The Cd-Te Phase Diagram

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ABSTRACT

The properties of the liquid phase in the Cd–Te system are fit using thermodynamic properties of CdTe(c) recently optimized by the author. These include a high temperature heat capacity significantly lower than commonly used such that the enthalpy of formation of CdTe(c) at its melting point is about 10 kJ/mol less negative than previously thought. An associated solution model with Cd, CdTe, and Te species is used. Seven adjustable parameters are sufficient to quantitatively fit the liquidus and partial pressures of Te_2 and Cd. Additional partial pressures for Te rich CdTe(c) near its melting point are extracted from an earlier study and tabulated. The parameters giving good fits to the liquidus and partial pressures give only a fair fit to the enthalpy of mixing of the liquid phase. Moreover, the parameters giving a good fit to the enthalpy give poor fits to the other data. The sensitivity of the different data types to changes in the interaction parameters of the associated solution model is established. A variation of ± 160 J/g atom in the enthalpy parameter determining the CdTe–Te interaction is sufficient to double the fractional standard deviation between experimental and calculated partial pressures of Te_2 over Te rich CdTe(c) from 0.034 to 0.07. Because the degree of association is near its maximum, the measures of fit to the data are insensitive to changes in the parameters determining the Cd–Te interaction.

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1. Introduction

The Cd–Te system is similar to about eighty other binary systems in forming a single narrow homogeneity range compound at 50 at.% and showing extremely narrow terminal solid solutions. Although many of the thermodynamic properties of CdTe(c) are well established, recently measured high temperature heat capacities [1,2] are considerably smaller than assumed earlier. This prompted us to reanalyze the high temperature data [3] and led to an enthalpy of formation at the melting point about 10 kJ/mol less negative. As a result the analyses of the phase diagram by Jianrong et al. [4], by the present author and coworkers [5,6] and in recent studies [7,8] are in need of revision. A separate analysis by Yamaguchi et al. [9] used their measured heat capacity, while we used an average of that with a closely similar one from Malkova et al. [1]. However, Yamaguchi et al. also used their measured value of −112 kJ/mol for the standard enthalpy of formation at 298 K, which is about 12 kJ/mol more negative than most of the other published values. Moreover, this value has been shown [3] to be inconsistent with high temperature partial pressures obtained from Knudsen cell and optical density measurements.

In common with the previous studies we assume the existence of Cd, Te, and CdTe species in the melt. We consider the experimental data to fall in three sets: the heats of mixing for the Te rich liquid from Yamaguchi et al. [9], liquidus points from various sources, and partial pressures. The latter consist of the partial pressure of diatomic tellurium along the Te rich leg of the CdTe(c) three phase curve, that for 55, 60, and 65 at.% Te liquids [10], and the partial pressure of cadmium along high temperature portions of both the Te rich [3,11] and Cd rich [10] legs of the CdTe(c) three phase curve. In discussing the partial pressure of Cd a number of additional experimental points are obtained from an earlier study [10]. A best fit is obtained to each of these data sets separately using the trial and error simplex method of Nelder and Mead [12]. Then the liquid phase interaction parameters so obtained are used to obtain the measure of fit to the other data. In this way a sense of the consistency of the data sets with one another is obtained. We find that the parameters giving a best fit to the partial pressures alone also give a fit to the liquidus points within a degree of the best fit obtained by fitting the liquidus points alone. However, even after the heats of mixing are adjusted to be consistent with a standard enthalpy of formation of −100.27 kJ/mol at 298.15 K, the best fit parameters for the partial pressures give a fit of only 16% to the enthalpy of mixing and the calculated values are less negative than those observed by about 5 kJ/g atom near 50 at.%. On the other hand, the interaction parameters obtained by a best fit to the heats of mixing give very poor fits to the liquidus points and partial pressures. Next a best fit to the liquidus points and the partial pressures considered together is obtained and a number of data for which there no measurements are then generated. The sensitivity of the different data types to changes in the parameters

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Table 1
Analytical formulae for the Gibbs energy of formation of CdTe(c) from its condensed phase elements and, in the last row, from Cd (g) and 1/2 Te$_2$ (g).

ΔG_f^0 (J/mol) $= A + BT + CT^2 + DT^3 + ET \ln(T) + F/T$						
Temp range (K)	A	B	C	D	E	F
298–594.2	−100,889	15.3341	3.4210E−03	2.7966E−07	−1.8300	5.8550E+04
594.2–722.65	−104,820	−21.7759	−2.6440E−03	2.79667E−07	5.5800	5.8550E+04
722.65–833	−76,940	−721.020	−6.3519E−02	0	112.645	5.8550E+04
833–1365	−118,058	−57.0652	−4.2525E−03	0	13.9150	5.8550E+04
298–1365	−297,496	289.970	2.36150E−03	−9.5700E−07	−13.419	5.8550E+04

is determined and estimates obtained for the uncertainty in the parameters.

In the interests of brevity a number of shorthand notations are substituted for more exact wording as follows. The partial pressure along the CdTe(c) three phase curve will also be referred to as partial pressure over Te saturated or Cd saturated CdTe(c). The standard deviation between observed and calculated liquidus points will be called the measure of fit to the liquidus. Similarly the fractional standard deviation between observed and calculated partial pressures will be referred to as the measure of fit for that data type.

2. Thermodynamic properties of the elements and of CdTe(c)

The necessary properties for Cd are from Hultgren [13] and have also been adopted by SGTE [14]. They are

m.pt. 594.2; enthalpy of Fusion $= 6192$ J/mol

$C_p = 22.30 + 0.01213T$; $298 < T < 594.2$ K

$C_p = 29.71$; $T > 594.2$ K

Cd(c); $S_{298}^0 = 51.80$ J/mol K

Cd(g); $S_{298}^0 = 167.63$ (J/mol K)

Cd(c) $\rightarrow$ Cd(g); $\Delta H_{298}^0 = 111,960$ J/mol

$\log_{10} P_{Cd}$ (atm) $= 5.119 - 6317/T$; $T > 594.2$ K.

The corresponding quantities for Te are taken from our third law analysis of the crystal–liquid–vapor equilibrium [15]. The heat capacity for the liquid is quite different from that given by Mills [16]. It is close to that adopted by Davidov et al. [17]. The enthalpy and entropy of liquid Te calculated with our heat capacity and that of Davidov et al. differ by less than 0.5% between 722.65 and 1365 K. However, our vapor pressures are 7%–20% higher than those adopted by Davidov et al. above 722.65 K and closer to the experimental values [18]. The necessary data are

m.pt. $= 722.65$ K; enthalpy of fusion $= 17,489$ J/mol

$C_p = 24.610 + 0.003217T + 1.678(10^{-6})T^2$;

$\quad 298 < T < 722.65$

$C_p = 131.7 - 0.1185T$; $722.65 < T < 833$

$C_p = 32.94$; $T > 833$ K

Te(c); $S_{298}^0 = 49.1$ J/mol K

Te$_2$(g); $S_{298}^0 = 258.66$ J/mol K

Te(c) $\rightarrow \dfrac{1}{2}$Te$_2$(g); $\Delta H_{298}^0 = 81,031$ J/mol

$\log_{10} P$ (atm) $= 4.3985 - 5267.68/T - 368,192.2/T^2$;

$\quad 722.65 < T < 1434$ K.

We originally gave four equations for the vapor pressure in the above range [15]. We subsequently found [3] that these can be approximated to better than 2% by the single equation given. In this temperature range the vapor is 99% or more Te$_2$(g).

For CdTe(c) we use the results of our recent analysis [3]. The coefficients for the standard Gibbs energy of formation between

298 and 1365 K are given in Table 1. Some properties entailed in this Gibbs energy and some additional properties are

m.pt. $= 1365$ K; enthalpy of fusion $= 43,500$ J/mol

$C_p = 48.740 + 0.008505T - 1.171(10^5)/T^2$;

$\quad 298 < T < 1365$ K

$\Delta H_{f,298}^0 = -100,270$ J/mol, $\Delta S_{f,298}^0 = -4.5333$ J/mol K.

The heat capacity is an average of one recommended by Malkova et al. [1] and one measured by Yamaguchi et al. [2].

3. Associated solution model

We assume liquid phase species, Cd, CdTe, and Te with mole fractions, y_1, y_2, and y_3. The enthalpy of mixing from the elemental liquid components, Cd and Te, is given by

$$\Delta H_{Mix} = -y_2 \Delta H_D + \sum_{j=1}^{3} \sum_{i=1}^{3} [Q_{ij} y_i y_j + C_{ij} y_i y_j^2] \tag{1}$$

where

$$Q_{ij} = A_{ij} - B_{ij}(T - T_m); \qquad C_{ij} = F_{ij} - G_{ij}(T - T_m) \tag{2}$$

$$\begin{aligned} \Delta H_D &= \Delta H_{D,0} - \Delta H_{D,1}(T - T_m); \\ \Delta S_D &= \Delta S_{D,0} - \Delta H_{D,1} \ln(T/T_m) \end{aligned} \tag{3}$$

and where ΔH_D is the enthalpy of dissociation of the species CdTe into Cd and Te, A_{ij}, B_{ij}, F_{ij}, and G_{ij} are constants to be determined by a fit to experimental data and T_m is the melting point of CdTe(c). In addition

$$Q_{ij} = Q_{ji}; \qquad Q_{jj} = 0; \quad \text{and} \quad C_{ij} = -C_{ji}. \tag{4}$$

The excess entropy of mixing is defined by a completely analogous expression in which the enthalpy of dissociation is replaced by the entropy of dissociation, ΔS_D, and the parameters Q_{ij} and C_{ij} are replaced, respectively, by

$$P_{ij} = D_{ij} - B_{ij} \ln(T/T_m) \quad \text{and} \quad U_{ij} = H_{ij} - G_{ij} \ln(T/T_m). \tag{5}$$

The excess entropy of mixing is

$$\Delta S_{Mix}^x = -y_2 \Delta S_D + \sum_{j=1}^{3} \sum_{i=1}^{3} [P_{ij} y_i y_j + U_{ij} y_i y_j^2]. \tag{6}$$

The expressions for the relative, partial molar enthalpies are given below. Again the equations for the relative, partial molar excess entropies are analogous and the relative partial molar excess Gibbs energies or chemical potentials can be constructed from the corresponding enthalpies and entropies using standard thermodynamic formulae. The enthalpies are given by

$$\bar{h}_k = -\delta_{k2} \Delta H_D + \sum_{j=1}^{3} [2Q_{jk} y_j - C_{jk} y_j(y_j - 2y_k)] - COM;$$

$$k = 1, 2, 3 \tag{7}$$

where $\delta_{k2} = 1$, if $k = 2$ and 0 otherwise. The term COM is common to all three partial molar enthalpies and is given by

$$COM = \sum_{j=1}^{3} \sum_{i=1}^{3} (Q_{ij} + 2C_{ij}y_j)y_i y_j. \tag{8}$$

In addition three equations were required to hold at the melting point of CdTe(c):

$$\bar{\mu}_1 + \bar{\mu}_3 = \Delta G_f^o(T_m); \qquad X_{Te} = 1/2 \tag{9}$$

$$2\Delta H_{Mix}/(1 + Z) = \Delta H_f^o(T_m) + \Delta H_{Fusion} \tag{10}$$

$$\bar{\mu}_2 = \Delta G_f^0(T_m) \tag{11}$$

where $\bar{\mu}_1, \bar{\mu}_2, \bar{\mu}_3$ are the relative chemical potentials of, respectively, the Cd, CdTe, and Te species, $\Delta G_f^0(T_m)$ and $\Delta H_f^0(T_m)$ are the standard Gibbs energy and standard enthalpy of formation of CdTe(c) from Cd and Te liquids at the melting point, ΔH_{Fusion} is the enthalpy of fusion per mole of CdTe(c), Z is the mole fraction of the CdTe species at the melting point, and ΔH_{Mix} is the enthalpy of mixing of the liquid per mole of species and from liquid Cd and Te. These equations ensure that the sum of the enthalpy of formation and that of fusion of the solid equals the enthalpy of mixing of the liquid and that a similar equation between the corresponding entropy quantities is satisfied. These equations introduce another parameter, Z, but fix the parameters ΔH_D and ΔS_D and one other in terms of the others. We chose A_{12}.

4. Methodology

At a given temperature the mole fractions of the cadmium and tellurium species in the liquid phase can be written in terms of that of the molecular species, CdTe, and the atomic fraction of the Te component, x. Using the mass action law for the equilibrium among these species one can then obtain an implicit equation for y_2, the mole fraction of CdTe, in which the equilibrium constant itself contains y_2 and the interaction parameters through the activity coefficients. This equation is:

$$x(1 - x)y_2^2 - [(1 - x)^2 + x^2 + \kappa]y_2 + x(1 - x) = 0. \tag{12}$$

The effective equilibrium constant arises from equating the chemical potentials of the Cd and Te liquid phase species to that of the CdTe species and is given by,

$$\kappa = (\gamma_2/\gamma_1\gamma_3) \exp((-\Delta H_D + T\Delta S_D)/RT) \tag{13}$$

and the activity coefficients of the species are given in terms of their partial molar enthalpies and excess entropies by

$$RT \ln \gamma_j = \bar{h}_j - T\bar{s}_j^x. \tag{14}$$

This nonlinear equation was solved by the Newton–Raphson method starting with an approximation for the equilibrium constant in which the activity coefficients are all set to unity. Usually one or two iterations were sufficient to ensure that the sum of the absolute value of the fractional difference in successive values for y_2 and the absolute value of Eq. (12) for y_2 was less than 1.0E−08.

The Simplex method of Nelder and Mead [12] was used to vary some or all of the interaction parameters in a search for a best fit to the data. A measure of fit was defined for each data type as the standard deviation between observed and calculated temperatures for the liquidus and the fractional standard deviation for the partial pressures and the enthalpies of mixing. For the partial pressures, measures of fit were calculated separately for the partial pressure of tellurium along the CdTe three phase curve, that of cadmium, the partial pressure of tellurium for 55, 60, and 60 at.% Te liquids, and the enthalpies of mixing. In this way the goodness of a fit to

Table 2
Line 1 gives the best fits to the individual data types. Line 2 gives the best overall fit. The subscript 2 refers to the partial pressure of diatomic tellurium. ΔH refers to the enthalpy of mixing of the liquid phase.

σ_T	$\sigma_{2,3Phase}$	$\sigma_{Cd,3Phase}$	$\sigma_{2,Liquid}$	$\sigma_{\Delta H}$
8.7 °C	0.034	0.15	0.041	0.067
10.8	0.034	0.15	0.041	0.10

each data type could be seen and by adjusting the data weights, discussed below, the importance of each data type in establishing the parameters changed. The Simplex method varied the available parameters in order to minimize an overall measure of fit defined as follows: the square of the standard deviation for each data type was multiplied by its weighting factor, these were summed, and finally the square root taken. The weighting factors were taken as the reciprocal of the square of an estimated accuracy of a data type. This was 10 °C for the liquidus points, 0.05 for the tellurium partial pressures, 0.10 for those of cadmium, and 0.15 for the enthalpies of mixing. The 10% accuracy for the cadmium partial pressures is high because of the scatter of the pressure values along the Te rich leg of the three phase curve.

Initially, the parameters, C_{ij} and U_{ij}, multiplying factors cubic in the species mole fractions, and the temperature dependence of the remaining parameters, B_{ij}, were set equal to zero. Following Jianrong et al. [4], A_{13} and D_{13} representing the interaction of the Cd and Te species, were also set to zero leaving four parameters free.

5. Results

Best fits were obtained to the liquidus points alone, then to all the partial pressures, and finally to the enthalpies of mixing. The results are shown in the first line of Table 2. The second line shows the fits to each data type achieved when the parameters are determined by fitting the liquidus and the partial pressures together. It can be seen that these are as good as the individual fits for the partial pressures and almost as good for the liquidus points. However, in order to accomplish this it was necessary to include the parameters for the cubic interaction between CdTe and Te, namely F_{23} and H_{23}. For the enthalpy of mixing the compromise fit is decidedly poorer than the best fit. Not shown in Table 2 is the fact that the parameters giving the best fit to the enthalpies give poor fits to the other data types e.g. 91 °C to the liquidus points, 0.46 for the fractional standard deviation of the tellurium partial pressures on the CdTe(c) three phase curve, and 0.52 to the tellurium pressures over the Te rich liquids. The fit to the cadmium pressures is equal to the best attained, 0.15. One can conclude that within the framework of the liquid model and thermodynamic properties used here that the enthalpy of mixing data is inconsistent with the liquidus points and the tellurium partial pressures.

The parameters giving the best fits shown in line 2 are

$$\begin{aligned}
&\Delta H_D = 89{,}678.3; \qquad \Delta S_D = 17.2551; \qquad H_{D1} = 0.0; \\
&Z = 0.94776 \qquad Q_{12} = 30{,}541.2 - 17.4110\,T; \\
&Q_{13} = 0; \qquad Q_{23} = 5530.78 - 1.99000\,T \\
&C_{23} = 4376.12 - 2.05634\,T.
\end{aligned} \tag{15}$$

Here the enthalpy and entropy of dissociation for the CdTe species as well as the constant term in Q_{12} are determined by the other parameters and by the auxiliary conditions given by Eqs. (9)–(11). Thus for this fit six parameters plus Z were varied. As can be seen the parameters A_{13} and D_{13} are zero.

Fig. 1 shows the calculated liquidus as the solid curve and the experimental points from various sources as symbols. The three points from the optical density measurements might be expected
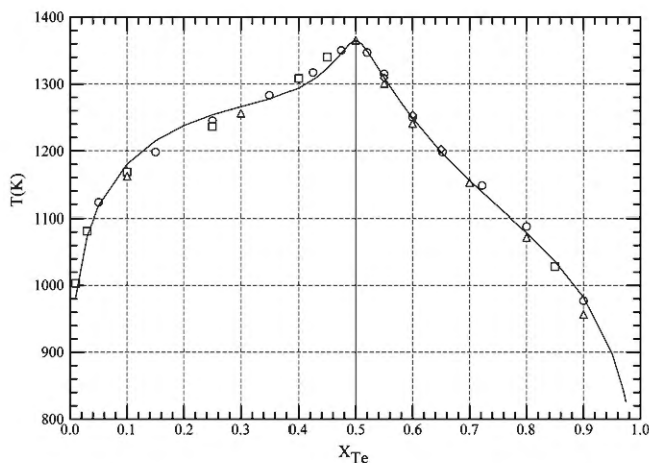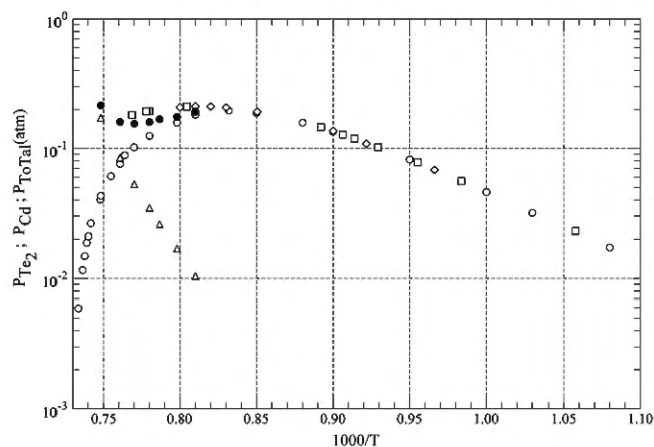
Fig. 1. CdTe(c) liquidus. Solid curve is calculated. Experimental points are shown as circles, [11]; squares, [19]; triangles, [20] and diamonds, [10]. The vertical line at $X = 0.50$ represents the narrow homogeneity compound CdTe(c).
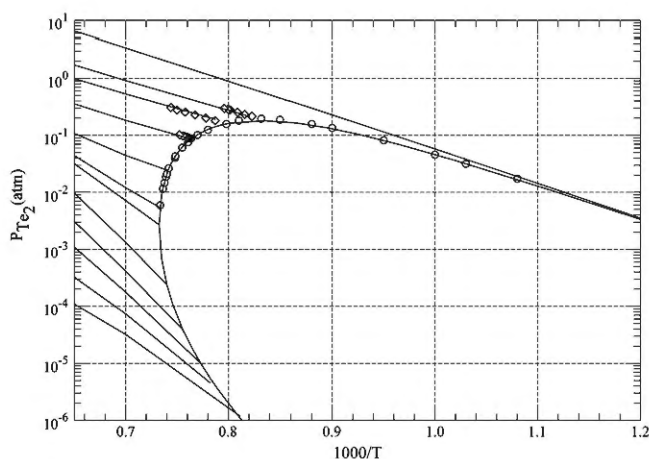
Fig. 2. Partial pressure of Te_2 along the three phase curve for CdTe(c) and for a number of liquids. Solid curves and lines are calculated. Liquid compositions in at.% Te for the line segments on the left and from top to bottom are 100, 65, 60, 55, 52, 50.5, 50.0, 48, 45, 40, 30, and 20. Circles are experimental [10] three phase points. Diamonds are experimental points for 65, 55, and 60 at.% Te liquids.

Fig. 3. Circles show the partial pressure of Te_2 along the three phase curve for CdTe(c) from optical density measurements [10]. Squares and diamonds show the total pressure from silica Bourdon gauge measurements [21,22]. Triangles show values for the Cd pressure calculated by us from P_2 and the Gibbs energy of formation of CdTe(c) as explained in the text. Filled circles are the sum of this Cd pressure and that of Te_2 at the same temperature for comparison with the measured total pressure.

Fig. 3 shows the experimental values of P_2 along the Te rich three phase curve from Ref. [10] as circles along with total pressures measured with a silica Bourdon gauge by Greenberg and coworkers as squares [21] and diamonds [22]. Up to about $1000/T = 0.85$ the measurements all agree to within a few percent. To see to what extent the data from Ref. [10] are consistent with the total pressure measurements at higher temperatures we have calculated values for P_{Cd} for a number of values of P_2 from Ref. [10] with the equation

$$P_{Cd} = \exp(\Delta G_f^0/RT)/P_2^{1/2}. \tag{16}$$

Eq. (16) follows from the fact that the homogeneity range of CdTe(c) is sufficiently narrow that the Gibbs energy of formation is essentially independent of composition. These are shown as triangles. The standard Gibbs energy of formation of CdTe(c) in J/mol and from Cd (g) and Te_2 (g) is given by the last line in Table 1.

The filled circles show the sum of the Cd and Te_2 pressures. It can be seen that our calculation for the total pressure is below that of Greenberg by 14%–17% at the highest two temperatures. The total pressure measurements were not included in the data fit but are shown to verify the accuracy of the optical density measurements.

Fig. 4 shows the partial pressure of Cd along the CdTe(c) three phase curve and for various liquids for which there is no data. Again the solid curves and lines are calculated. The uppermost line is the vapor pressure of Cd. Diamonds represent points from Lorenz [11] obtained by measuring the onset of freezing under fixed cadmium pressure and with a calibrated Pt–Pt10%Rh thermocouple. The agreement with other points is excellent although similar measurements under fixed tellurium pressure do not agree with the results shown in Figs. 2 and 3. Experimental points shown as circles are from Fig. 5 of Ref. [10] for the Cd leg of the three phase curve and for three points from Table I and Fig. 4 of Ref. [3] for the Te rich leg. Reexamination of the data collected for Ref. [10] from two optical cells has yielded an additional 17 values for the cadmium pressure on the Te rich leg of the three phase curve. These are listed in Table 3 and are at high temperatures where P_2 is decreasing with increasing temperature. At P_2 equal to or less than 0.06 atm the broadening by Te_2 of the 325.7 nm Cd peak or the UV wing of the 228.7 nm peak is insignificant as demonstrated by the agreement of the product $P_2^{1/2}P_{Cd}$ with values obtained from congruently subliming CdTe. Ten Cd pressures from one cell were obtained from the

to be more accurate than the results of thermal analysis since they are from a static measurement and are identified as sharp breaks in the slope of log (P_2) vs. $1000/T$. The corresponding calculated point for 55 at.% Te at 1037 is 1° high, that for 60 at.% at 976 is 4° low, and that for 65 at.% at 928 is 1° low. The calculated liquidus is about 10°–20° low between 40 and 45 at.% Te and about 15° high between 10 and 25 at.% Te. With the number of adjustable parameters limited to seven it proved necessary to forgo a closer fit in order to optimize the fit to the partial pressure of tellurium over Te rich CdTe(c). The calculated eutectics are 99.20 at.% Te and 447.6 °C and 3.8E−06 at.% Te and 321 °C.

The calculated partial pressure of Te_2 along the CdTe(c) three phase curve and for a number of liquids are shown as the solid curve and line segments in Fig. 2. The uppermost line is the vapor pressure of Te. Circles show the experimental points along the three phase curve and are given in Table I of Ref. [10]; diamonds show the experimental points for the 55, 60, and 65 at.% liquids and are given in Table II of Ref. [10]. (There are corrections necessary for the next to last column of Table I of Ref. [10] for P_2. These are 0.06 for 0.6 as the 1st entry and 0.0068 for 0.068 and 0.0056 for 0.056 for the last two entries. These are obvious from Fig. 3 of that Ref.) The fractional standard deviation is 0.034 for the three phase curve and 0.041 for the liquids.
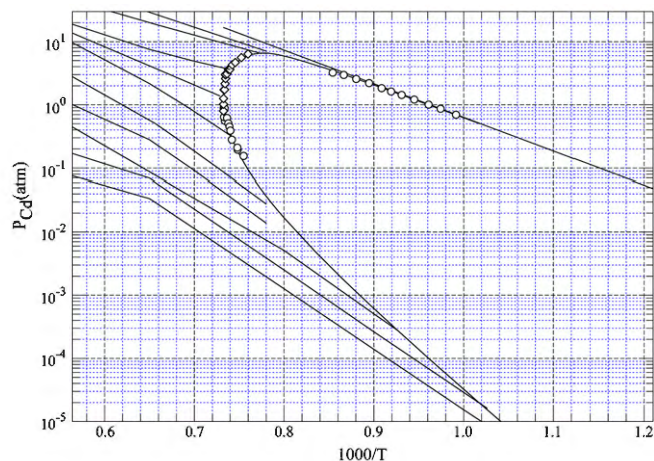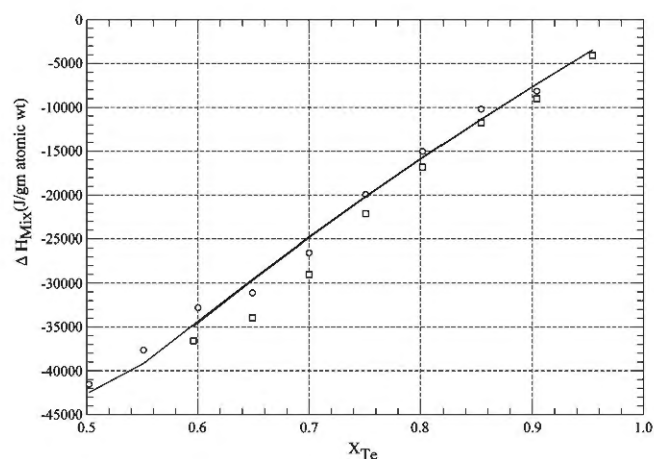
Fig. 4. Partial pressure of Cd along the three phase curve for CdTe(c) and for a number of liquids. Solid curve and lines are calculated. Liquid compositions in at.% Te from top to bottom are 0, 30, 40, 48, 50, 52, 60, 70, 80, 90, and 95. Circles [10] and diamonds [11] are experimental.

Fig. 5. Enthalpy of mixing of $Cd_{(1−X)}Te_X$ liquids at 1400 and 1259 K in J/g atomic weight and as a function of the atomic fraction of Te. Experimental points [9] are shown as circles for 1400 K and squares for 1259 K. The solid curves are calculated. That for 1259 K ends at 60 at.% Te where it is barely distinguishable from the curve for 1400 K. A gram atomic weight of $Cd_{1−X}Te_X$ contains one Avogadro number of atoms in the proportion of X atoms of Te for every $1 − X$ atoms of Cd.

Table 3
Partial pressures of Cd and Te_2 over Te saturated CdTe(c).

| 1000/T	P_{Cd} (atm)	P_2 (atm)	1000/T	P_{Cd}	P_2	1000/T	P_{Cd}	P_2
0.7549	0.155	0.060	0.7317	0.875	0.0056	0.7391	0.45	0.019
0.7483	0.195	0.042	0.7321	0.900	0.0056	0.7402	0.39	0.040
0.7418	0.285	0.025	0.7327	0.890	0.0056	0.7566	0.17	0.60
0.7340	0.565	0.011	0.7336	0.880	0.0061			
0.7331	0.640	0.007	0.7364	0.620	0.012			
0.7315	0.890	0.0055	0.7378	0.510	0.015			

optical densities at 240, 280, and 325.7 nm. Seven Cd pressures were obtained from the optical density at the 325.7 nm peak. The fractional standard deviation of 0.10 is to a large extent set by the scatter of the experimental points along the Te rich leg of the three phase curve.

For 50 at.% Te and 1365 K the cadmium pressure is 1.19 atm while, from Fig. 2, it is 3.2E−03 for diatomic tellurium.

Yamaguchi et al. [9] have measured the temperature increase of the enthalpy for various Te rich compositions from 298 to 1400 K and from these calculated the enthalpy of mixing for the liquid phase at 1259 and 1400 K. To obtain the enthalpies of mixing of
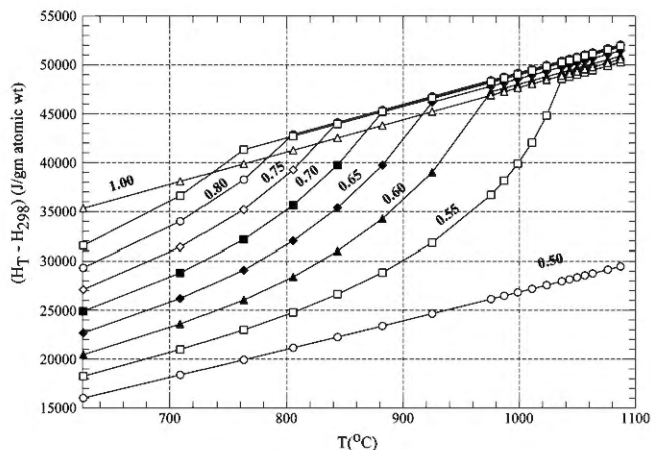
Fig. 6. Increase of the enthalpy of various Te rich compositions above that at 298 K as a function of temperature. Labels give the atomic fraction of Te.
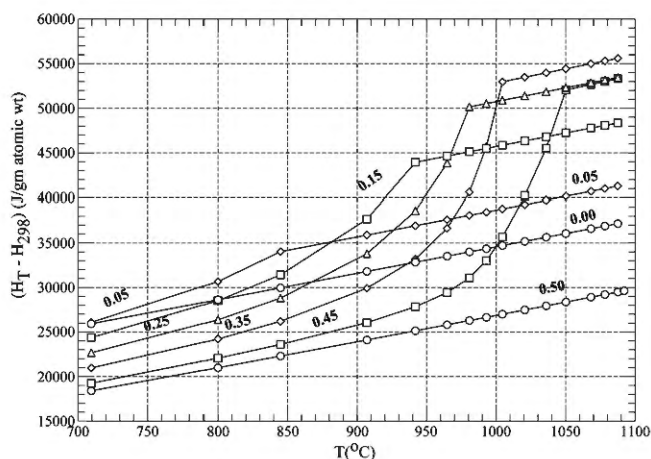
Fig. 7. Similar to Fig. 6 but for compositions containing less than 50 at.% Te. Labels give the atomic fraction of Te.

the liquid phase one needs [9] the enthalpies of Cd and Te as a function of temperature and the enthalpy of formation of CdTe(c) at 298 K. The latter appears as the term $(1 − X)\Delta H^0_{f,298}$, where X is the atom fraction of Te in the liquid. (See Eq. (9) of Ref. [9]). We have adjusted the values of Yamaguchi et al. given as a graph by using our value of −100.27 kJ/mol in place of their −112 for the enthalpy of formation at 298 K. Fig. 5 shows our calculated value at 1400 K as the solid upper line. That at 1259 K is the essentially coinciding dashed line. The adjusted experimental values are shown as circles and squares. There is fair agreement at 1400 K but the experimental values at 1259 K are more negative than the calculated ones by as much as 5 kJ/g atom.

For completeness we show calculated values for the enthalpy of various compositions as a function temperature in Fig. 6 for Te rich compositions and in Fig. 7 for Cd rich compositions. The low temperature parts of the curves correspond to two phase mixtures of CdTe(c) and a Te rich or Cd rich liquid. The high temperature, straight line parts correspond to liquids of the labeled composition. Yamaguchi et al. give a three-dimensional plot of their experimental results for Te rich compositions but we have not been able to scale these accurately for comparison. It appears that our calculated results would be only in rough agreement.

6. Discussion

Except for the enthalpy of mixing for the liquid phase, we believe that the experimental data have been fit to within

Table 4

Best fit parameter values and changes in them required to approximately double the measure of fit to the value shown. σ_2 is the measure of fit to the partial pressure of Te_2 over Te saturated CdTe(c). σ_T is the measure of fit to the liquidus points in degree centigrade. $\sigma_{2,Liq}$ is the measure of fit to the partial pressure of Te_2 over Te rich liquids.

Parameter	Best fit value	$\sigma_T = 20$	$\sigma_2 = 0.07$	$\sigma_{2,Liq} = 0.08$
A_{23}	5530.7	−1011; +949	−231; +229	−411; +229
D_{23}	1.99	−0.81; +0.83	−0.17; +0.19	−0.28; +0.31
A_{13}	0.00	−22,000; +32,000	−22,000; 17,000	−29,000; >+50,000
D_{13}	0.00	−21.5; +20	−12; +14	<−50; +24
D_{12}	17.411	−0.82; +1.6	−0.93; +0.72	<−1.1; >+2.1
F_{23}	4376.1	−3466; +2274	−426; +774	−2216; +3840
H_{23}	2.056	−0.14; +2.67	−0.49; 0.34	−1.0; +1.74
Z	0.9477	−0.0084; +0.0061	−0.0045; 0.0061	<−0.011; +0.0073

their probable accuracy. A question arises as to how closely the interaction parameters are fixed as a result. To explore this question the parameters given in Eq. (15) were changed away from their best fit values one at a time and the change in the measure of fit noted. In this process the parameters A_{12}, ΔH_{D0}, and ΔS_{D0} are also varied to satisfy the constraints imposed by Eqs. (9)–(11). As mentioned earlier, these ensure consistency between the thermodynamic properties of CdTe(c) at its melting point and those of its coexisting liquid. It was found that the measure of fit to P_2 over Te saturated CdTe(c) and that over the liquidus were the most sensitive to changes in the parameters. The fits to P_{Cd} over Cd and Te saturated CdTe(c) and that to the enthalpy of mixing of the liquid were the least sensitive. The measure of fit to P_2 over the 55, 60, and 65 at.% liquids was intermediate in sensitivity. In the case of the enthalpy of mixing the term $y_2\Delta H_D$, occurring in Eq. (7) for the partial molar enthalpy of the compound species CdTe, dominates. Thus relatively large changes in the other parameters cause relatively small changes in the enthalpy of mixing and the measure of fit. In the case of P_{Cd} the observed partial pressures correspond to a relatively small range in atom fraction of Te. For P_{Cd} over Cd saturated CdTe(c) the atomic fraction of Te varies between 0.03 and 0.09. For that at high temperature the atomic fraction of Te varies between 0.44 and 0.54. Evidently, because of the small temperature and composition ranges covered by the observed data they can be fit equally well by a range of parameters.

As an example of the varied sensitivity of different data types we consider the effect of A_{23}. Changing A_{23} from its best fit value of 5530 by about ±1000 J/g atom doubles the measure of fit to the liquidus to 20 °C. Changing it by only ±160 doubles the measure of fit to P_2 over Te saturated CdTe(c) to 0.07, and changing it by ±370 increases the measure of fit of P_2 over the Te rich liquid from 0.041 to 0.08. Presumably the narrowest range applies and A_{23} is determined to within ±160 J/g atom. The results for all the parameters are shown in Table 4 which lists the best fit value for the parameter and the change downwards and upwards required to approximately double the measure of fit for three data types. The parameter changes required to change the measure of fit to the partial pressure of cadmium along the CdTe(c) three phase curve or that to the enthalpy of mixing are much larger and not shown. The changes are approximately symmetric about the best fit value in some cases and are generally smallest for P_2 over Te saturated CdTe(c). Of particular note is the very weak dependence of the measures of fit on A_{13} and D_{13}, both of which are zero in the best fit given in Eq. (15). The reason for this is that the mole fraction of the CdTe liquid species is near its maximum value over an extended range of composition and therefore the mole fraction of either the Cd species or that of the Te species is near zero. As a result the contributions of $A_{13}y_1y_3$ and $D_{13}y_1y_3$ to the chemical potentials are minor for a large range of A_{13} and D_{13} near their best fit values of zero.

In fitting the partial pressure of Te_2 or Cd the corresponding chemical potential is involved and in fitting the liquidus points the sum of the chemical potentials of species Cd and Te is set equal to the Gibbs energy of formation of CdTe(c). The parameters appear in the chemical potentials as $Q_{ij} − P_{ij}T$ and $C_{ij} − U_{ij}T$. Because we have not used the full complexity of the model here these reduce to $A_{ij} − D_{ij}T$ and $F_{23} − H_{23}T$.

Corresponding values of A_{ij} and D_{ij} are found to fall along a straight line so that larger changes in either are required to give a given increase in the measure of fit provided the changes occur together. As an example, provided A_{23} and D_{23} are changed together the former must be either decreased by 2530 or increased by 4770 J/g atom in order to double the measure of fit to P_2 over Te saturated CdTe(c) to 0.07. As noted above and in Table 4 the change is about one-tenth of this when A_{23} is changed alone.

Finally, we comment on our use of a 1092 °C melting point. Yamaguchi et al. [9] obtain a 1095 melting point from enthalpy measurements and Jianrong et al. [4] allowed the melting point to be a variable in their fitting process and found a better fit with 1095 than with 1092 °C. If we use 1095 we find that although the liquidus can only be fit to within 11.3 °C, the points at 35, 42.5, and 47.5 at.% Te are fit better than before and to within −6 °C, −9 °C, and −0.5 °C, respectively. The measure of fit to P_2 over Te saturated CdTe(c) is slightly worse at 0.06 as is that for P_{Cd} over Te saturated CdTe(c) at 0.192. However, the three calculated values for the tellurium pressure between 1090 and 1082.4 are high by 10%–20%. The calculated values for the cadmium pressure between 1089 and 1090 are low by 10%–50%. We believe that the better fit to these partial pressures at high temperature justifies the use of the 1092 °C melting point.

7. Conclusions

The fit to the tellurium partial pressures to within 4% obtained here has been at the expense of a slightly poorer fit to the liquidus line in the 40–47 at.% Te range and to only a moderately good fit to the heats of mixing for the Te rich liquid phase. The results suggest that a careful redetermination of the melting point would be useful. Possible outcomes would be to confirm the 1092 °C value supported by the partial pressure measurements and used here. Alternatively the higher 1095 °C value obtained by Yamaguchi et al. [2] and used also by Jianrong et al. [4] to improve the liquidus fit in the 40–47 at.% Te range might be confirmed requiring a reanalysis. A redetermination of the heat of mixing would also be useful. Confirmation of the results from Yamaguchi et al. [9] would require an extension of the model that possibly could be met by the adoption of the more complicated temperature dependence the model allows and the use of more interaction parameters. The cadmium and tellurium partial pressures calculated here as well as the calculated temperature dependence of the enthalpy of various Cd–Te compositions would be of some use in deciding the most profitable temperature and composition ranges to be studied.

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