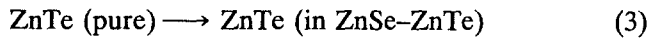
were unsuccessful owing to the irreversible nature of the cell. The irreversibility of the cell (2) is due to the deficiency of Te which is caused by vaporization of Te from ZnTe<sub>x</sub>Se<sub>1-x</sub> alloy electrodes. In order to prevent the possible loss of Te, activity of Te was maintained at unity by adding 10 at.% excess Te in both the left-hand and right-hand side electrodes. A number of additional experiments were also conducted in which the alloy electrodes contained 5 and 15 at.% excess Te. The e.m.f. values were found to be independent of the amount of excess tellurium. Hence, in order to maintain the consistency throughout the entire measurements, the experiments were carried out with the cell (1) containing 10 at.% excess Te in equilibrium with ZnTe and ZnTe<sub>x</sub>Se<sub>1-x</sub> electrodes.

After charging the reaction compartment with electrolyte, the cell assembly was flushed with argon for 1 h and then heated in a vertical tube furnace. The temperature of the cell was controlled to an accuracy of better than  $\pm 0.5 \text{ K}$  by a digital temperature controller. The temperature and cell e.m.f. were both measured by a digital electrometer (Keithley, USA; model 617) at an input impedance of greater than  $2 \times 10^{12} \Omega$ . The cell attained equilibrium after 24 h and thereafter the e.m.f. values remained reversible for over 30 h. The following general criteria for reversibility were applied to ensure the correct reversible cell e.m.f.: (i) the time-independent e.m.f. at a constant temperature; (ii) the reproducibility of e.m.f. values whether approached from the higher or lower temperature side; (iii) 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 galvanic cell (1) indicates the absence of any side or exchange reaction within the cell. After a constant e.m.f. had been attained at one temperature, the temperature was changed and sufficient time was allowed for reestablishment 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.

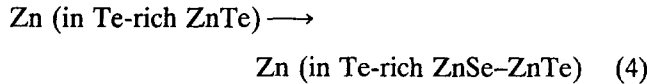
### 3. Results and discussion

#### 3.1. Activity of components

In order to realize the reaction



the cell (1) has been employed. The virtual cell reaction in the galvanic cell (1) may be represented as follows:



The activities  $a_{\text{Zn}}$  of Zn in the two electrodes are related to the e.m.f. of the cell (1):

$$-nFE = RT \ln \frac{a_{\text{Zn (in Te-rich ZnSe-ZnTe)}}}{a_{\text{Zn (in Te-rich ZnTe)}}} \quad (5)$$

where  $n$  is the number of electrons (2 in the present case) transferred during reaction (4),  $E$  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 mass action law for the general reaction



is

$$K = \frac{a_{\text{ZnTe}}}{a_{\text{Zn}} a_{\text{Te}}} \quad (7)$$

Since each electrode of the cell is saturated with the solid or liquid Te (i.e.  $a_{\text{Te}} = 1$ ),

$$a_{\text{Zn}} = K^* a_{\text{ZnTe}} \quad (8)$$

where  $K$  and  $K^*$  are constants. Thus from Eqs. (5) and (8)  $a_{\text{ZnTe}}$  in the system may be calculated as follows:

$$-nFE = RT \ln a_{\text{ZnTe (in Te-rich ZnSe-ZnTe)}} \quad (9)$$

The reversible cell e.m.f. values measured in the temperature range 710–845 K are listed in Table 1. The variation in e.m.f. with temperature for nine compositions as shown in Fig. 1 was calculated by the least-squares method and summarized in Table 1 in the form of linear equation ( $E = A + BT$ ). The error limits shown in Table 1 are the maximum deviations from the average values of cell e.m.f. based on two independent runs.

From the e.m.f. values measured at different temperatures activities of ZnTe in Te-saturated ZnSe–ZnTe solid solutions were calculated and summarized in Table 2 and also plotted in Fig. 2 at a typical temperature of 845 K. The corresponding values of the activity coefficient  $\gamma_{\text{ZnTe}}$  of ZnTe as calculated by using the relation

$$\gamma_{\text{ZnTe}} = \frac{a_{\text{ZnTe}}}{x_{\text{ZnTe}}} \quad (10)$$

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

$x_{\text{ZnTe}}$	E.m.f. (mV) at the following temperatures				Coefficients of $E = A + BT$	
	710 K	755 K	800 K	845 K	-A (mV)	B (mV K <sup>-1</sup> )
0.1	31.13 ±1.00	38.98 ±1.20	48.38 ±1.30	58.54 ±1.50	114.86	0.2036
0.2	20.51 ±0.80	25.85 ±0.90	31.76 ±1.00	36.67 ±1.10	65.28	0.1209
0.3	15.76 ±0.70	18.21 ±0.75	23.15 ±0.90	26.67 ±0.90	44.14	0.0836
0.4	11.87 ±0.60	13.60 ±0.65	17.68 ±0.75	20.80 ±0.80	37.35	0.0687
0.5	10.37 ±0.55	12.05 ±0.65	14.66 ±0.70	16.56 ±0.70	23.18	0.0471
0.6	8.32 ±0.50	9.67 ±0.55	11.35 ±0.60	13.02 ±0.65	16.67	0.0351
0.7	7.15 ±0.40	7.73 ±0.45	8.97 ±0.50	10.24 ±0.55	9.64	0.0234
0.8	5.20 ±0.35	5.68 ±0.35	6.24 ±0.40	6.96 ±0.40	4.07	0.0130
0.9	2.86 ±0.25	3.12 ±0.25	3.50 ±0.30	3.81 ±0.30	2.26	0.0072

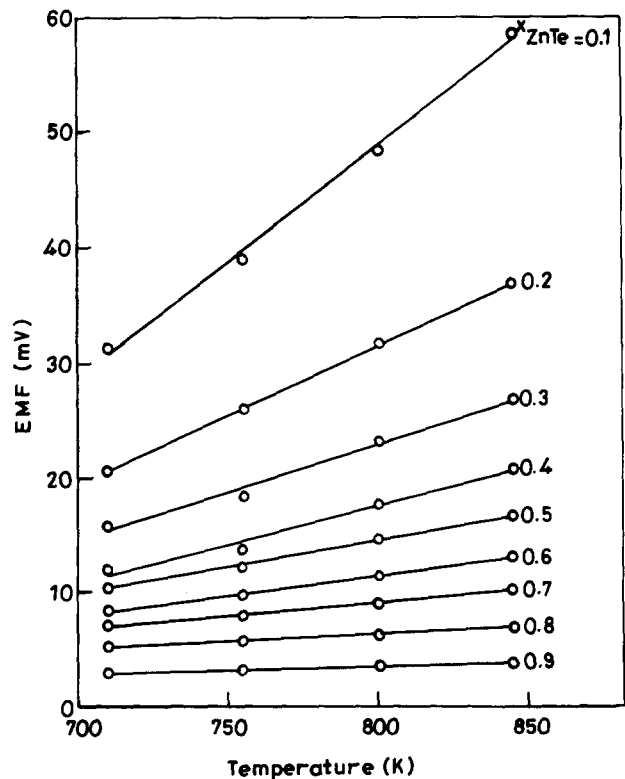


Fig. 1. E.m.f. vs. temperature plot of the galvanic cell (1).

are presented in Fig. 3 at 845 K. The plots of activity and activity coefficient (Figs. 2 and 3) exhibit positive deviation from Raoult's law up to 90 mol.% ZnTe,

Table 2  
Activity values of ZnTe and ZnSe in Te-saturated ZnSe–ZnTe solid solutions

$x_{\text{ZnTe}}$	$a_{\text{ZnTe}}$				$a_{\text{ZnSe}}$			
	710 K	755 K	800 K	845 K	710 K	755 K	800 K	845 K
0.1	0.3614 ± 0.0120	0.3016 ± 0.0114	0.2456 ± 0.0095	0.2002 ± 0.0084	0.9198	0.9153	0.9117	0.9045
0.2	0.5114 ± 0.0135	0.4516 ± 0.0127	0.3979 ± 0.0117	0.3651 ± 0.0112	0.8736	0.8560	0.8416	0.8160
0.3	0.5973 ± 0.0138	0.5712 ± 0.0134	0.5108 ± 0.0135	0.4806 ± 0.0120	0.8316	0.7931	0.7770	0.7462
0.4	0.6783 ± 0.0135	0.6582 ± 0.0133	0.5987 ± 0.0131	0.5647 ± 0.0125	0.7776	0.7356	0.752	0.6846
0.5	0.7124 ± 0.0130	0.6904 ± 0.0139	0.6535 ± 0.0134	0.6345 ± 0.0123	0.7460	0.7075	0.6675	0.6225
0.6	0.7618 ± 0.0126	0.7428 ± 0.0127	0.7194 ± 0.0126	0.6993 ± 0.0126	0.6872	0.6132	0.5944	0.5524
0.7	0.7915 ± 0.0105	0.7884 ± 0.0110	0.7708 ± 0.0113	0.7548 ± 0.0115	0.6396	0.5775	0.5226	0.4791
0.8	0.8436 ± 0.0098	0.8397 ± 0.0091	0.8344 ± 0.0097	0.8259 ± 0.0092	0.5250	0.4656	0.4096	0.3640
0.9	0.9107 ± 0.0075	0.9085 ± 0.0070	0.9034 ± 0.0079	0.9006 ± 0.0075	0.3300	0.2956	0.2514	0.2140

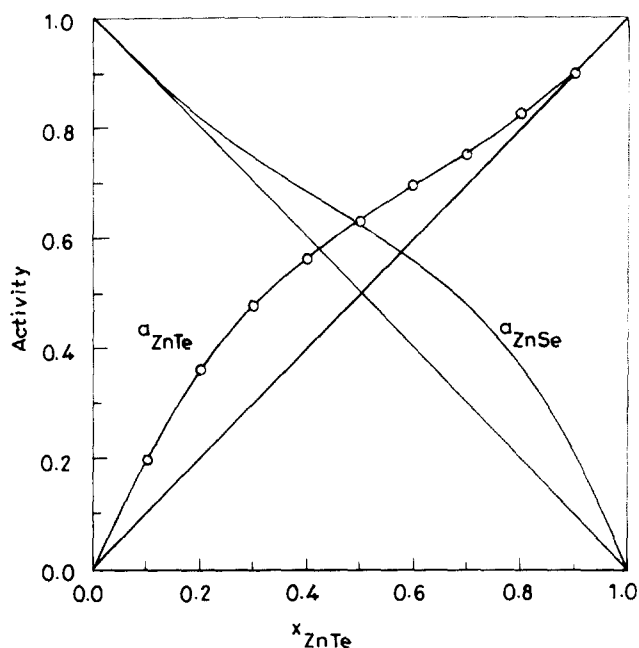


Fig. 2. Activity–composition relations in Te-saturated ZnSe–ZnTe solid solutions at 845 K.

which indicates the clustering of Se and Te in the second nearest neighbourhood (at the electronegative sublattice). Beyond 90 mol.% ZnTe, the system obeys Raoult's law.

The activity of ZnSe in the system has been calculated by using the following form of Gibbs–Duhem integration [12]:

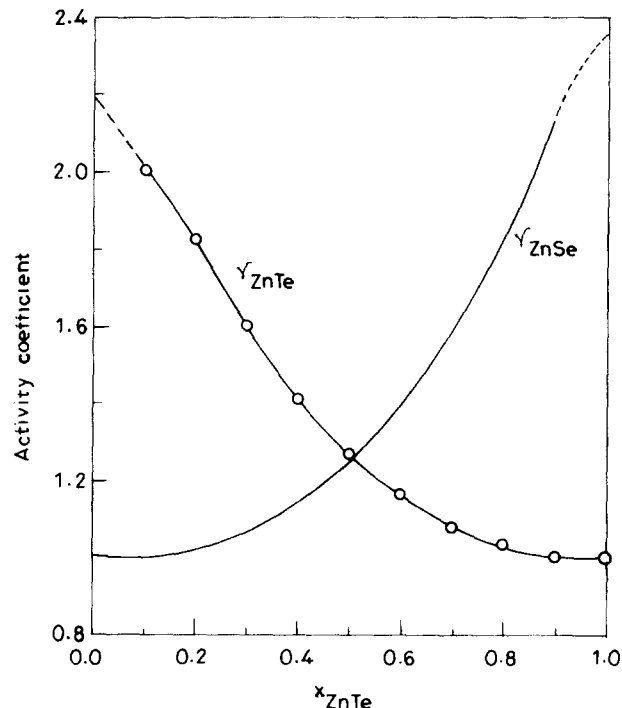


Fig. 3. Activity coefficient–composition relations in Te-saturated ZnSe–ZnTe solid solutions at 845 K.

$$\ln \gamma_{\text{ZnSe}} = -\alpha_{\text{ZnTe}} x_{\text{ZnTe}} x_{\text{ZnSe}} - \int_1^{x_{\text{ZnSe}}} \alpha_{\text{ZnTe}} dx_{\text{ZnSe}} \quad (11)$$

where

$$\alpha_{\text{ZnTe}} = \frac{\ln \gamma_{\text{ZnTe}}}{(1 - x_{\text{ZnTe}})^2}$$

The activity values of ZnSe in Te-saturated ZnSe–ZnTe solid solutions, so obtained, have also been incorporated in Table 2. The values of  $a_{\text{ZnSe}}$  and  $\gamma_{\text{ZnSe}}$  (at a typical temperature of 845 K) are also plotted in Figs. 2 and 3. These figures show positive deviation from Raoult's law up to 87 mol.% ZnSe, beyond which the system obeys Raoult's law.

From Table 2 it is clear that the values of the activity of ZnTe and ZnSe in Te-saturated ZnSe–ZnTe solid solutions decrease with the increase in temperature. This is consistent with the existing hypothesis of positive deviation. The continuous variation in activity and activity coefficient of both of the binary components, i.e. ZnTe and ZnSe, with composition (Figs. 2 and 3) confirms that the system ZnSe–ZnTe is completely miscible in the solid state and consists of a single phase throughout the entire range of composition. This is in conformity with the results of Aven and Garwacki [13], Larach et al. [14] and Mizetskaya et al. [15].

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

From the e.m.f. values measured at any temperature (Table 1) the partial molar free energy  $\Delta\tilde{G}_{\text{ZnTe}}^{\text{M}}$  of ZnTe in Te-saturated ZnSe–ZnTe solid solutions was calculated by using the relation

$$\Delta\tilde{G}_{\text{ZnTe}}^{\text{M}} = RT \ln a_{\text{ZnTe}} = -nFE \quad (12)$$

The values of partial molar enthalpy  $\Delta\tilde{H}_{\text{ZnTe}}^{\text{M}}$  and entropy  $\Delta\tilde{S}_{\text{ZnTe}}^{\text{M}}$  of ZnTe in Te-saturated ZnSe–ZnTe solid solutions were obtained respectively from the intercept and slope of  $\Delta\tilde{G}_{\text{ZnTe}}^{\text{M}}$  vs.  $T$  plots. In the calculation of  $\Delta\tilde{H}_{\text{ZnTe}}^{\text{M}}$  and  $\Delta\tilde{S}_{\text{ZnTe}}^{\text{M}}$ , the heat capacity contribution to the formation of solid solutions in the narrow temperature range 710–845 K has been neglected. The excess partial molar thermodynamic quantities were computed as follows:

$$\Delta\tilde{G}_{\text{ZnTe}}^{\text{XS}} = \Delta\tilde{G}_{\text{ZnTe}}^{\text{M}} - \Delta\tilde{G}_{\text{id}}^{\text{M}} = RT \ln \gamma_{\text{ZnTe}} \quad (13)$$

$$\Delta\tilde{H}_{\text{ZnTe}}^{\text{XS}} = \Delta\tilde{H}_{\text{ZnTe}}^{\text{M}} \text{ as } \Delta\tilde{H}_{\text{id}}^{\text{M}} = 0 \quad (14)$$

and

$$\Delta\tilde{S}_{\text{ZnTe}}^{\text{XS}} = \Delta\tilde{S}_{\text{ZnTe}}^{\text{M}} - \Delta\tilde{S}_{\text{id}}^{\text{M}} = - \frac{\partial(\Delta\tilde{G}_{\text{ZnTe}}^{\text{XS}})}{\partial T} \quad (15)$$

where  $\Delta\tilde{G}_{\text{id}}^{\text{M}}$ ,  $\Delta\tilde{H}_{\text{id}}^{\text{M}}$  and  $\Delta\tilde{S}_{\text{id}}^{\text{M}}$  refer to the corresponding values for the partial molar quantities of ZnTe expected from the system ZnSe–ZnTe if it behaved in ideal manner, i.e.

$$\Delta\tilde{G}_{\text{id}}^{\text{M}} = -T \Delta\tilde{S}_{\text{id}}^{\text{M}} = RT \ln x_{\text{ZnTe}} \quad (16)$$

Various partial molar thermodynamic quantities, i.e.  $\Delta\tilde{G}_{\text{ZnTe}}^{\text{M}}$ ,  $\Delta\tilde{G}_{\text{ZnTe}}^{\text{XS}}$ ,  $\Delta\tilde{H}_{\text{ZnTe}}^{\text{M}}$ ,  $\Delta\tilde{S}_{\text{ZnTe}}^{\text{M}}$  and  $\Delta\tilde{S}_{\text{ZnTe}}^{\text{XS}}$ , thus computed, are summarized in Table 3. All the partial molar thermodynamic quantities in the form of  $\Delta\tilde{G}_{\text{ZnTe}}^{\text{M}}$ ,  $\Delta\tilde{G}_{\text{ZnTe}}^{\text{XS}}$ ,  $\Delta\tilde{H}_{\text{ZnTe}}^{\text{M}}$ ,  $T \Delta\tilde{S}_{\text{ZnTe}}^{\text{M}}$  and  $T \Delta\tilde{S}_{\text{ZnTe}}^{\text{XS}}$  as a function of the alloy composition  $x_{\text{ZnTe}}$  at 845 K are plotted in Fig. 4. For comparison values of  $\Delta\tilde{G}_{\text{id}}^{\text{M}}$  and  $T \Delta\tilde{S}_{\text{id}}^{\text{M}}$  are also presented in the figure.

The analogous thermodynamic parameters for the second component (ZnSe), i.e.  $\Delta\tilde{G}_{\text{ZnSe}}^{\text{M}}$ ,  $\Delta\tilde{G}_{\text{ZnSe}}^{\text{XS}}$ ,  $\Delta\tilde{H}_{\text{ZnSe}}^{\text{M}}$ ,  $\Delta\tilde{S}_{\text{ZnSe}}^{\text{M}}$  and  $\Delta\tilde{S}_{\text{ZnSe}}^{\text{XS}}$  have also been calculated from the estimated values of  $a_{\text{ZnSe}}$  and  $\gamma_{\text{ZnSe}}$  (based on Gibbs-Duhem integration) and are listed in Table 4.

The excess partial molar thermodynamic parameters  $\Delta\tilde{Q}_i^{\text{XS}}$  of components at infinite dilution can be estimated according to the procedure discussed by Chiotti [16]. The method based on  $x_i \Delta\tilde{Q}_i^{\text{XS}}$  vs.  $x_i$  plots presents a specific advantage in determining excess partial molar quantities at infinite dilution because such plots have zero intercepts at  $x_i = 0$  as well as  $x_i = 1$ . Hence, any excess partial molar thermodynamic quantity  $\Delta\tilde{Q}_i^{\text{XS}(0)}$  at infinite dilution can be estimated accurately from the slope of  $x_i \Delta\tilde{Q}_i^{\text{XS}}$  vs.  $x_i$  plots at  $x_i \rightarrow 0$ . All the terminal values for ZnTe, i.e.  $\Delta\tilde{G}_{\text{ZnTe}}^{\text{XS}(0)}$ ,  $\Delta\tilde{H}_{\text{ZnTe}}^{\text{M}(0)}$  and  $\Delta\tilde{S}_{\text{ZnTe}}^{\text{XS}(0)}$ , and for ZnSe, i.e.  $\Delta\tilde{G}_{\text{ZnSe}}^{\text{XS}(0)}$ ,  $\Delta\tilde{H}_{\text{ZnSe}}^{\text{M}(0)}$  and  $\Delta\tilde{S}_{\text{ZnSe}}^{\text{XS}(0)}$ , obtained by this method have been incorporated in Tables 3 and 4. The limiting values for the component ZnTe have also been plotted in Fig. 4.

The integral molar thermodynamic quantities  $\Delta Q$  ( $\Delta G^{\text{M}}$ ,  $\Delta G^{\text{XS}}$ ,  $\Delta H^{\text{M}}$ ,  $\Delta S^{\text{M}}$  and  $\Delta S^{\text{XS}}$ ) of formation of the solid solutions in the system ZnSe–ZnTe were calculated from the partial molar quantities of ZnTe and ZnSe using the relationship

$$\Delta Q = x_{\text{ZnTe}} \Delta\tilde{Q}_{\text{ZnTe}} + x_{\text{ZnSe}} \Delta\tilde{Q}_{\text{ZnSe}} \quad (17)$$

The integral molar quantities so obtained (at different temperatures) are summarized in Table 5 and also presented in Fig. 5 in a suitable form as a function of composition at a typical temperature of 845 K. For comparison values of  $\Delta\tilde{G}_{\text{id}}^{\text{M}}$  and  $T \Delta\tilde{S}_{\text{id}}^{\text{M}}$  are also included in the figure. All the integral quantities vary roughly parabolically with composition. A high value of positive entropy of mixing clearly reflects the formation of solid solutions with substantially disordered atomic distribution from the well-ordered ZnTe and ZnSe compounds. This may also be partly due to clustering of Te and Se at the electronegative sublattices. From Table 5 it is clear that the negative values of integral molar free energy of formation of ZnSe–ZnTe solid solutions increase with increase in temperature at each composition. Thus the thermodynamic stability of the system increases with temperature.

Table 3  
Partial and excess molar thermodynamic quantities of ZnTe in Te-saturated ZnSe–ZnTe solid solutions

$x_{\text{ZnTe}}$	$-\Delta\bar{G}_{\text{ZnTe}}^{\text{M}} (\text{kJ mol}^{-1})$				$\Delta\bar{G}_{\text{ZnTe}}^{\text{XS}} (\text{kJ mol}^{-1})$				$\Delta\bar{H}_{\text{ZnTe}}^{\text{M}} (\text{kJ mol}^{-1})$	$\Delta\bar{S}_{\text{ZnTe}}^{\text{M}} (\text{J K}^{-1} \text{mol}^{-1})$	$\Delta\bar{S}_{\text{ZnTe}}^{\text{XS}} (\text{J K}^{-1} \text{mol}^{-1})$
	710 K	755 K	800 K	845 K	710 K	755 K	800 K	845 K			
0.0	–	–	–	–	8.423	7.693	6.731	5.567	23.419	–	21.09
0.1	6.008 $\pm 0.199$	7.524 $\pm 0.242$	9.339 $\pm 0.262$	11.300 $\pm 0.301$	7.584 $\pm 0.199$	6.929 $\pm 0.242$	5.976 $\pm 0.262$	4.877 $\pm 0.301$	22.170	39.30	20.16
0.2	3.959 $\pm 0.157$	4.990 $\pm 0.179$	6.129 $\pm 0.199$	7.079 $\pm 0.218$	5.542 $\pm 0.157$	5.113 $\pm 0.179$	4.577 $\pm 0.199$	4.230 $\pm 0.218$	12.600	23.34	9.94
0.3	3.042 $\pm 0.138$	3.515 $\pm 0.149$	4.468 $\pm 0.178$	5.148 $\pm 0.177$	4.065 $\pm 0.138$	4.042 $\pm 0.149$	3.541 $\pm 0.178$	3.311 $\pm 0.177$	8.520	16.16	6.14
0.4	2.291 $\pm 0.119$	2.625 $\pm 0.128$	3.412 $\pm 0.147$	4.015 $\pm 0.157$	3.118 $\pm 0.119$	3.128 $\pm 0.128$	2.684 $\pm 0.147$	2.424 $\pm 0.157$	7.209	13.24	5.61
0.5	2.002 $\pm 0.108$	2.325 $\pm 0.128$	2.830 $\pm 0.137$	3.196 $\pm 0.138$	2.091 $\pm 0.108$	2.026 $\pm 0.128$	1.781 $\pm 0.137$	1.674 $\pm 0.138$	4.474	9.09	3.32
0.6	1.606 $\pm 0.099$	1.866 $\pm 0.103$	2.190 $\pm 0.118$	2.513 $\pm 0.128$	1.411 $\pm 0.099$	1.340 $\pm 0.103$	1.207 $\pm 0.118$	1.079 $\pm 0.128$	3.218	6.78	2.51
0.7	1.380 $\pm 0.079$	1.429 $\pm 0.089$	1.731 $\pm 0.099$	1.976 $\pm 0.108$	0.747 $\pm 0.079$	0.745 $\pm 0.089$	0.640 $\pm 0.099$	0.528 $\pm 0.108$	1.861	4.52	1.69
0.8	1.004 $\pm 0.069$	1.097 $\pm 0.068$	1.204 $\pm 0.078$	1.344 $\pm 0.079$	0.316 $\pm 0.069$	0.306 $\pm 0.068$	0.280 $\pm 0.078$	0.221 $\pm 0.079$	0.786	2.51	0.69
0.9	0.552 $\pm 0.049$	0.602 $\pm 0.049$	0.676 $\pm 0.058$	0.736 $\pm 0.058$	0.070 $\pm 0.049$	0.056 $\pm 0.049$	0.027 $\pm 0.058$	0.007 $\pm 0.058$	0.436	1.39	0.05

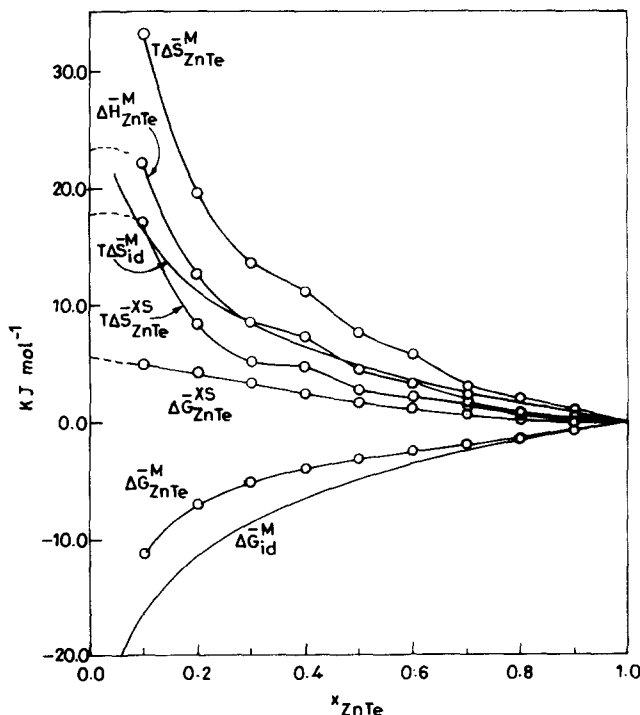


Fig. 4. Partial and excess molar thermodynamic quantities of ZnTe in Te-saturated ZnSe–ZnTe solid solutions at 845 K.

### 3.3. Solution model

The  $\alpha$  functions for both of the components ZnTe and ZnSe in the system have been plotted as function

of composition at different temperatures in Fig. 6. From the figure it is clear that

$$\alpha_{\text{ZnTe}} \neq \alpha_{\text{ZnSe}} \quad (18)$$

In addition to this the  $\alpha$  functions are also found to vary with composition in a considerable manner. These behaviours of  $\alpha$  functions reflect that the system ZnSe–ZnTe does not follow a regular solution model. The considerable positive values of excess entropy also highlight the non-regular behaviour of the system. Further, the system does not satisfy Darken's quadratic formalism [17], as the data cannot be presented according to either form of the following equations:

$$\ln(\gamma_{\text{ZnTe}}/\gamma_{\text{ZnTe}}^{(0)}) = \alpha_{\text{ZnSe}}(x_{\text{ZnTe}}^2 - 2x_{\text{ZnTe}}) \quad (19)$$

$$\ln(\gamma_{\text{ZnSe}}/\gamma_{\text{ZnSe}}^{(0)}) = \alpha_{\text{ZnTe}}(x_{\text{ZnSe}}^2 - 2x_{\text{ZnSe}}) \quad (20)$$

Hence the thermodynamic behaviour of the ZnSe–ZnTe system has been analysed in the light of Darken's stability and excess stability parameters. Darken [17] has defined 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; by definition, the stability is:

$$\frac{d^2 \Delta G^{\text{M}}}{dx_{\text{ZnTe}}^2} = -2RT \frac{d \ln a_{\text{ZnTe}}}{d(1-x_{\text{ZnTe}})^2} \quad (21)$$

Table 4

Partial and excess molar thermodynamic quantities of ZnSe in Te-saturated ZnSe–ZnTe solid solutions

$x_{\text{ZnTe}}$	$-\Delta\bar{G}_{\text{ZnSe}}^{\text{M}}$ (kJ mol <sup>-1</sup> )				$\Delta\bar{G}_{\text{ZnSe}}^{\text{XS}}$ (kJ mol <sup>-1</sup> )				$\Delta\bar{H}_{\text{ZnSe}}^{\text{M}}$ (kJ mol <sup>-1</sup> )	$\Delta\bar{S}_{\text{ZnSe}}^{\text{M}}$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta\bar{S}_{\text{ZnSe}}^{\text{XS}}$ (J K <sup>-1</sup> mol <sup>-1</sup> )
	710 K	755 K	800 K	845 K	710 K	755 K	800 K	845 K			
0.0	–	–	–	–	7.905	7.598	6.703	6.034	18.109	–	14.12
0.1	6.544	7.650	9.138	10.832	7.048	6.803	6.132	5.345	16.323	31.99	12.84
0.2	3.804	4.798	5.937	7.100	5.697	5.304	4.768	4.207	13.643	24.50	11.12
0.3	2.638	3.446	4.316	5.170	4.469	4.111	3.692	3.289	10.735	18.81	8.78
0.4	2.214	3.070	3.460	4.169	3.194	2.682	2.634	2.268	7.579	13.90	6.28
0.5	1.730	2.172	2.689	3.330	2.362	2.179	1.922	1.539	6.706	11.82	6.06
0.6	1.485	1.928	2.229	2.662	1.531	1.279	1.168	0.927	4.545	8.52	4.27
0.7	1.089	1.455	1.678	2.057	1.017	0.784	0.694	0.499	3.833	6.95	3.65
0.8	0.798	0.976	1.147	1.429	0.520	0.425	0.337	0.139	2.479	4.59	2.74
0.9	0.493	0.556	0.615	0.705	0.128	0.106	0.086	0.035	0.609	1.54	0.66

Table 5

Integral and excess molar thermodynamic quantities of Te-saturated ZnSe–ZnTe solid solutions

$x_{\text{ZnTe}}$	$-\Delta\bar{G}^{\text{M}}$ (kJ mol <sup>-1</sup> )				$\Delta\bar{G}^{\text{XS}}$ (kJ mol <sup>-1</sup> )				$\Delta\bar{H}^{\text{M}}$ (kJ mol <sup>-1</sup> )	$\Delta\bar{S}^{\text{M}}$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta\bar{S}^{\text{XS}}$ (J K <sup>-1</sup> mol <sup>-1</sup> )
	710 K	755 K	800 K	845 K	710 K	755 K	800 K	845 K			
0.1	1.045	1.253	1.487	1.765	0.874	0.788	0.675	0.519	2.765	5.32	2.61
0.2	1.430	1.779	2.143	2.559	1.524	1.363	1.185	0.957	4.503	8.34	4.18
0.3	1.675	2.073	2.515	2.984	1.931	1.761	1.548	1.343	5.239	9.71	4.40
0.4	1.807	2.207	2.742	3.203	2.166	2.019	1.774	1.526	5.611	10.41	4.81
0.5	1.866	2.249	2.760	3.263	2.226	2.103	1.852	1.607	5.590	10.46	4.69
0.6	1.849	2.348	2.698	3.175	2.124	1.877	1.778	1.555	4.962	9.30	4.02
0.7	1.757	2.078	2.507	2.934	1.872	1.755	1.556	1.356	4.523	8.81	3.82
0.8	1.564	1.837	2.151	2.495	1.392	1.306	1.178	1.018	3.357	6.91	2.78
0.9	1.151	1.307	1.527	1.746	0.767	0.731	0.638	0.541	2.025	4.45	1.33

and the excess stability is

$$\frac{d^2 \Delta G^{\text{XS}}}{dx_{\text{ZnTe}}^2} = -2RT \frac{d \ln \gamma_{\text{ZnTe}}}{d(1-x_{\text{ZnTe}})^2} \quad (22)$$

Thus the values of stability and excess stability of the pseudobinary system ZnSe–ZnTe may be calculated by multiplying the slopes of respectively  $\ln a_{\text{ZnTe}}$  vs.  $(1-x_{\text{ZnTe}})^2$  and  $\ln \gamma_{\text{ZnTe}}$  vs.  $(1-x_{\text{ZnTe}})^2$  plots by  $-2RT$ . The plot of  $\ln \gamma_{\text{ZnTe}}$  vs.  $(1-x_{\text{ZnTe}})^2$  has been observed to follow the following formalism:

$$\begin{aligned} \ln \gamma_{\text{ZnTe}} = & -0.0085 + 0.9529(1-x_{\text{ZnTe}})^2 \\ & + 0.1565(1-x_{\text{ZnTe}})^4 \\ & - 0.3976(1-x_{\text{ZnTe}})^8 \end{aligned} \quad (23)$$

Hence the values of excess stability have been calculated by multiplying the first derivative of Eq. (23) with respect to  $(1-x_{\text{ZnTe}})^2$  by  $-2RT$ . The values of Darken's stability have been calculated by adding the values of excess stability to the ideal stability, defined as

$$\frac{RT}{x_{\text{ZnTe}}(1-x_{\text{ZnTe}})} \quad (24)$$

The stability and excess stability of the ZnSe–ZnTe system together with the ideal stability parameters obtained have been plotted in Fig. 7 at a typical temperature of 845 K. From the figure it is clear that the system ZnSe–ZnTe is less stable than the ideal system. This is because of the positive deviation of the system from Raoult's law. The clustering of Se and Te at the electronegative sites decreases the stability of the solid solutions to a considerable extent. Further, calculations at different temperatures reflect that the values of Darken's stability of the system increase with the increase in temperature. This is associated with the decrease in negative values of excess stability. Hence the system behaves in a more ideal manner at the higher temperatures. The positive values of stability and smooth variation in excess stability with composition further indicate that the system ZnSe–ZnTe is completely miscible in the solid state and consists of a single-phase field throughout the entire range of composition in the temperature range 710–845 K.

#### 4. Conclusions

Activities of ZnTe and ZnSe in Te-saturated ZnSe–ZnTe solid solutions in the temperature range

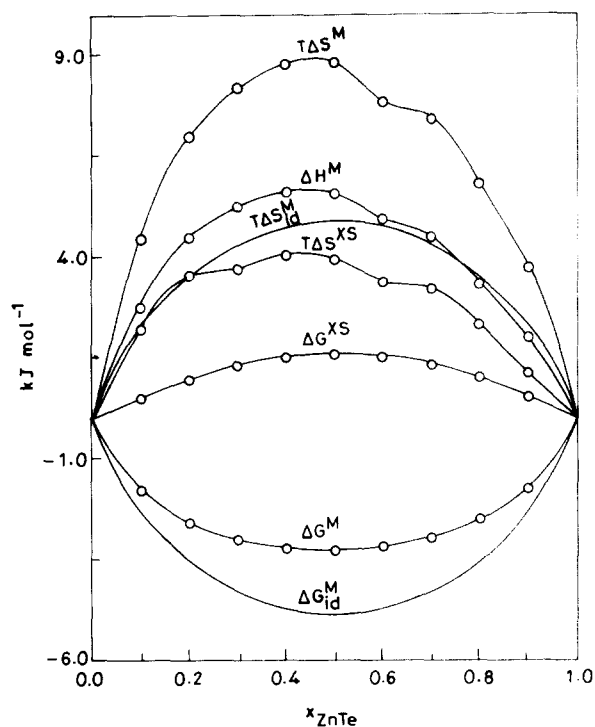


Fig. 5. Integral and excess molar thermodynamic quantities of Te-saturated ZnSe-ZnTe solid solutions at 845 K.

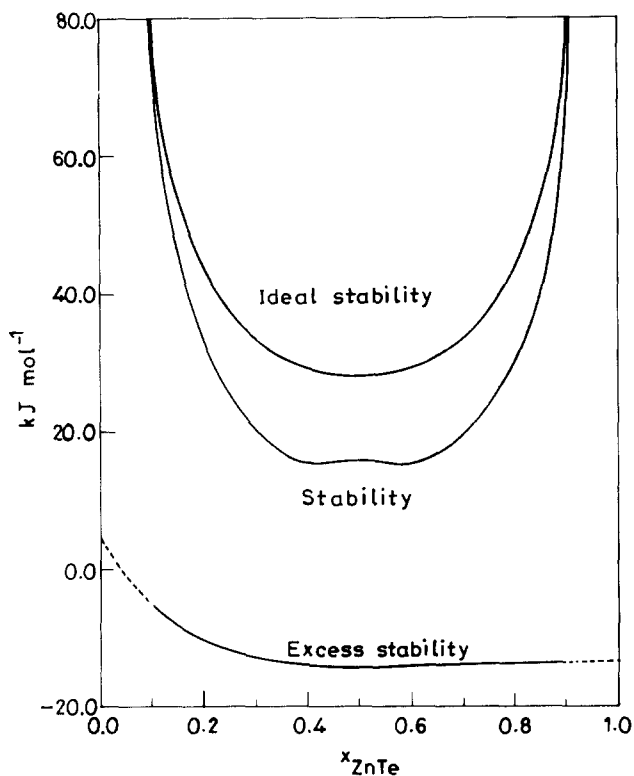


Fig. 7. Stability and excess stability functions of ZnSe-ZnTe solid solutions at 845 K.

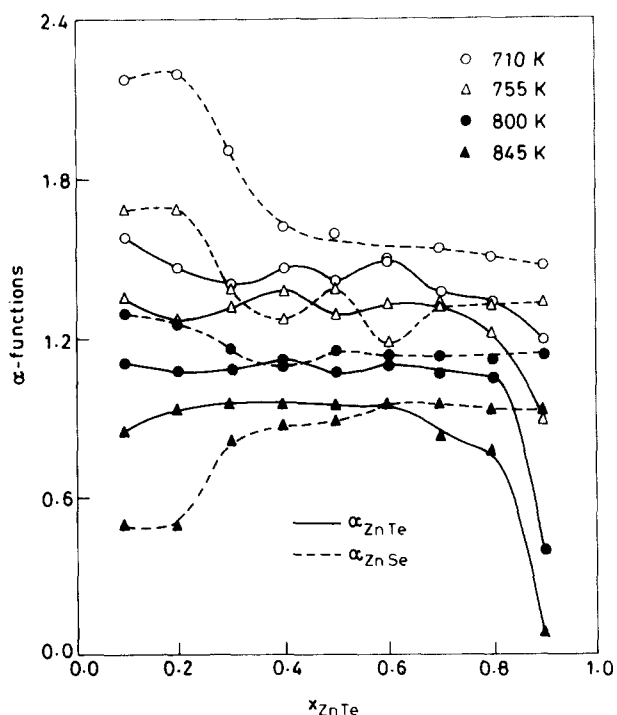


Fig. 6. Plots of  $\alpha_{ZnTe}$  and  $\alpha_{ZnSe}$  vs.  $x_{ZnTe}$  at different temperatures.

710-845 K exhibit positive deviation from Raoult's law and decrease with the increase in temperature. The partial, integral and excess molar thermodynamic quan-

ties obtained from electrochemical measurements include  $\Delta\bar{G}_{ZnTe}^M$ ,  $\Delta\bar{G}_{ZnSe}^M$ ,  $\Delta G^M$ ,  $\Delta\bar{G}_{ZnTe}^{XS}$ ,  $\Delta\bar{G}_{ZnSe}^{XS}$ ,  $\Delta G^{XS}$ ,  $\Delta\bar{H}_{ZnTe}^M$ ,  $\Delta\bar{H}_{ZnSe}^M$ ,  $\Delta H^M$ ,  $\Delta\bar{S}_{ZnTe}^M$ ,  $\Delta\bar{S}_{ZnSe}^M$ ,  $\Delta S^M$ ,  $\Delta\bar{S}_{ZnTe}^{XS}$ ,  $\Delta\bar{S}_{ZnSe}^{XS}$  and  $\Delta S^M$ . The excess partial molar thermodynamic quantities and activity coefficients at infinite dilution, i.e.  $\Delta\bar{G}_{ZnTe}^{XS(0)}$ ,  $\Delta\bar{G}_{ZnSe}^{XS(0)}$ ,  $\Delta\bar{H}_{ZnTe}^{M(0)}$ ,  $\Delta\bar{H}_{ZnSe}^{M(0)}$ ,  $\Delta\bar{S}_{ZnTe}^{XS(0)}$ ,  $\Delta\bar{S}_{ZnSe}^{XS(0)}$ ,  $\gamma_{ZnTe}^{(0)}$  and  $\gamma_{ZnSe}^{(0)}$  have been calculated by Chiotti's method.

The increase in negative values of integral molar free energy of formation with the increase in temperature suggests that the feasibility of formation of solid solutions in the system ZnSe-ZnTe increases with temperature at each composition.

The system ZnSe-ZnTe does not follow a regular solution model. The thermodynamic data cannot be interpreted in terms of Darken's quadratic formalism. Detailed analyses of thermodynamic data and stability parameters suggest that the system ZnSe-ZnTe is completely miscible in the solid phase throughout the entire range of composition. The thermodynamic stability of the system has been found to increase with the increase in temperature.

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