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# Thermodynamic behaviour of zinc and cadmium in liquid-Te-saturated CdTe–ZnTe solid solutions

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**Abstract**

The activity of zinc in liquid-tellurium-saturated CdTe–ZnTe solid solutions in the temperature 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 cadmium was estimated from hypothetical e.m.f. values and also by Gibbs–Duhem integration. The activity values of Zn and Cd calculated at different temperatures were used to obtain various partial and excess molar thermodynamic quantities, namely $\Delta\bar{G}^{M}_{Zn}$, $\Delta\bar{G}^{xs}_{Zn}$, $\Delta\bar{H}^{M}_{Zn}$, $\Delta\bar{S}^{M}_{Zn}$, $\Delta\bar{S}^{xs}_{Zn}$, $\Delta\bar{G}^{M}_{Cd}$, $\Delta\bar{G}^{xs}_{Cd}$, $\Delta\bar{H}^{M}_{Cd}$, $\Delta\bar{S}^{M}_{Cd}$ and $\Delta\bar{S}^{xs}_{Cd}$. The thermodynamic data obtained in the present investigation are consistent with the view that the CdTe–ZnTe system consists of a single phase throughout the entire range of composition.

*Keywords:* Binary system; Cadmium; EMF; Solid solution; Thermodynamics; Zinc

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## 1. Introduction

The thermodynamic properties of the CdTe–ZnTe sysetm have been studied by Zabdyr [1] and Katayama et al. [2]. Recently, thermodynamic investigations of liquid-Te-saturated $Zn_xCd_{1-x}Te$ solid solutions, based on an electrochemical

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technique using LiCl–KCl + 5 wt% $ZnCl_2$ as molten salt electrolyte have been reported from our laboratory [3]. Employing the same assembly, the activity of zinc was determined by measuring the open circuit e.m.f. of the galvanic cell

$$Zn(l)|LiCl{-}KCl + 5wt\%ZnCl_2|Zn_xCd_{1-x}Te(s) + Te(l) \tag{1}$$

Details about the materials, preparation and characterization of the solid solutions, and the experimental procedure for attainment of the correct reversible cell e.m.f. have been described elsewhere [3–6]. As $ZnCl_2$ is more stable than $CdCl_2$, the activity of cadmium cannot be obtained by operating the cell

$$Cd(l)|LiCl{-}KCl + 5wt\%CdCl_2|Zn_xCd_{1-x}Te(s) + Te(l) \tag{2}$$

due to the displacement reaction between the electrolyte and solid solution electrodes. Therefore, the activity of cadmium in the CdTe–ZnTe system was estimated by an indirect method (hypothetical e.m.f.). Using the activity values of CdTe [3] in $Zn_xCd_{1-x}Te$ solid solutions (obtained by Gibbs–Duhem integration), the corresponding e.m.f. values were calculated. Addition of these e.m.f. to the e.m.f. of the cell

$$Cd(l)|LiCl{-}KCl + 5wt\%CdCl_2|CdTe(s) + Te(l) \tag{3}$$

reported in the literature [4] yields the e.m.f. corresponding to cell (2), from which the activity of Cd in $Zn_xCd_{1-x}Te$ solid solutions was calculated. The activity of cadmium was also calculated independently by Gibbs–Duhem integration.

## 2. Results and discussion

### *2.1. Thermodynamic behaviour of zinc in liquid-Te-saturated CdTe–ZnTe solid solutions*

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

$$Zn(pure) \longrightarrow Zn(in\ Zn_xCd_{1-x}Te) \tag{4}$$

The activity $a_{Zn}$ of zinc in $Zn_xCd_{1-x}Te$ solid solution was calculated from the relation

$$a_{Zn} = \exp(-nFE/RT) \tag{5}$$

where $n$ is the number of electrons (two 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 reversible cell e.m.f. values measured in the temperature range 743–848 K are listed in Table 1. The variation of e.m.f. with temperature for all nine compositions was obtained by the least-squares method and also summarized in the form of a linear equation ($E = a + bT$). The error limits shown in the table are the maximum deviation from the average values based on two independent runs. From the e.m.f. values measured at different temperatures, the activity of zinc in liquid-tellurium-saturated

Table 1
E.M.F. (in mV) of galvanic cell (1) at different temperatures

| $x_{Zn}$ | E.M.F. | | | | $E = a + bT$ | |
|---|---|---|---|---|---|---|
| | 743 K | 778 K | 808 K | 848 K | $a$ | $-b$ |
| 0.05 | $603.67 \pm 1.65$ | $599.87 \pm 1.90$ | $595.77 \pm 1.96$ | $592.65 \pm 2.07$ | 683.05 | 0.1071 |
| 0.10 | $588.67 \pm 1.54$ | $583.97 \pm 1.77$ | $579.08 \pm 1.82$ | $574.20 \pm 1.74$ | 692.36 | 0.1396 |
| 0.15 | $582.61 \pm 1.30$ | $586.64 \pm 1.57$ | $571.32 \pm 1.63$ | $564.57 \pm 1.75$ | 710.56 | 0.1722 |
| 0.20 | $578.82 \pm 1.16$ | $572.69 \pm 1.39$ | $566.38 \pm 1.45$ | $559.18 \pm 1.53$ | 719.25 | 0.1888 |
| 0.25 | $575.84 \pm 1.11$ | $570.13 \pm 1.33$ | $563.35 \pm 1.36$ | $555.41 \pm 1.47$ | 722.81 | 0.1972 |
| 0.30 | $574.17 \pm 1.03$ | $567.76 \pm 1.26$ | $560.57 \pm 1.29$ | $551.68 \pm 1.32$ | 735.43 | 0.2164 |
| 0.35 | $571.79 \pm 1.01$ | $565.11 \pm 1.24$ | $557.99 \pm 1.27$ | $549.37 \pm 1.27$ | 732.23 | 0.2155 |
| 0.40 | $570.61 \pm 0.90$ | $563.05 \pm 1.20$ | $555.38 \pm 1.25$ | $546.11 \pm 1.25$ | 741.30 | 0.2299 |
| 0.45 | $567.85 \pm 0.89$ | $560.19 \pm 1.12$ | $552.17 \pm 1.12$ | $542.69 \pm 1.15$ | 747.81 | 0.2418 |
| 0.50 | $565.18 \pm 0.65$ | $557.21 \pm 0.85$ | $548.89 \pm 0.85$ | $538.86 \pm 0.85$ | 753.36 | 0.2529 |

Table 2
Activity and activity coefficient of Zn in liquid-Te-saturated CdTe–ZnTe solid solutions at different temperatures

| $x_{Zn}$ | $a_{Zn} \times 10^9$ | | | | $\gamma_{Zn} \times 10^8$ | | | | $\ln \gamma_{Zn} = A/T + B$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 743 K | 778 K | 808 K | 848 K | 743 K | 778 K | 808 K | 848 K | $-A$ | $B$ |
| 0.05 | 6.424 | 16.812 | 36.764 | 89.787 | 12.848 | 33.623 | 73.529 | 179.570 | 15870.9 | 5.498 |
| 0.10 | 10.265 | 27.019 | 59.388 | 148.795 | 10.265 | 27.019 | 59.338 | 148.800 | 15807.7 | 5.219 |
| 0.15 | 12.406 | 33.626 | 74.223 | 193.683 | 8.270 | 22.417 | 49.482 | 129.120 | 16497.7 | 5.896 |
| 0.20 | 13.965 | 37.833 | 85.543 | 224.481 | 6.983 | 18.916 | 42.771 | 112.240 | 16697.8 | 5.992 |
| 0.25 | 15.328 | 40.836 | 93.324 | 248.890 | 6.131 | 16.334 | 37.330 | 99.556 | 16768.9 | 5.949 |
| 0.30 | 16.149 | 43.829 | 101.084 | 275.650 | 5.383 | 14.610 | 33.695 | 91.883 | 17060.1 | 6.210 |
| 0.35 | 17.396 | 47.436 | 108.863 | 293.646 | 4.970 | 13.553 | 31.104 | 83.899 | 16991.1 | 6.042 |
| 0.40 | 18.391 | 50.443 | 117.341 | 321.060 | 4.598 | 12.661 | 29.335 | 80.265 | 17199.1 | 6.241 |
| 0.45 | 19.675 | 54.937 | 128.679 | 352.575 | 4.372 | 12.208 | 28.595 | 78.350 | 17355.6 | 6.406 |
| 0.50 | 21.386 | 60.047 | 141.396 | 391.554 | 4.277 | 12.009 | 28.279 | 78.311 | 17483.1 | 6.554 |

$Zn_xCd_{1-x}Te$ solid solutions was calculated; they are listed in Table 2 and also presented in Fig. 1. The corresponding values of the activity coefficient of Zn ($\gamma_{Zn}$) were calculated using the relation

$$\gamma_i = a_i/x_i \tag{6}$$

and are also presented in Table 2 in the form of a linear equation ($\ln \gamma_{Zn} = A/T + B$). The activity as well as the activity coefficient both increase with increase in temperature. The logarithmic plots of the activity coefficient with the inverse of temperature, shown in Fig. 2, establish a linear relationship at each composition.

The activity–composition plots shown in Fig. 1 exhibit large negative deviations from Raoult's law at each composition and temperature. This indicates that the Zn–Te interactions are much stronger than those of Cd–Cd, Zn–Zn and Cd–Zn

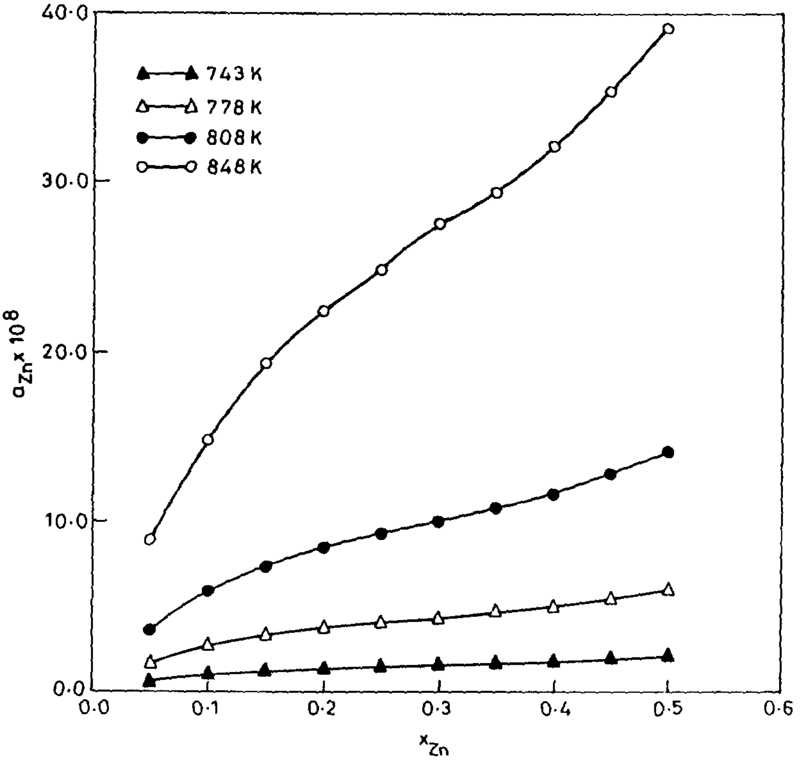

Fig. 1. $a_{Zn}$ vs. $x_{Zn}$ relations in liquid-Te-saturated CdTe–ZnTe solid solutions.

and, hence, zinc atoms can have tellurium atoms as nearest neighbours. The Zn–Te interactions decrease with increasing concentration of ZnTe in $Zn_xCd_{1-x}Te$ solid solutions, which is reflected in Fig. 1 in the appreciable increase of $a_{Zn}$ with increasing molar concentration of ZnTe at each temperature. The change in activity is more pronounced at higher temperatures.

From the e.m.f. values of the galvanic cell (1) measured at any temperature (Table 1), the partial molar free energy of mixing of Zn, $\Delta\bar{G}^{M}_{Zn}$, in liquid-Te-saturated CdTe–ZnTe systems was calculated by the relation

$$\Delta\bar{G}^{M}_{i} = RT \ln a_i = -nFE \tag{7}$$

The values of the partial molar enthalpy ($\Delta\bar{H}^{M}_{Zn}$) and entropy ($\Delta\bar{S}^{M}_{Zn}$) of cadmium in liquid-Te-saturated CdTe–ZnTe systems were obtained respectively from the intercept and slope of the $\Delta\bar{G}^{M}_{Zn}$ vs. $T$ plots. The excess partial molar quantities of Zn were calculated as follows

$$\Delta\bar{G}^{XS}_{i} = \Delta\bar{G}^{M}_{i} - \Delta\bar{G}^{M}_{i} = RT \ln \gamma_i \tag{8}$$

$$\Delta\bar{H}^{XS}_{i} = \Delta\bar{H}^{M}_{i} \qquad (\text{because } \Delta\bar{H}^{M}_{id} = 0) \tag{9}$$

$$\Delta\bar{S}^{XS}_{i} = \Delta\bar{S}^{M}_{i} - \Delta\bar{S}^{M}_{id} = -\frac{\partial(\Delta G_i)}{\partial T} \tag{10}$$

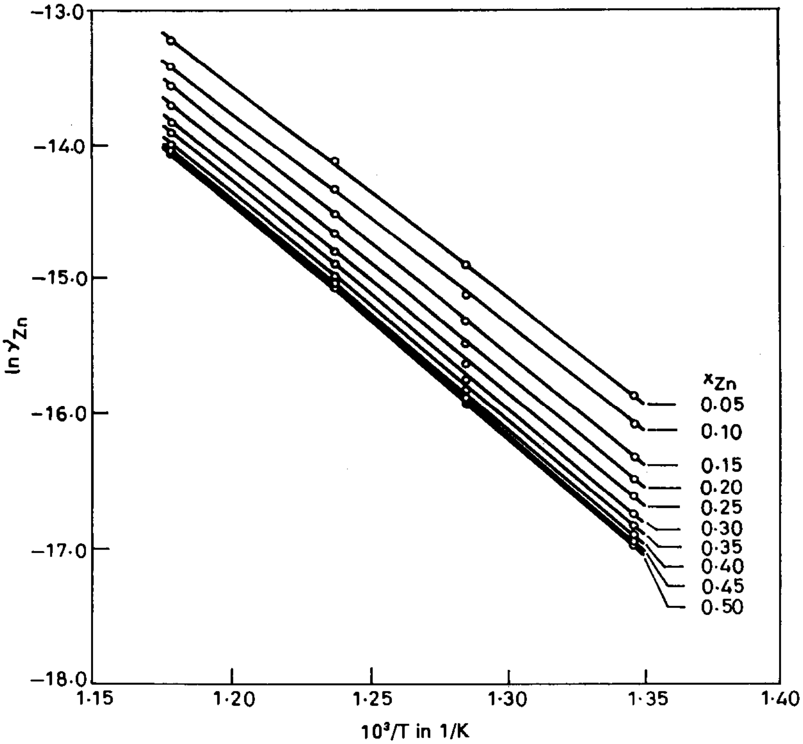

Fig. 2. ln $\gamma_{Zn}$ vs. $1/T$ relations in liquid-Te-saturated CdTe–ZnTe solid solutions.

Various partial thermodynamic quantities, $\Delta\bar{G}^{M}_{Zn}$, $\Delta\bar{G}^{XS}_{Zn}$, $\Delta\bar{H}^{M}_{Zn}$, $\Delta\bar{S}^{M}_{Zn}$ and $\Delta\bar{S}^{XS}_{Zn}$, are summarized in Table 3. The variation of $\Delta\bar{G}^{M}_{Zn}$, $\Delta\bar{G}^{XS}_{Zn}$, $\Delta\bar{H}^{M}_{Zn}$, $T\Delta\bar{S}^{M}_{Zn}$ and $T\Delta\bar{S}^{XS}_{Zn}$, with composition $x_{Zn}$ is shown in Fig. 3 at a typical temperature of 848 K. From Table 3 it is clear that negative values of the partial molar free energy of mixing of zinc decrease with increasing temperature. The continuous variation of activity (Fig. 1) and of various other thermodynamic properties (Fig. 3) with composition indicates that the system CdTe–ZnTe consists of a single-phase field throughout the entire range of composition. This is in conformity with the results of Steininger [7] and Woolley and Ray [8].

The equilibrium vapour pressure of zinc $p_{Zn}$ over liquid-tellurium-saturated $Zn_xCd_{1-x}Te$ solid solutions was calculated from the relation

$$P_i = P_i^\circ a_i \qquad (11)$$

where $P_i^\circ$ is the vapour pressure of pure component at the same temperature, taken from the literature [9]. From the activity values at different temperatures listed in Table 2, the vapour pressures of zinc were obtained and are presented in the form of empirical linear equations in Table 4 and also shown in Fig. 4. Like the activity values, the equilibrium partial pressures of zinc over liquid-tellurium-saturated

Table 3
Partial molar thermodynamic quantities of Zn in liquid-Te-saturated CdTe–ZnTe solid solutions in the temperature range 743–848 K

| $x_{Zn}$ | $-\Delta\bar{G}^M_{Zn}$ in kJ mol$^{-1}$ | | | | $-\Delta\bar{H}^M_{Zn}$ in kJ mol$^{-1}$ | $-\Delta\bar{S}^M_{Zn}$ in J K$^{-1}$mol$^{-1}$ |
|---|---|---|---|---|---|---|
| | 743 K | 778 K | 808 K | 848 K | | |
| 0.05 | 116.57 | 115.84 | 114.93 | 114.45 | 132.09 | 20.95 |
| 0.10 | 113.68 | 112.77 | 111.83 | 110.88 | 133.70 | 26.96 |
| 0.15 | 112.51 | 111.35 | 110.33 | 109.02 | 137.22 | 33.26 |
| 0.20 | 111.78 | 110.59 | 109.37 | 107.98 | 138.89 | 33.47 |
| 0.25 | 111.20 | 110.10 | 108.79 | 107.25 | 139.58 | 38.08 |
| 0.30 | 110.88 | 109.64 | 108.25 | 106.53 | 142.02 | 41.62 |
| 0.35 | 110.42 | 109.13 | 107.75 | 106.09 | 141.40 | 41.79 |
| 0.40 | 110.07 | 108.73 | 107.25 | 105.46 | 143.15 | 44.41 |
| 0.45 | 109.66 | 108.18 | 106.63 | 104.80 | 144.41 | 46.70 |
| 0.50 | 109.14 | 107.60 | 105.99 | 103.94 | 146.28 | 49.87 |

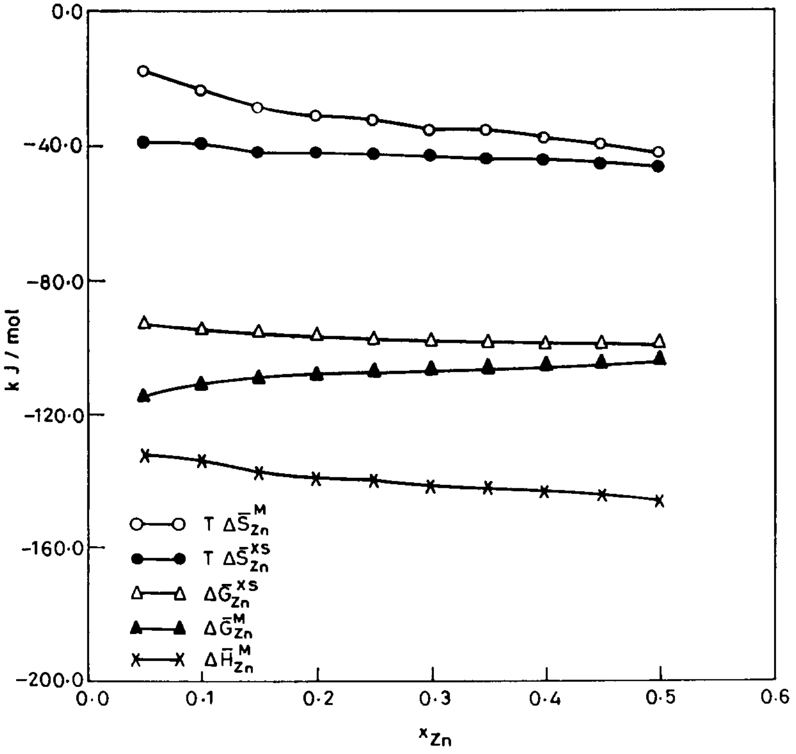

Fig. 3. Patial and excess molar thermodynamic quantities of Zn in liquid-Te-saturated CdTe–ZnTe solid solutions at 848 K.

Table 4

Equilibrium vapour pressure of Zn over liquid-Te-saturated CdTe–ZnTe solid solutions in the temperature range 743–848 K

| $x_{Zn}$ | $\ln(p_{Zn}/\text{atm}) = a/T + b$ | |
|---|---|---|
| | $-a$ | $b$ |
| 0.05 | 30154.4 | 14.687 |
| 0.10 | 29863.9 | 14.831 |
| 0.15 | 30782.1 | 16.185 |
| 0.20 | 30986.3 | 16.575 |
| 0.25 | 31053.1 | 16.749 |
| 0.30 | 31344.9 | 17.193 |
| 0.35 | 31275.4 | 17.178 |
| 0.40 | 31483.4 | 17.511 |
| 0.45 | 31672.2 | 17.839 |
| 0.50 | 31767.3 | 18.047 |

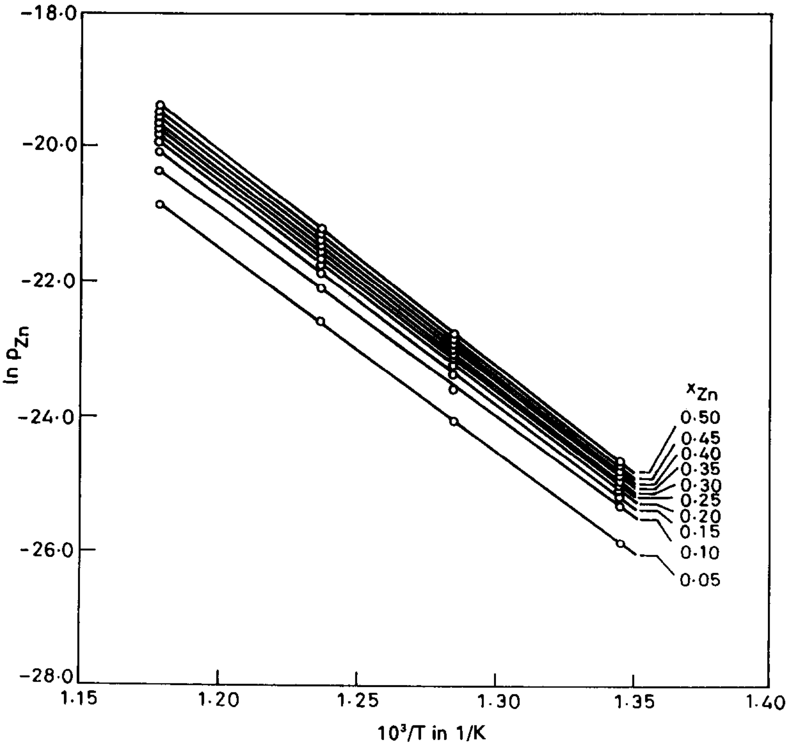

Fig. 4. ln/$p_{Zn}$ vs. $1/T$ relations in liquid-Te-saturated CdTe–ZnTe solid solutions.

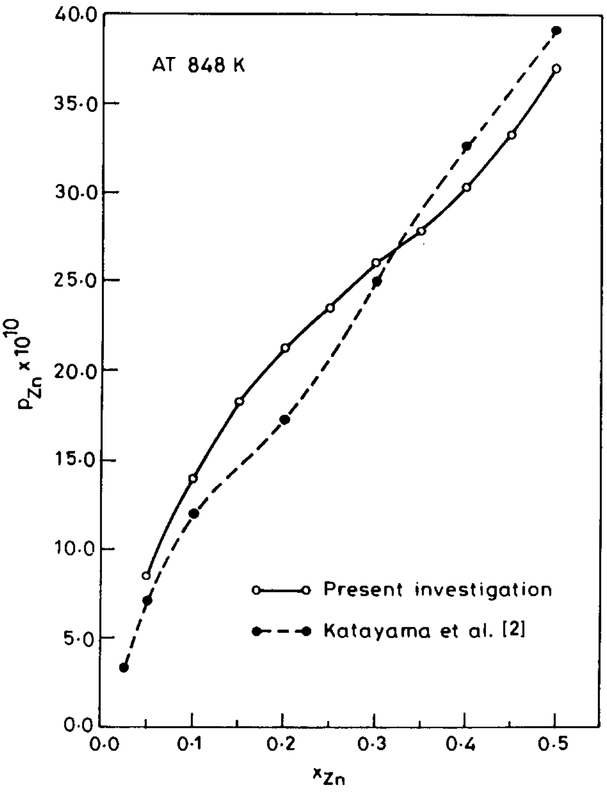

Fig. 5. $p_{Zn}$ vs. $x_{Zn}$ relations in liquid-Te-saturated CdTe–ZnTe solid solutions at 848 K.

CdTe–ZnTe solid solutions increase with increasing concentration of ZnTe at each temperature. The variation of partial pressure of zinc with composition at 848 K shown in Fig. 5 is in good agreement with the results of Katayama et al. [2].

### *2.2. Thermodynamic behaviour of cadmium in liquid-Te-saturated CdTe–ZnTe solid solutions*

The hypothetical e.m.f. of the galvanic cell (2) estimated in the temperature range 743–848 K is listed in Table 5. From the e.m.f. values estimated at different temperatures the activities of Cd in liquid-Te-saturated $Zn_xCd_{1-x}Te$ solid solutions were calculated using Eq. (5). The activity values of Cd in the CdTe–ZnTe system are summarized in Table 6 and their variation with composition $x_{Cd}$ at different temperatures is presented in Fig. 6. The corresponding values of the activity coefficient $\gamma_{Cd}$ of cadmium were calculated using Eq. (6) and are also presented in Table 6. The logarithmic plots of activity coefficient with the inverse of temperature, shown in Fig. 7, establishes a linear relationship ($\ln \gamma_{Cd} = A/T + B$) at each composition.

Table 5
E.M.F. (in mV) of galvanic cell (2) (hypothetical) at different temperatures

| $x_{Cd}$ | E.M.F. | | | | $E = a + bT$ | |
|---|---|---|---|---|---|---|
| | 743 K | 778 K | 808 K | 848 K | $a$ | $-b$ |
| 0.05 | 529.11 ± 1.55 | 527.92 ± 1.75 | 525.83 ± 1.91 | 522.79 ± 2.25 | 575.04 | 0.0612 |
| 0.10 | 516.30 ± 1.44 | 511.05 ± 1.62 | 506.92 ± 1.77 | 502.14 ± 1.99 | 616.19 | 0.1348 |
| 0.15 | 510.83 ± 1.20 | 504.68 ± 1.42 | 498.88 ± 1.58 | 492.13 ± 1.90 | 639.05 | 0.1789 |
| 0.20 | 506.43 ± 1.06 | 499.75 ± 1.24 | 494.03 ± 1.40 | 487.72 ± 1.68 | 643.92 | 0.1792 |
| 0.25 | 504.37 ± 1.01 | 496.83 ± 1.18 | 490.61 ± 1.31 | 483.15 ± 1.62 | 654.40 | 0.2023 |
| 0.30 | 501.95 ± 0.93 | 494.74 ± 1.11 | 488.14 ± 1.24 | 480.07 ± 1.47 | 657.40 | 0.2092 |
| 0.35 | 499.93 ± 0.91 | 492.64 ± 1.09 | 485.50 ± 1.22 | 476.40 ± 1.44 | 667.55 | 0.2253 |
| 0.40 | 497.97 ± 0.85 | 490.25 ± 1.05 | 482.97 ± 1.20 | 473.74 ± 1.40 | 670.29 | 0.2317 |
| 0.45 | 495.42 ± 0.79 | 487.45 ± 0.92 | 479.98 ± 1.07 | 470.64 ± 1.30 | 671.63 | 0.2370 |
| 0.50 | 492.52 ± 0.55 | 484.06 ± 0.70 | 476.81 ± 0.80 | 467.15 ± 1.00 | 672.30 | 0.2417 |

Table 6
Activity and activity coefficient of Cd in liquid-Te-saturated CdTe–ZnTe solid solutions at different temperatures

| $x_{Cd}$ | $a_{Cd} \times 10^8$ | | | | $\gamma_{Cd} \times 10^7$ | | | | $\ln \gamma_{Cd} = A/T + B$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 743 K | 778 K | 808 K | 848 K | 743 K | 778 K | 808 K | 848 K | $-A$ | $B$ |
| 0.05 | 6.602 | 14.391 | 27.429 | 60.795 | 13.204 | 28.782 | 54.857 | 121.590 | 13335.4 | 4.398 |
| 0.10 | 9.851 | 23.808 | 47.226 | 107.000 | 9.851 | 23.808 | 47.226 | 107.000 | 14317.1 | 5.447 |
| 0.15 | 11.687 | 28.793 | 59.499 | 140.740 | 7.792 | 19.195 | 39.666 | 93.830 | 14935.0 | 5.890 |
| 0.20 | 13.410 | 33.356 | 68.397 | 161.300 | 6.705 | 16.678 | 34.198 | 80.650 | 14953.2 | 6.061 |
| 0.25 | 14.302 | 36.393 | 75.372 | 179.990 | 5.721 | 14.557 | 30.149 | 71.990 | 15201.4 | 6.064 |
| 0.30 | 15.425 | 38.735 | 81.009 | 195.800 | 5.142 | 12.912 | 27.003 | 65.270 | 15264.4 | 6.093 |
| 0.35 | 16.430 | 41.241 | 87.394 | 216.500 | 4.694 | 11.783 | 24.970 | 61.860 | 15491.4 | 6.272 |
| 0.40 | 17.468 | 44.289 | 93.983 | 232.860 | 4.367 | 11.072 | 23.496 | 58.210 | 15558.4 | 6.292 |
| 0.45 | 18.916 | 48.149 | 102.410 | 253.480 | 4.204 | 10.700 | 22.759 | 56.330 | 15591.1 | 6.299 |
| 0.50 | 20.711 | 53.275 | 112.180 | 278.900 | 4.142 | 10.655 | 22.436 | 55.780 | 15602.7 | 6.303 |

The activity coefficient of Cd in liquid-Te-saturated $Zn_xCd_{1-x}Te$ solid solutions was calculated by a Gibbs–Duhem equation of the following form

$$\ln \gamma_{Cd} = \ln \gamma_{Cd}(\text{at } x_{Cd} = 0.5) - \int_{x_{Cd}=0.5}^{x_{Cd}=x_{Cd}} (x_{Zn}/x_{Cd})\, d(\ln \gamma_{Zn}) \qquad (12)$$

where $a_{Te} = 1$ and $\gamma_{Te} = 1$, i.e. $\ln \gamma_{Te} = 0$). The values of $\gamma_{Cd}$ and $a_{Cd}$ calculated at different temperatures are listed in Table 7. The $a_{Cd}$ values obtained by Gibbs–Duhem integration at 848 K are compared with those estimated by hypothetical e.m.f. in Fig. 8. The two values are in excellent agreement.

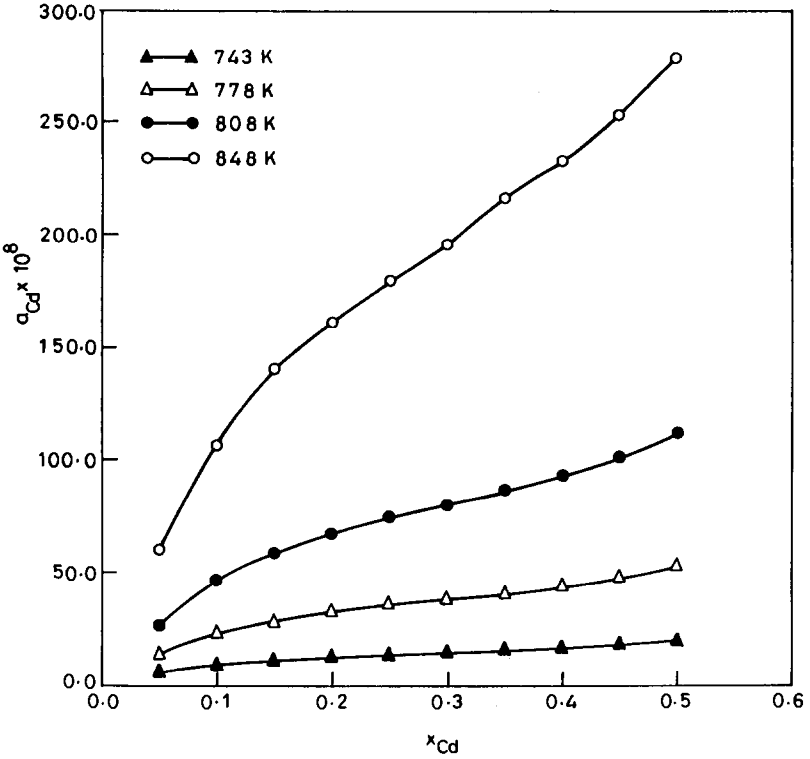

Fig. 6. $a_{Cd}$ vs. $x_{Cd}$ relations in liquid-Te-saturated CdTe–ZnTe solid solutions.

Table 7
Activity and activity coefficient of Cd in liquid-Te-saturated CdTe–ZnTe solid solutions at different temperatures (obtained by Gibbs–Duhem integration)

| $x_{Cd}$ | $a_{Cd} \times 10^8$ | | | | $\gamma_{Cd} \times 10^7$ | | | |
|---|---|---|---|---|---|---|---|---|
| | 743 K | 778 K | 808 K | 848 K | 743 K | 778 K | 808 K | 848 K |
| 0.05 | 7.043 | 14.516 | 28.408 | 67.186 | 14.086 | 29.033 | 56.816 | 134.370 |
| 0.10 | 10.177 | 23.507 | 48.122 | 114.850 | 10.177 | 23.507 | 48.122 | 114.850 |
| 0.15 | 11.866 | 29.695 | 60.025 | 149.850 | 7.910 | 19.797 | 40.017 | 99.900 |
| 0.20 | 13.589 | 34.328 | 68.746 | 168.110 | 6.795 | 17.164 | 34.373 | 84.050 |
| 0.25 | 14.260 | 37.326 | 75.599 | 182.620 | 5.704 | 14.164 | 30.239 | 73.050 |
| 0.30 | 15.718 | 39.538 | 80.814 | 197.900 | 5.239 | 13.179 | 26.938 | 65.970 |
| 0.35 | 16.429 | 42.014 | 87.020 | 213.720 | 4.694 | 12.004 | 24.863 | 61.060 |
| 0.40 | 17.592 | 45.189 | 93.750 | 233.250 | 4.398 | 11.297 | 23.438 | 58.310 |
| 0.45 | 19.111 | 48.929 | 101.580 | 253.910 | 4.247 | 10.873 | 22.574 | 56.430 |
| 0.50 | 20.711 | 53.275 | 112.180 | 278.900 | 4.142 | 10.655 | 22.436 | 55.780 |

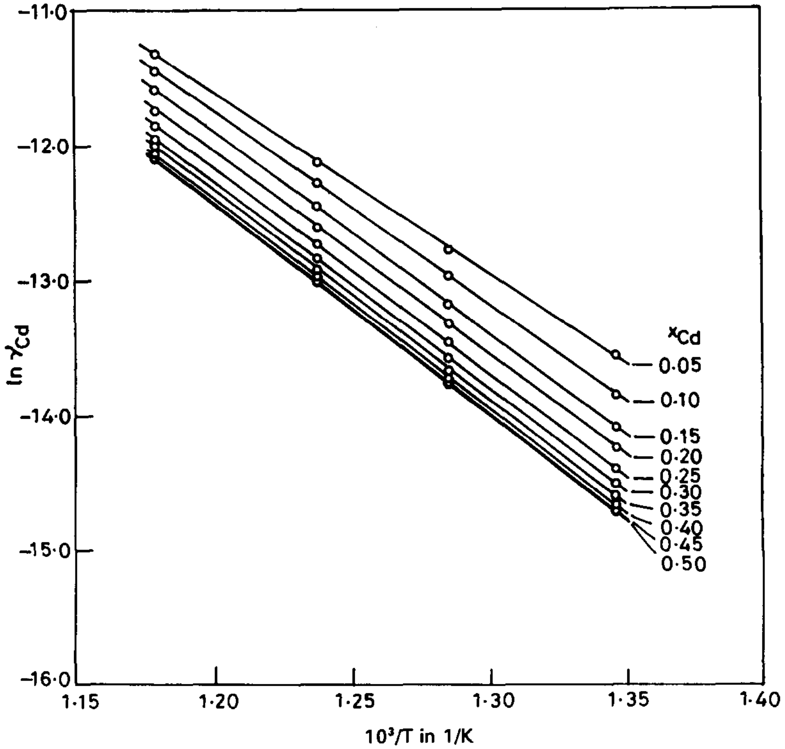

Fig. 7. ln $\gamma_{Cd}$ vs. $1/T$ relations in liquid-Te-saturated CdTe–ZnTe solid solutions.

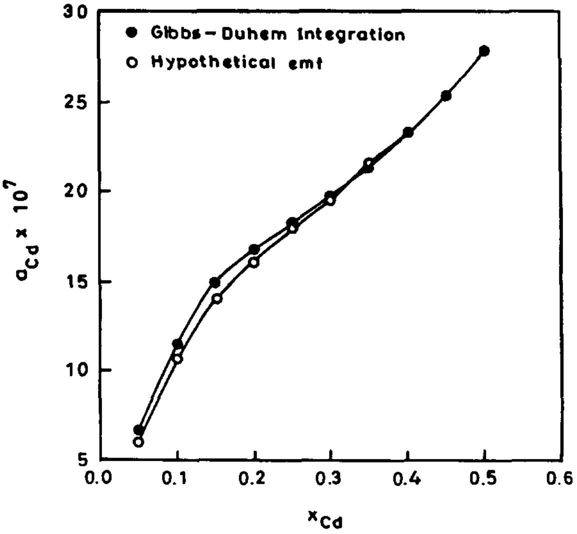

Fig. 8. $a_{Cd}$ vs. $x_{Cd}$ relations (obtained by two independent methods) in liquid-Te-saturated CdTe–ZnTe solid solutions at 848 K.

The activity–composition plots shown in Fig. 6 exhibit strong negative deviation from Raoult's law at each composition and temperature. This indicates that Cd–Te interactions are much stronger than the metal–metal interactions, of Cd–Cd, Zn–Zn and Cd–Zn. Hence cadmium atoms can have tellurium as nearest neighbours. These interactions decrease with increasing concentration of CdTe in the alloy. It is clear from the figure that the activity values of Cd increase appreciably with increasing molar concentration of CdTe at each temperature. The change in activity is more pronounced at higher temperatures.

From the activity values $a_{\mathrm{Cd}}$ at any temperature (Tables 6 and 7), the partial molar free energy of mixing of Cd, $\Delta\bar{G}^{\mathrm{M}}_{\mathrm{Cd}}$, was calculated using Eq. (7). The values of partial molar enthalpy ($\Delta\bar{H}^{\mathrm{M}}_{\mathrm{Cd}}$) and entropy ($\Delta\bar{S}^{\mathrm{M}}_{\mathrm{Cd}}$) of mixing of Cd in liquid-tellurium-saturated $\mathrm{Zn}_x\mathrm{Cd}_{1-x}\mathrm{Te}$ solid solutions were obtained respectively from the intercept and slope of $\Delta\bar{G}^{\mathrm{M}}_{\mathrm{Cd}}$ vs. $T$ plots (by the least-squares method). The excess partial thermodynamic quantities, namely $\Delta\bar{G}^{\mathrm{XS}}_{\mathrm{Cd}}$, $\Delta\bar{H}^{\mathrm{XS}}_{\mathrm{Cd}}$ and $\Delta\bar{S}^{\mathrm{XS}}_{\mathrm{Cd}}$, were calculated using Eqs. (8)–(10). Various partial molar thermodynamic quantities, namely $\Delta\bar{G}^{\mathrm{M}}_{\mathrm{Cd}}$, $\Delta\bar{H}^{\mathrm{M}}_{\mathrm{Cd}}$ and $\Delta\bar{S}^{\mathrm{M}}_{\mathrm{Cd}}$, are summarized in Table 8. The variation of $\Delta\bar{G}^{\mathrm{M}}_{\mathrm{Cd}}$, $\Delta\bar{G}^{\mathrm{XS}}_{\mathrm{Cd}}$, $\Delta\bar{H}^{\mathrm{M}}_{\mathrm{Cd}}$, $T\Delta\bar{S}^{\mathrm{M}}_{\mathrm{Cd}}$ and $T\Delta\bar{S}^{\mathrm{XS}}_{\mathrm{Cd}}$ at 848 K with composition $x_{\mathrm{Cd}}$ is shown in Fig. 9. From Table 8, it is clear that the negative values of partial molar free energy descrease with increasing temperature. The continuous variation of activity (Fig. 6) and the various thermodynamic properties (Fig. 9) with composition indicates that the system CdTe–ZnTe consists of a single-phase field throughout the entire range of composition.

The equilibrium vapour pressures of cadmium ($p_{\mathrm{Cd}}$) over liquid-tellurium-saturated $\mathrm{Zn}_x\mathrm{Cd}_{1-x}\mathrm{Te}$ solid solutions at different temperatures calculated from Eq. (11) are presented in the form of an empirical linear equation in Table 9 and also shown graphically in Fig. 10. Like the activity values, the equilibrium vapour pressures of cadmium over CdTe–ZnTe solutions, increase with increasing concen-

Table 8

Partial molar thermodynamic quantities of Cd in liquid-Te-saturated CdTe–ZnTe solid solutions in the temperature range 743–848 K

| $x_{\mathrm{Cd}}$ | $-\Delta\bar{G}^{\mathrm{M}}_{\mathrm{Cd}}$ in kJ mol$^{-1}$ | | | | $-\Delta\bar{H}^{\mathrm{M}}_{\mathrm{Cd}}$ in kJ mol$^{-1}$ | $-\Delta\bar{S}^{\mathrm{M}}_{\mathrm{Cd}}$ in J K$^{-1}$mol$^{-1}$ |
|---|---|---|---|---|---|---|
| | 743 K | 778 K | 808 K | 848 K | | |
| 0.05 | 102.18 | 101.95 | 101.54 | 100.96 | 111.05 | 11.82 |
| 0.10 | 99.70 | 98.69 | 97.89 | 96.97 | 118.99 | 26.04 |
| 0.15 | 98.65 | 97.46 | 96.34 | 95.03 | 124.35 | 34.60 |
| 0.20 | 97.80 | 96.51 | 95.40 | 94.18 | 123.41 | 34.00 |
| 0.25 | 97.40 | 95.94 | 94.75 | 93.30 | 126.36 | 39.04 |
| 0.30 | 96.93 | 95.54 | 94.26 | 92.71 | 126.95 | 40.40 |
| 0.35 | 96.54 | 95.13 | 93.75 | 91.99 | 128.91 | 43.51 |
| 0.40 | 96.16 | 94.67 | 93.27 | 91.48 | 129.44 | 44.75 |
| 0.45 | 95.67 | 94.13 | 92.69 | 90.88 | 129.70 | 45.77 |
| 0.50 | 95.11 | 93.48 | 92.08 | 90.21 | 129.78 | 46.66 |

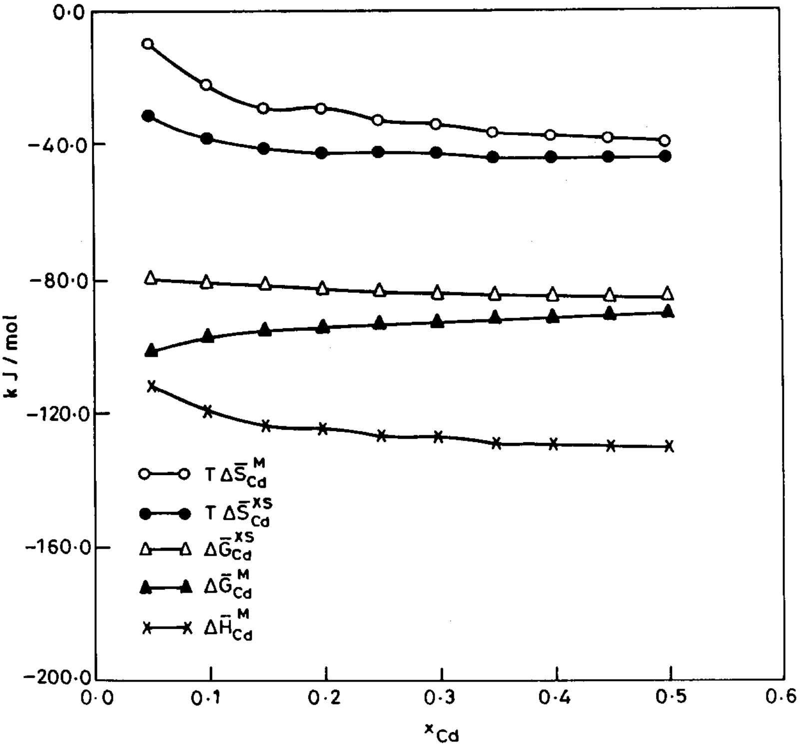

Fig. 9. Partial and excess molar thermodynamic quantities of Cd in liquid-Te-saturated CdTe–ZnTe solid solutions at 848 K.

Table 9
Equilibrium vapour pressure of Cd over liquid-Te-saturated CdTe–ZnTe solid solutions in the temperature range 743–848 K

| $x_{Cd}$ | $\ln(p_{Cd}/\text{atm}) = a/T + b$ | |
|---|---|---|
| | $-a$ | $b$ |
| 0.05 | 25737.1 | 13.410 |
| 0.10 | 26719.3 | 15.153 |
| 0.15 | 27337.0 | 16.172 |
| 0.20 | 25355.3 | 16.289 |
| 0.25 | 27604.3 | 16.716 |
| 0.30 | 27666.5 | 16.716 |
| 0.35 | 27893.6 | 17.231 |
| 0.40 | 27960.4 | 17.384 |
| 0.45 | 27993.3 | 17.509 |
| 0.50 | 28004.1 | 17.618 |

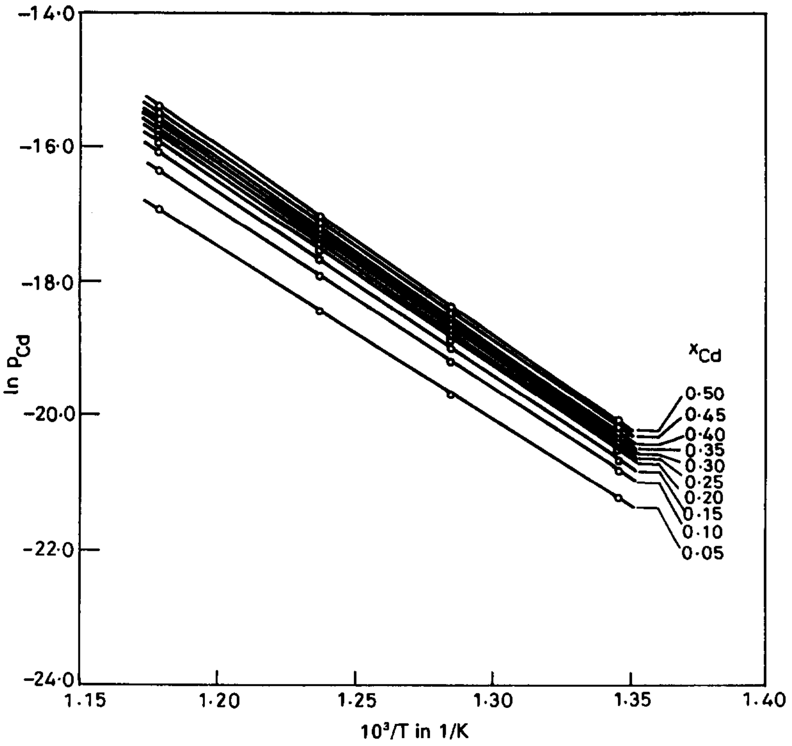

Fig. 10. $\ln p_{\mathrm{Cd}}$ vs. $1/T$ relations in liquid-Te-saturated CdTe–ZnTe solid solutions.

tration of CdTe at each temperature. It is observed from Tables 4 and 9 that the equilibrium vapour pressures of Cd are larger than those of Zn over the solid solutions at all temperatures.

## 3. Conclusions

The activities of both zinc and cadmium over $\mathrm{Zn}_x\mathrm{Cd}_{1-x}\mathrm{Te}$ solid solutions at different temperatures and compositions exhibit large negative deviations from Raoult's law. This indicates that Zn–Te as well as Cd–Te interactions are much stronger than Cd–Zn, Cd–Cd and Zn–Zn interactions, and that both Zn and Cd tend to have Te atoms as nearest neighbours. Both $a_{\mathrm{Zn}}$ and $a_{\mathrm{Cd}}$ have been found to increase with temperature and the change in activities is more pronounced at higher temperatures. The continuous variation of activity and activity coefficient of zinc and cadmium with composition indicates that the system CdTe–ZnTe is completely miscible and consists of a single-phase field throughout the entire range of composition in the temperature range 743–848 K.

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