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High Temperature Thermodynamic Data for CdTe(c)

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Abstract

The high temperature heat capacity, Gibbs energy of formation, and standard enthalpy and entropy of formation at 298 K are combined with thermodynamic data for Cd and revised data for Te to provide an internally consistent data set for CdTe(c). Equations are given for the Gibbs energy of formation from Cd(g) and Te₂(g) and from the solid or liquid elements as a function of temperature. These give values similar to those used before. However, the derived enthalpy and entropy of formation are significantly different due to a revised heat capacity for CdTe(c). The standard enthalpy and entropy of formation at 298.15 K from the gases are –293262 J/mol and –200.593 J/mol K, respectively. From the solid elements they are –100270 and –4.5334.

Introduction

Recently, high temperature heat capacity determinations for CdTe(c) by Malkova et al.[1] and by Yamaguchi et al.[2] and by others at lower temperatures have been reviewed by Pavlova et al.[3] Here we wish to extend this study of the thermodynamic properties of CdTe(c) to include experimental

values for the high temperature Gibbs energy of formation. The standard enthalpy and entropy of formation at 298.15 are also required, but both are fairly well established. Earlier assessments of the entire Cd-Te system by Jianrong et al.[4] in 1995 and by the author and coworkers.[5,6] depended in part on an estimate of the heat capacity of CdTe(c) made by Mills.[7] which was based on the heat content measurements by Mezaki et al.[8] According to Pavlova et al.,[3] this heat capacity is high by as much as 15 J/mol K at the 1365 K melting point. Besides, assessments of the entire system are more complicated than necessary to establish the thermodynamic properties of the CdTe(c) phase itself. For our purposes, the properties of cadmium and tellurium are of course required. Those of cadmium are well established. For tellurium, we use this author's third law analysis[9] of the crystal-liquid-vapor equilibrium for Te. A heat capacity for the liquid determined by Medzhidov and Rasulov[10] was used which is much different than that used in previous thermodynamic calculations. A review of the heat capacity of Te by Davydov et al.[11] was shown[12] to give closely similar results.

Formation of CdTe(c) from Its Cd(g) and Te₂(g)

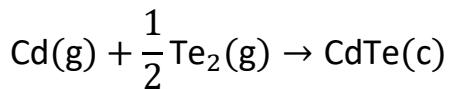
Partial Pressure Data

The predominant vapor species over CdTe(c) are cadmium and diatomic tellurium. The partial pressures of Cd(g) and Te₂(g) over congruently subliming CdTe(c) have been determined by measuring the UV-VIS optical absorbance of the coexisting vapor.[13] The smoothed values for the partial pressure of diatomic tellurium are given by,

$$\log_{10} P_2(\text{atm}) = -10,000/T + 6.346; 1051-1230\text{K.}$$

(1)

Here and henceforth the partial pressure of diatomic tellurium will be written as P_2 . At each measurement temperature, Eq 1 is used to calculate a partial pressure of diatomic tellurium. That of cadmium is taken as twice this. The standard Gibbs energy of formation for the reaction:



(2)

is given by:

$$\Delta G_f^\circ = RT \ln (f_{\text{Cd}} P_{\text{Cd}} f_2^{1/2} P_2^{1/2}),$$

(3)

where f_j is the fugacity coefficient of gaseous species j . These fugacity coefficients account for the nonideality of the vapor phase and can be expressed in terms of virial coefficients. It is assumed that the pressures involved are low enough that the second virial coefficient suffices. Then if the virial coefficients are written as B_{JK} one has[14]:

$$\begin{aligned} \ln f_{\text{Cd}} &= P_{\text{Cd}}(1 + P_2/P_T)B_{\text{Cd}} + (P_2^2/P_T)(2B_{\text{Cd-Te}_2} - B_{\text{Te}_2}) \\ \ln f_2 &= P_2(1 + P_{\text{Cd}}/P_T)B_{\text{Te}_2} + (P_{\text{Cd}}^2/P_T)(2B_{\text{Cd-Te}_2} - B_{\text{Cd}})' \end{aligned}$$

(4)

where P_T is the total pressure. Studies of tellurium vapor[15] have given its second virial coefficient as,
 $B_{Te_2} = -440.397/T + 0.26899; T > 900K.$

(5)

The second virial coefficient for Cd(g) is calculated here. For the ground state we use a Leonard-Jones 6-12 potential determined from optical absorbance measurements[16] of the 228.7 nm line at a number of temperatures and cadmium pressures. These gave an energy minimum of 0.0475 eV and a separation at zero potential energy of 0.4295 nm. A published[17] series solution was evaluated numerically to generate the virial coefficient as a function of temperature. The numerical result was fit with a standard deviation of 5E-05 by the equation:

$$B_{Cd} = 9.4649/T^{1.25} - 2662.6/T^2; 800-1436K.$$

(6)

Finally, the virial coefficient for the Cd-Te₂ interaction was assumed to be the average of those for Cd-Cd and Te₂-Te₂,

$$B_{Cd-Te_2} = (1/2)(B_{Cd} + B_{Te_2}).$$

(7)

Table 1 gives the temperature and value of the Gibbs energy according to Eq 3. The fugacity coefficient correction is negative and reaches its largest absolute value of 27 J/mol at 1245.2 K.

Table 1 Gibbs energy of formation of CdTe(c) from gaseous and from condensed phase elements

| T, K | $-\Delta G_{f,298}^{\circ}, J/mol, \text{ from gases, Eq 2 and 3}$ | $-\Delta G_{f,298}^{\circ}, J/mol, \text{ from solid or liquid elements, Eq 15 and 16}$ |
|--------|--|---|
| 1052.6 | 89289 | 81067 |
| 1078.8 | 84376 | 79872 |
| 1096.5 | 81049 | 79065 |
| 1133.8 | 74008 | 77313 |
| 1154.7 | 70091 | 76356 |
| 1165.5 | 68071 | 75852 |
| 1179.2 | 65472 | 75189 |
| 1201.9 | 61229 | 74127 |
| 1216.6 | 58436 | 73386 |
| 1245.2 | 53075 | 72043 |

Calculated with partial pressure data from ref 13

The smoothed partial pressures of Te₂ and Cd over Te-saturated CdTe as determined from optical absorbance measurements[18] are given in Table 2. The Gibbs energy of formation of CdTe from Cd(g) and Te₂ as calculated with Eq 3 and that from the liquid elements (discussed later) are also listed. The fugacity correction is negative, is essentially all due to tellurium, and is 210 J/mol or less in magnitude.

Table 2 Gibbs energy of formation of CdTe(c) from gaseous and from condensed phase elements

| <i>T</i> , K | <i>P</i> ₂ , atm | <i>P</i> _{Cd} , atm | $-\Delta G_{f,298}^{\circ}$, J/mol from gaseous elements | $-\Delta G_{f,298}^{\circ}$, J/mol from solid or liquid elements |
|--------------|-----------------------------|------------------------------|---|---|
| 1337.0 | 0.042 | 0.190 | 36158 | 67957 |
| 1351.0 | 0.023 | 0.310 | 34448 | 68204 |
| 1360.0 | 0.012 | 0.480 | 33458 | 68472 |
| 1366.1 | 0.0068 | 0.68 | 32933 | 68800 |

Partial pressure data from ref 18

The first three columns of Table 3 give the temperature and partial pressure of Te₂ obtained from Knudsen cell measurements by Goldfinger and Jeunehomme.[19] The Gibbs energies are from an equation given in the caption of their Fig. 6 and are calculated for each temperature in that figure, which is a plot of log *K* versus 1000/*T*. The partial pressure of Te₂ is calculated from this Gibbs energy assuming an effusion steady state in which the flux of Te₂ out from the Knudsen cell in moles/sec is one-half that of Cd. Then inside the cell the pressures are related by,

$$P_{Cd} = 2(M_{Cd}/M_{Te_2})^{1/2}P_2 = 1.327P_2.$$

(8)

The quantities within the square root are the atomic weight of Cd and molecular weight of diatomic tellurium. The Gibbs energy was recalculated with these partial pressures according to Eq 3. The correction for a non ideal vapor was <1 J/mol.

Table 3 Partial pressures from Knudsen cell measurements of reference 19 and Gibbs energy of formation

| <i>T</i> , K | <i>P</i> ₂ , atm | <i>P</i> _{Cd} , atm | $-\Delta G_{f,298}^{\circ}$, J/mol from gaseous elements | $-\Delta G_{f,298}^{\circ}$, J/mol from solid or liquid elements |
|--------------|-----------------------------|------------------------------|---|---|
| 733.1 | 3.84E-7 | 5.09E-7 | 140610 | 92192 |
| 781.9 | 5.32E-7 | 7.06E-7 | 139030 | 91895 |
| 794.8 | 8.50E-7 | 1.13E-6 | 136680 | 91438 |
| 813.7 | 1.64E-6 | 2.17E-6 | 133280 | 90776 |
| 829.1 | 2.74E-6 | 3.64E-6 | 130460 | 90187 |
| 845.2 | 4.59E-6 | 6.09E-6 | 127570 | 89629 |
| 860.3 | 7.33E-6 | 9.73E-6 | 124830 | 89670 |
| 877.7 | 1.23E-5 | 1.63E-5 | 121700 | 88459 |
| 895.6 | 2.05E-5 | 2.73E-5 | 118440 | 87785 |
| 905.8 | 2.72E-5 | 3.61E-5 | 116620 | 87423 |
| 916.2 | 3.60E-5 | 4.78E-5 | 114750 | 87055 |
| 926.8 | 4.77E-5 | 6.33E-5 | 112820 | 86656 |
| 950.6 | 8.78E-5 | 1.16E-4 | 108490 | 85727 |
| 960.1 | 1.11E-4 | 1.47E-4 | 106790 | 85375 |
| 979.7 | 1.77E-4 | 2.35E-4 | 103240 | 84630 |
| 1006.5 | 3.26E-4 | 4.32E-4 | 98412 | 83623 |

The corrected Gibbs energies from the above three sources are shown in Fig. 1 and can be seen to fall close to the same straight line. A least squares fit to the data gives a standard deviation is 303 J/mol and is represented by:

$$\Delta G_f^\circ(\text{J/mol}) = -284730 + 185.80T.$$

(9)

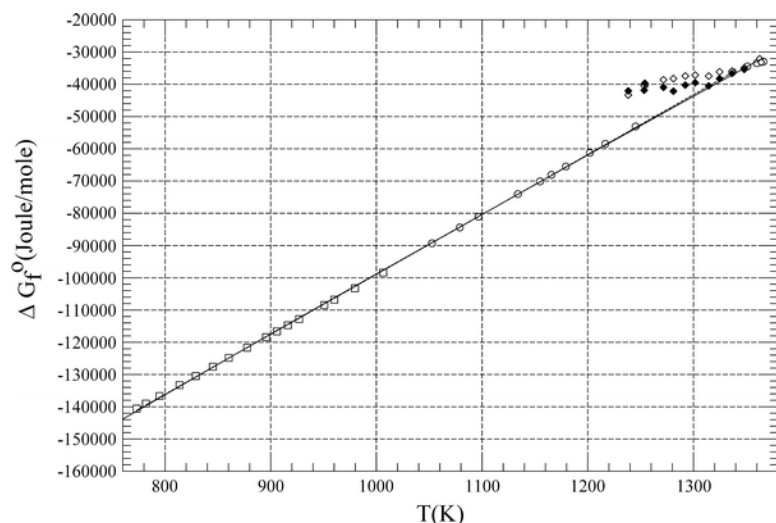


Fig. 1 Gibbs energy of formation of CdTe(c) from gaseous cadmium and diatomic tellurium each at 1 atm. *Squares*; ref 19, Knudsen cell. *circles*; ref 13, optical absorption. *Circles at and above 1245 K*, ref 18, vapor over Te-saturated CdTe (c). *Dashed line* from second law analysis, Eq 9. *Solid line* from third law analysis with $\Delta H_{f,298}^\circ = -293262 \text{ J/mol}$ and $S_{298}^\circ(\text{CdTe(c)}) = 96.367$ or $\Delta S_{f,298}^\circ = -200.593 \text{ J/mol K}$

The diamonds at high temperature are for Te-saturated CdTe[20] and were not included in the least squares fit. For the open diamonds the partial pressure was calculated from the Cd peak at 325.7 nm while for the closed diamonds it was calculated from the absorbance at 240.0 nm in the far wing of the strongly absorbing 228.7 nm peak. The fugacity correction ranges from -77 to -200 J/mol at 1348 K. For these points the partial pressure of diatomic tellurium is decreasing from 0.131 atm at 1238 K to 0.0248 atm at 1348 K. With increasing temperature the points approach and then coincide with the least squares line. The discrepancy at the lowest temperatures is most likely due to the fact that the absorbance at the Cd peaks has not been corrected for pressure broadening by Te_2 . It would appear that this effect is negligible from about 1330 K upward. These data have not been included in the analysis except as an indication that the pressure broadening is negligible for the four circles from Table 2 at the highest temperatures.

Third Law Analysis

At equilibrium between CdTe(c) and the vapor phase, the chemical potential of cadmium must be the same in both phases, as must be that of tellurium. Moreover, the chemical potential of tellurium is equal to one-half that of the gaseous, diatomic tellurium molecule. Adding the two equations for the chemical potentials and applying standard thermodynamic formulae one arrives at the equation,

$$\Delta G_f^{\circ} = \Delta H_{f,298}^{\circ} - TS_{298}^{\circ} + (H_T^{\circ} - H_{298}^{\circ})_{\text{CdTe}} - T(S_T^{\circ} - S_{298}^{\circ})_{\text{CdTe}} - (H_T^{\circ} - H_{298}^{\circ})_{\text{Cd(g)}} + TS_{T,\text{Cd(g)}}^{\circ} - (1/2)(H_T^{\circ} - H_{298}^{\circ})_{\text{Te}_2(\text{g})} + (1/2)TS_{T,\text{Te}_2(\text{g})}^{\circ}$$

(10)

where ΔG_f° is the standard Gibbs energy of formation of CdTe(c) from the gases as given by Eq 3. Our choice of the standard entropy at 298 K for CdTe(c) as a parameter, rather than the standard entropy of the reaction, is arbitrary and of no fundamental significance. If the heat capacity of CdTe(c), the chemical potentials of Cd(g) and Te₂(g), and $\Delta H_{f,298}^{\circ}$ and S_{298}° are known, then at each temperature one can calculate a value for the right side of Eq 10 for comparison with the experimental value of the Gibbs energy. Here we treat the enthalpy of formation and the entropy of CdTe(c) at 298 K as variables. Although values exist for them in the literature we expect that small adjustments will be necessary to minimize the standard deviation between the values of the standard Gibbs energy calculated with Eq 10 and those observed. Before discussing this minimization we indicate the values used for the other quantities in the right side of Eq 10.

The sources of the quantities in Eq 10 that are assumed to be known are as follows. With a value of 20.786 J/mol K for the constant pressure heat capacity[21] of Cd(g) above 298.15 K and a standard entropy at 298.15 K of 167.63 J/mol K one arrives at the results:

$$\begin{aligned} (\Delta H_T^{\circ} - \Delta H_{298}^{\circ}) &= 20.7861(T - 298.15) \\ S_{T,\text{Cd(g)}}^{\circ} &= 49.201 + 20.7861\ln(T) \end{aligned}$$

(11)

Similarly, for T above 298 K the thermodynamic properties of Te₂ (g, 1 atm) were calculated by Mills[7] from spectroscopic constants. These properties can be simply but accurately given between 400 and 1400 K using the constant pressure heat capacity:

$$C_p(\text{J/molK}) = 29.070 + 0.02645T - 1.1484(10^{-5})T^2.$$

(12)

With this result and a standard entropy at 298.15 K of 258.66 J/mol K, one has,

$$\begin{aligned} (H_T^{\circ} - H_{298}^{\circ})_{\text{Te}_2(\text{g})} &= 29.070(T - 298.15) + 0.013228(T^2 - 298.15^2) - 3.828(10^{-6})(T^3 - 298.15^3) \\ S_{T,\text{Te}_2(\text{g})}^{\circ} &= 85.645 + .026456T - 5.742(10^{-6})T^2 + 29.070\ln(T) \end{aligned}$$

(13)

Because we have found that constant pressure heat capacities for CdTe(c) given by Yamaguchi et al.[2]. and by Pavlova et al.[3] give close to the same fits to the data used here we use a heat capacity that is the average of these two:

$$C_p = 48.740 + .008505T - 1.171(10^5)/T^2.$$

(14)

The heat capacities given by Pavlova, by Yamaguchi, and in our study[6] of the Cd-Te system are all 50 ± 0.5 J/mol K at 298 K. However, they differ significantly at the 1365 K melting point where they are, respectively, 58.7, 62.0, and 70. We also note that the heat contents calculated with the heat capacity given by Yamaguchi et al. are larger than those calculated with that given by Pavlova et al., but by <1 J/mol between 298 and 800 K and by only 1 kJ/mol at 1365 K.

The linear theory of adjustment[22] was used to obtain the values at 298 K for the standard enthalpy of formation of and the entropy for CdTe(c) which minimize the standard deviation between calculated and observed values for the Gibbs energy. The 95% confidence levels in these quantities were also obtained. Then the Simplex trial and error method of Nelder and Mead[23] was used to calculate the standard deviation and the value for the enthalpy for fixed values of the entropy in the neighborhood of the best fit.. The best fit to the left side of Eq 10 is attained with $\Delta H_{298}^{\circ} = -294,008$ J/mol, $S_{298}^{\circ} = 95.64$ J/mol K, and a standard deviation of 410 J/mol. However, as is shown in Fig. 2, there is a wide range of enthalpy and entropy values falling along a straight line which give almost equally good fits. The standard deviation rises rapidly with small departures from this line. As has been pointed out,[24] this is a feature of linear least squares fits to a set of data made over a temperature range small compared to the average temperature of the measurements themselves. Moreover, if the enthalpy is expressed as a linear function of the entropy, then the slope (coefficient of the entropy) is the reciprocal of the average value of $1/T$ of the measurements, 1007.9 in this case. This best fit line is useful in attaining consistency with the quantities for the formation from the condensed phase elements since it turns out to be necessary to move away from the very best fit. It is also useful in graphically demonstrating that the uncertainties in the enthalpy and entropy are strongly correlated. Along this best fit line the literature value of $-293,000$ J/mol for the enthalpy change corresponds to a standard entropy at 298 for CdTe(c) of 96.6 and $\sigma = 440$, just above the minimum value. Similarly, the literature value of 95 for the entropy corresponds to an enthalpy of formation of $-294,600$ and a standard deviation of 420, again just above the minimum attained. However, the paired literature values of $-293,000$ and 95 are off the best fit line and correspond to $\sigma = 1702$. This is about four times the minimum value. It is apparent that a small adjustment is required in these parameters. Further discussion is delayed until the Gibbs energy of formation from the condensed phase elements is analyzed.

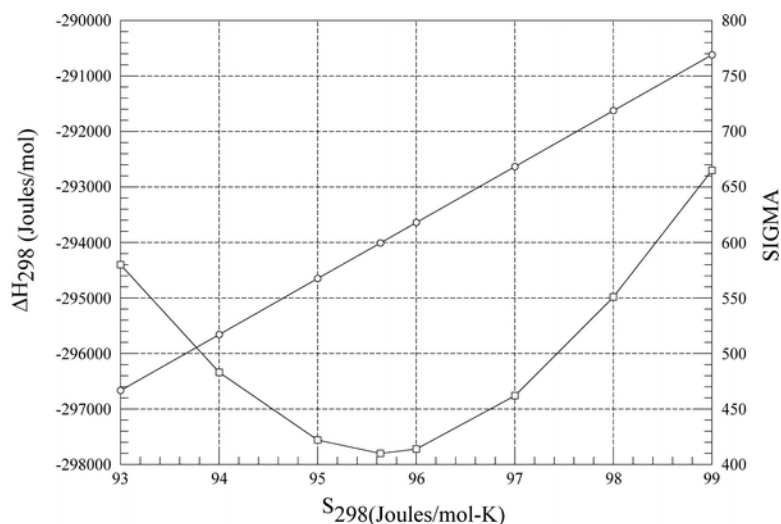
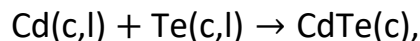


Fig. 2 The parabola-like curve shows the best fit between the observed Gibbs energies of formation in Fig. 1 and third law values as a function of the standard entropy of CdTe(c) at 298 K. The best fit or standard deviation between observed and calculated values is given by the right vertical axis. The straight line shows corresponding values of the standard enthalpy of formation and the standard entropy of CdTe(c) at 298 K that give a best fit for a fixed value of the entropy

Formation of CdTe(c) from Its Condensed Phase Elements

Calculation of the Gibbs Energy of Formation from Data

For the reaction,



(15)

the Gibbs energy of formation is given by,

$$\Delta G_f^\circ = RT \ln (P_{\text{Cd}} f_{\text{Cd}} / P_{\text{Cd}}^\circ f_{\text{Cd}}^\circ) + (1/2) RT \ln (P_2 f_2 / P_2^\circ f_2^\circ),$$

(16)

where the superscript circle indicates a partial pressure or fugacity in the vapor over the pure element. For cadmium, the necessary properties are taken from Hultgren et al.[21] and have also been adopted by SGTE.[25] They are:

$$C_p = 22.30 + .01213T; 298 < T < 594.2; \text{m.pt.} 594.2\text{K}; \text{Enthalpy of fusion} = 6192\text{J/mol}$$

$$C_p = 29.71; T > 594.2\text{K}$$

$$\text{Cd(c)}; S_{298}^\circ = 51.80 \text{ J/molK}; \text{Cd(g)}; S_{298}^\circ = 167.63$$

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

$$\log_{10} P_{\text{Cd}}(\text{atm}) = 5.119 - 5317/T; T > 594.2\text{K}$$

(17)

The corresponding quantities for tellurium are taken from our third law analysis[9] of the crystal-liquid-vapor equilibrium. As mentioned earlier, the heat capacity above the melting point is quite different from that given by Mills[7] and used in previous studies. It is close to that adopted by Davydov et al.[11] The enthalpy and entropy of Te(l) calculated with our heat capacity and that of Davydov et al. differ by <0.5% between 722.65 and 1365 K. However, our vapor pressures are 7-20% higher than those adopted by Davydov et al. and closer to the experimental values. The necessary thermodynamic data for tellurium are:

$$\begin{aligned}
& \text{m. pt.} = 722.65\text{K}; \text{ heat of fusion} = 17,489 \text{ J/mol} \\
& C_p = 24.610 + 0.003217T + 1.678(10^{-6})T^2; 298 < T < 722.65 \\
& C_p = 131.7 - 0.1185T; 722.65 < T < 833\text{K} \\
& C_p = 32.94; T > 833\text{K} \\
& \text{Te(c)}; S_{298}^{\circ} = 49.1\text{J/mol K} \quad \text{Te}_2(\text{g}); S_{298}^{\circ} = 258.66 \\
& \text{Te(c)} \rightarrow \frac{1}{2}\text{Te}_2(\text{g}); \Delta H_{f,298}^{\circ} = 81,031\text{J/mol}
\end{aligned}$$

(18)

We originally gave[9] four equations for the vapor pressure between 722.65 and 1434 K. We now find that these can be approximated to better than two percent by the single equation:

$$\log_{10} P(\text{atm}) = 4.3985 - 5267.68/T - 368192.2/T^2; 722.65 < T < 1434\text{K}$$

(19)

In this temperature range, the saturated vapor is 99% or better $\text{Te}_2(\text{g})$. [7]

With the above input data the Gibbs energy of formation from the gaseous elements in Table 1-3 were converted to Gibbs energies of formation from the condensed phase elements following the reaction in Eq 15. The results are shown in the last column of Table 1-3. For the entries shown in Table 1, the correction for vapor phase nonideality are all positive and range from 81 J/mol at 1052 K, 73 of which arise from the tellurium correction, and 375 J/mol at 1245 K, 343 of are from the tellurium term. In Table 2, the corrections are all about 550 J/mol with the tellurium contribution being about 500. The corrections for Table 3 are all positive and range from 47 J/mol at 1006 K, 43 of which are from the tellurium term, to 0.2 J/mol at 733 K. The corrected Gibbs energies are shown in Fig. 3 as symbols.

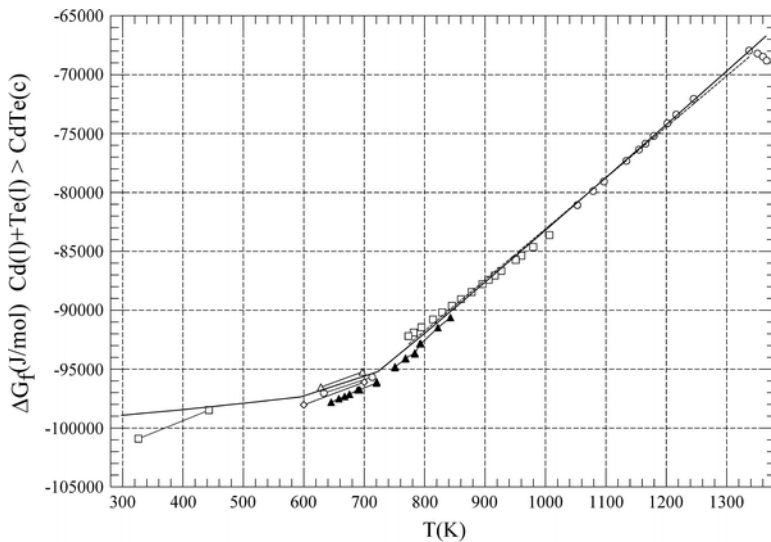


Fig. 3 Standard Gibbs energy of formation of CdTe(c) from its solid or liquid elements as a function of temperature. *Squares* and *circles* above 722.6 K as in Fig. 1. Line segments terminated by symbols and below 722.6 K are from emf measurements. *Squares*: ref 27, *circles*: ref 25, *diamonds*: ref 28, *triangles*: ref 26, *solid triangles*: ref 29; *Dashed line* is a second law analysis and is given by Eq 20. *Solid line* is a third law analysis with $\Delta H_{f,298}^{\circ} = -100270 \text{ J/mol}$ and $\Delta S_{f,298}^{\circ} = -4.53335 \text{ J/mol K}$

Also shown in Fig. 3 are data from emf measurements. There are four line segments below 722.6 K terminated by symbols.[25-28] The symbols indicate the temperature limits of the measurements. The measurements of Shamsuddin and Nasar[29] are shown as solid triangles between 640 and 845 K. They were extracted by us from a scaled plot of emf versus T . The cell electrodes were described as Cd(l) and CdTe(c) + Te(c,l). However, the CdTe(c)-Te(s) eutectic is close to 722.6 K so the anode description cannot be correct above about 722.6 K. Taking the authors description of the CdTe(c) electrode as containing 10% Te to have been calculated with CdTe and Te as components, then this electrode is about 52 at.% Te using Cd and Te as components. This composition falls in the two phase CdTe and Te rich liquid region up to over 1000 K. The Gibbs energy measured is then the difference in the chemical potential of Cd in CdTe (c) as Te rich as possible and that in pure Cd(l). To obtain the Gibbs energy of formation of CdTe (c) from its elements one must add a correction term, $\frac{1}{2}RT \ln P_2/P_2^0$, where P_2 is the partial pressure of diatomic tellurium over the "Te-saturated" CdTe(c) and P_2^0 is that over pure Te(l). The former partial pressure has been obtained from optical absorbance measurements[18] down to 934 K where it is 0.017 atm compared to 0.021 for pure Te(l). Thus, the correction term is -240 J/mol at 934 K and is expected to approach zero as the temperature is lowered to 722.6 K and the liquidus line approaches 100 at.% Te. We ignore this small correction here. It should be noted, as seen in Fig. 3, that the Gibbs energies from Shamsuddin and Nasar are more negative than those of all the others by about 2000 J/mole near 800 K and about 1000-2000 J/mol below 722.6 K.

A linear least squares fit to the data in Fig. 3 above 722.6 K and excluding that of Shamsuddin and Nasar gives,

$$\Delta G_f^\circ (\text{J/mol}) = -126372 + 43.2897T; \text{Std. dev.} = 415.$$

(20)

This equation is plotted as the dashed line in Fig. 3.

Third Law Analysis

The Gibbs energies for the formation of CdTe(c) from its condensed phase elements can be analyzed using an analogue of Eq 10. However, in contrast to Eq 10 we use the standard entropy of formation for the reaction given by Eq 15 as an adjustable parameter rather than the standard entropy of CdTe(c). The equation is:

$$\Delta G_f^\circ = \Delta H_{f,298}^\circ - T\Delta S_{f,298}^\circ + \Delta(H_T^\circ - H_{298}^\circ) - T\Delta(S_T^\circ - S_{298}^\circ)$$

where $\Delta(H_T^\circ - H_{298}^\circ) = (H_T^\circ - H_{298}^\circ)_{\text{CdTe(c)}} - (H_T^\circ - H_{298}^\circ)_{\text{Cd}} - (1/2)(H_T^\circ - H_{298}^\circ)_{\text{Te}_2}$

(21)

and where an equation analogous to the second of Eq 21 holds for the entropy. Knowing the heat capacities for CdTe(c) and its elements and the standard enthalpy and entropy of formation at 298 K, the right side of the equation can be calculated. Analogous to the discussion for the formation of CdTe(c) from the gases, the standard enthalpy and entropy of formation are considered as variable parameters. It is expected that these must be varied slightly from their literature values to achieve a

compromise of a good fit to the observed Gibbs energies and consistency with the results for the formation from the gases.

The values of $\Delta H_{f,298}^{\circ}$ and $\Delta S_{f,298}^{\circ}$ were determined which gave the smallest standard deviation between the observed values for ΔG_f° and those calculated with the right side of Eq 21. Then, the best fit was determined for fixed values of $\Delta S_{f,298}^{\circ}$. The results are shown in Fig. 4. Because the data from Shamsuddin and Nasar are more negative than all the other data, two determinations were made, one was including their data, the second omitting it. Excluding their data, the best fit to 33 points has a standard deviation of 416 J/mol with a standard enthalpy of formation of -100001 ± 726 J/mol and standard entropy of -4.245 ± 0.75 J/mol K, both at 298.15 K. Again, as shown in Fig. 4 there is a wide range of enthalpy-entropy values that fall along a straight line along which the standard deviation between experimental and calculated Gibbs energies of formation changes slowly. If one fixes the standard entropy at the literature value of -5.9 J/mol K then the corresponding enthalpy is -101645 J/mol with a fit of 528 J/mol. On the other hand if one fixes the standard enthalpy at the literature value of -100663 J/mol, then the corresponding entropy is -4.924 with a slightly better fit of 424 J/mol. If both the standard enthalpy and entropy are fixed at the literature values of -100663 and -5.9 , then the standard deviation of the fit more than doubles to 1148 J/mol.

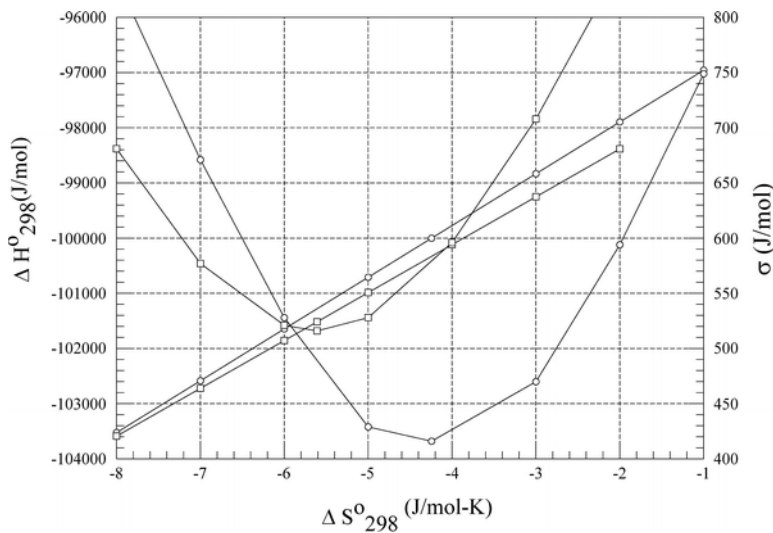


Fig. 4 Measure of fit for the standard Gibbs energy of formation of CdTe(c) from its condensed phase elements as a function of the standard entropy of formation at 298 K. Curves are analogous to those in Fig. 2. The curves shown with circles are from analyses using the data shown in Fig. 3 but excluding the data of ref 29. Those shown with squares include that data

Discussion

If one denotes Eq 2 for the formation of CdTe from Cd(g) and Te₂(g) as II and Eq 15 for its formation from the condensed phase elements as I, then the corresponding enthalpies and entropies of formation are related by the equations,

$$\Delta H_{f,298}^{\circ}(\text{II}) = \Delta H_{f,298}^{\circ}(\text{I}) - 192991$$

$$\Delta S_{f,298}^{\circ}(\text{II}) = \Delta S_{f,298}^{\circ}(\text{I}) - 196.06$$

$$S_{298}^{\circ}(\text{CdTe}) = \Delta S_{f,298}^{\circ}(\text{II}) + 296.96$$

(22)

Equations 17 and 18 for the thermodynamic properties of pure cadmium and tellurium have been used in Eq 22. Furthermore, since the standard deviation of the fit to the experimental Gibbs energies of formation increases rapidly as the enthalpy-entropy point is moved away from the best fit line shown in Fig. 2 and 4, acceptable values for these enthalpies and entropies must lie on these lines. The lines are given by,

$$\begin{aligned}\Delta H_{f,298}^{\circ}(\text{I}) &= 938.098 * \Delta S_{f,298}^{\circ}(\text{I}) - 96017.8 \\ \Delta H_{f,298}^{\circ}(\text{II}) &= 1007.98 * S_{298}^{\circ}(\text{CdTe}) - 390398\end{aligned}$$

(23)

The solution to Eq 22 and 23 are enthalpies and entropies that give the best fits to the experimental Gibbs energies of formation which are consistent with the thermodynamic data assumed for pure cadmium and tellurium and the assumed heat capacity of CdTe. They are,

| $\Delta H_{f,298}^{\circ}(\text{J/mol})$ | $\Delta S_{f,298}^{\circ}(\text{J/molK})$ | $S_{298}^{\circ}(\text{CdTe})$ | $\sigma(\text{J})$ |
|--|---|--------------------------------|--------------------|
| -100270 | -4.53335 | 96.367 | 420 |
| -293262 | -200.593 | 96.367 | 430 |

Here σ is the standard deviation between experimental and calculated standard Gibbs energies of formation and is close to the minimum attained in each case. The Gibbs energies obtained with the above parameters are shown as the solid lines in Fig. 1 and 3. They are in good agreement with the experimental points and the dashed lines representing second law fits. Analytical expressions for the Gibbs energy of formation are listed in Table 4. It should be noted that determinations for $\Delta H_{f,298}^{\circ}(\text{I})$ by metal solution calorimetry[30-32] are -101000 ± 418 , -101000 ± 836 , and $-99997 \pm 1255(\text{J/mol})$. The Gibbs energy of formation obtained here is in good agreement with the experimental values and with values used earlier by ourselves[5,6] and by Jianrong et al.[4] However, that from Yamaguchi et al.[30] is about 12 kJ/mol more negative since their measured value for $\Delta H_{f,298}^{\circ}(\text{I})$ is about 12 kJ/mol more negative than all the other published values. The fact that they do not fit the measured Gibbs energy of formation would seem to indicate an error in their value of $\Delta H_{f,298}^{\circ}(\text{I})$. The Gibbs energy is shown in Fig. 5 as a function of temperature. Fig. 6 and 7 show a similar comparison for, respectively, the enthalpy and entropy of formation. Now the results obtained by Jianrong et al. differ significantly at high temperature from those obtained here. At 1365 K, their enthalpy of formation is about 10 kJ/mol less negative while the entropy is about 9 J/mol K less negative. As mentioned earlier, this is because they used a heat capacity for CdTe that is about 16 J/mol K greater near 1365 K than that adopted here. Our earlier[6] analysis of the thermodynamic and phase diagram data for CdTe also used a heat capacity based upon the measurements of Mezaki et al.,[8] which have been judged to be too large by Pavlova et al.[3]

Table 4 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 $\frac{1}{2}\text{Te}_2(\text{g})$ $\Delta G_f^{\circ}(\text{J/mol}) = A + BT + CT^2 + DT^3 + ET\ln(T) + F/T$

| Temp. range, K | A | B | C | D | E | F |
|----------------|---|---|---|---|---|---|
|----------------|---|---|---|---|---|---|

| | | | | | | |
|---------------|---------|----------|-------------|-------------|---------|------------|
| 298-594.18 | -100889 | 15.3341 | 3.4210E-03 | 2.7966E-07 | -1.8300 | 5.8550E+04 |
| 594.18-722.65 | -104820 | -21.7759 | -2.6440E-03 | 2.79667E-07 | 5.5800 | 5.8550E+04 |
| 722.65-833 | -76940 | -721.020 | -6.3519E-02 | 0 | 112.645 | 5.8550E+04 |
| 833-1365 | -118058 | -57.0652 | -4.2525E-03 | 0 | 13.9150 | 5.8550E+04 |
| 298-1365 | -297496 | 289.970 | 2.36150E-03 | -9.5700E-07 | -13.419 | 5.8550E+04 |

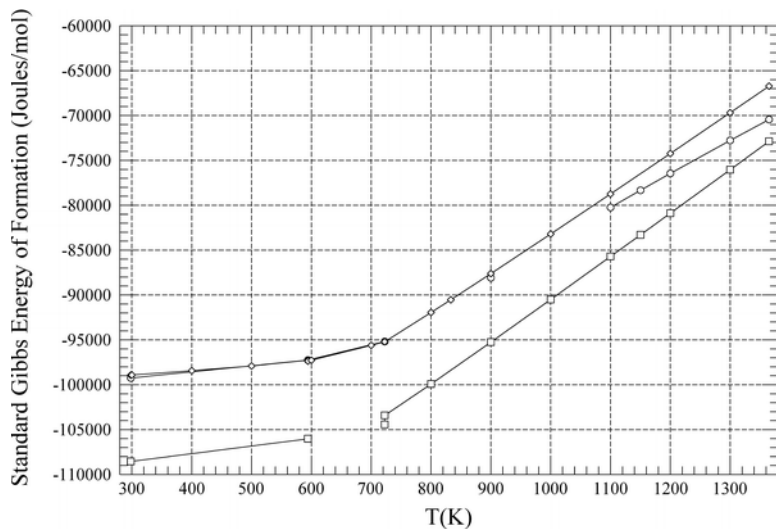


Fig. 5 The standard Gibbs energy of formation of CdTe as a function of temperature. *Circles*: ref 4, *squares*: ref 33, and *diamonds*: present work

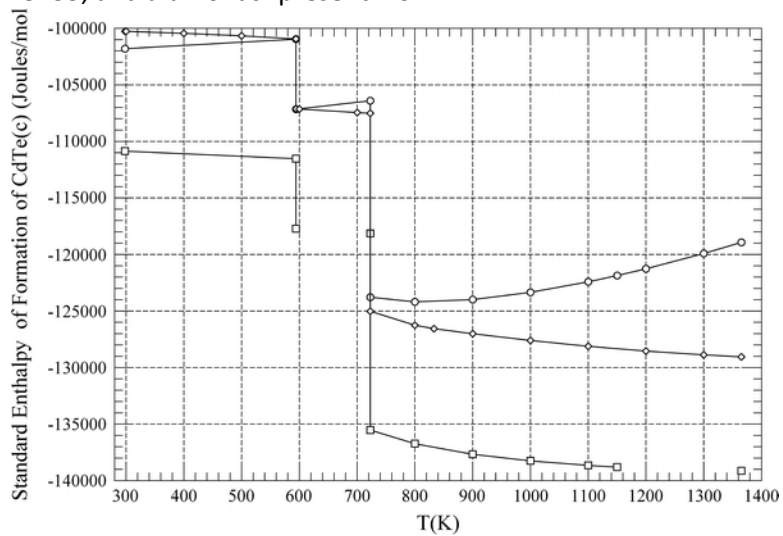


Fig. 6 The standard enthalpy of formation of CdTe as a function of temperature. *Circles*: ref 4, *squares*: ref 33, and *diamonds*: present work

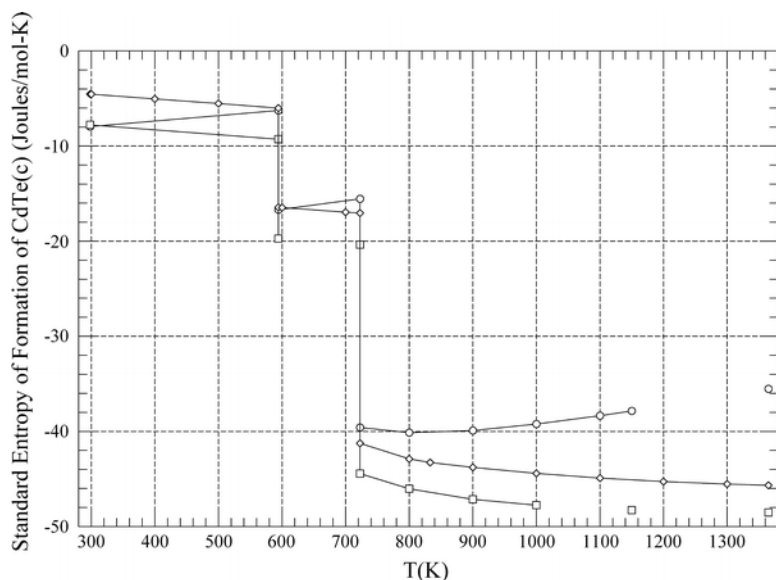


Fig. 7 The standard entropy of formation of CdTe. *Circles*: ref 4, *squares*: ref 33, and *diamonds*: present work

Conclusions

The thermodynamic data for CdTe(c) have been reanalyzed using newer high temperature heat capacities than used before. Although the standard enthalpy and entropy of formation are close to what has been accepted at 298.15 K, they diverge from previous values with increasing temperature. The results obtained here should be a more accurate representation of the thermodynamic properties of the solid, CdTe(c), which is of value in itself, but they also should be useful in any future analysis of the entire Cd-Te system in that only the model of the liquid phase need be established.

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