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High Temperature Thermodynamic Properties of ZnTe(s)

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Abstract

We have gathered the partial pressure, Knudsen cell, and emf measurements on ZnTe(s) from which the Gibbs energy of formation can be calculated. Published partial pressures of diatomic tellurium have been adjusted to take account of a subsequently published third law analysis of tellurium. The equation used to calculate the total pressure from the rate of mass loss from an extensive set of Knudsen cell measurements has been corrected to give a 5% increase in total pressure and the Gibbs energy of formation has been recalculated. A high temperature heat capacity for ZnTe(s) has been selected from the published data. The Gibbs energies of formation as a function of temperature have then been fit using a third law analysis to give two essentially equally good but extreme fits. In the first, the standard enthalpy of formation agrees with the calorimetric value of −119 kJ/mol but the standard entropy of ZnTe(s) is low by 2-3 J/mol K. In the second, the standard enthalpy of formation is more positive than the calorimetric values by about 3 kJ/mol but the standard entropy of ZnTe(s) is

82 J/mol K and close to the value from low temperature heat capacity measurements. We select values of −119.49 kJ/mol for the standard enthalpy of formation and 78.23 J/mol K for the standard entropy.

Introduction

Some time ago we analyzed the phase diagram and thermodynamic data for the Hg-Cd-Zn-Te system.[1,2] Since then we have reexamined the Cd-Te system[3,4] and now continue with the Zn-Te system. Consideration is confined to the thermodynamic properties of ZnTe(s) and includes data not considered before. In addition corrections are applied to our partial pressure data obtained from optical absorbance measurements which, though small, are apparently larger than the expected error. These corrections are necessitated because of revision of the vapor pressure of Te for temperatures near its 762.65 K melting point.[5] The primary data considered are emf, Knudsen cell, and optical absorption measurements that yield the Gibbs energy of formation. These are compared to each other and subjected to 3rd law analyses. The standard enthalpy of formation at 298 K and standard entropy of ZnTe(s) at 298 K obtained are compared to values from calorimetric methods. The extensive Knudsen cell data of Bardi and Trionfetti[6] and the partial pressures over congruently subliming ZnTe(s)[7] yield Gibbs energies that are close but different by about 1 kJ/mol. Both sets of data are examined to see if their difference can be removed.

The heat capacity of ZnTe(s) enters the analysis as basic input along with the thermodynamic properties of the elements and is discussed separately.

For the sake of brevity in the following discussion we will refer to ZnTe(s) in equilibrium with its Te rich or Zn rich liquidus somewhat inexactly as, respectively, Te saturated ZnTe(s) or Zn saturated ZnTe(s).

Thermodynamic Properties of Tellurium

The properties of tellurium necessary for our analysis are summarized below. Those for Te_2(g) were calculated by Mills[8] and for temperatures between 300 and 1400 K can be obtained starting with the constant pressure heat capacity:

$$C_{\mathrm{p}}(\text{J/mol K}) = 29.070 + 0.02645T - 1.1484(10^{-5})T^2$$

(1)

With this result and a standard entropy at 1 bar and 298.15 K of 258.77 J/mol K, one has,

$$\begin{aligned}(H_{\mathrm{T}}^{\circ} - H_{298.15}^{\circ}) &= 29.070(T - 298.15) + 0.013228(T^2 - 298.15^2) - 3.828(10^{-6})(T^3 - 298.15^3)\\ S_{\mathrm{T}}^{\circ}[\mathrm{Te_2(g)}] &= 85.754 + 0.026456T - 5.742(10^{-6})T^2 + 29.070\mathrm{Ln}(T)\end{aligned}$$

(2)

The properties for liquid and solid Te are taken from our third law analysis[5] of the crystal-liquid-vapor equilibrium and include a heat capacity just above the melting point much different than that used by Mills and in previous studies. With the exception of the vapor pressure the properties are close to those adopted by Davidov et al.[9] The properties are:

m.pt.	$= 722.65$K; Heat of fusion = 17,489J/mol
C_p	$= 24.610 + 0.003217T + 1.678(10^{-6})T^2; 298 < T < 722.65$
C_p	$= 131.7 - 0.1185T; 722.65 < T < 833$K
C_p	$= 32.94; T > 833$K
Te(c); S°_{298}	$= 49.1$J/molKTe$_2$(g); $S^\circ_{298} = 258.77$
Te(c)	$\rightarrow \frac{1}{2}$Te$_2$(g); $\Delta H^\circ_{f,298} = 81{,}031$J/mol

(3)

We originally gave four equations for the vapor pressure between 722.65 and 1434 K. As pointed out recently[3] these can be approximated to better than two percent by the single equation:

$$\log_{10} P_2(\text{bar}) = 4.40420 - 5267.68/T - 368192.2/T^2\,; 722.65 < T < 1434$$

(4)

In this range the vapor is 99% or better Te_2(g).[8] Above about 847 K this equation and that of Brooks[10] agree to within about 2%. Below 847 K Eq 4 gives values increasingly lower than Brooks', reaching about 15% at the melting point. Below the melting point the vapor pressure is given by

$$\log_{10} P_2(\text{bar}) = -8485.0/T + 8.649 - 6.81577(10^{-4})T$$

(5)

In our previous studies we have overlooked the results of Hultgren et al.[11] for Te. Over the 625-1190 K range for the partial pressures discussed in sections 5.1 and 5.2 below, their values for the vapor pressure of Te are less than given by Eq 4 and 5 by 20% at 625 K, 9% at 722.65, 3% at 900, and 1% between 1000 and 1200.

Thermodynamic Properties of Zn

The thermodynamic properties of Zn given by Hultgren et al.[12] in 1963 were modified in 1973.[11] The primary change was a small decrease in the standard enthalpy of vaporization at 298 K from 130729.1 to 130415.3 J/mol. This leads to a small increase in the vapor pressure, from 1.97E−04 to 2.09E−04 bar at the melting point. We choose the 1963 properties here so that the ratio P_{Zn}/P_2 we calculate for small ZnTe(s) samples heated to high temperatures[7] attains a limiting value of 2. This point is discussed again in section 5.1. The properties are:

m.pt.	$= 692.65$K; Heat of fusion $= 7384.8$J/mol
C_p(s)	$= 24.828 + .0028516T + 5.6051(10^{-6})T^2 - 66608/T^2\,; 298 < T < 692.65$K
C_p(L)	$= 31.38T > 692.65$K
C_p(g)	$= 20.786$
Zn(s): S°_{298}	$= 41.63$; Zn(g): $S^\circ_{298} = 160.98$J/molK
Zn(s) → Zn(g); ΔH°_{298}	$= 130729$J/mol
$\log_{10} P^\circ_{Zn}$(bar)	$= -6928.4/T + 8.4379 - 0.7532 \log_{10} T\,; 298 < T < 692.65$K
$\log_{10} P^\circ_{Zn}$(bar)	$= -6688.6/T + 9.5708 - 1.2743 \log_{10} T\,; 692.65 < T < 1700$K

(6)

Calorimetric Data for ZnTe(s)

The heat capacity of ZnTe(s) from various sources[13-18] and for temperatures above 170 K is shown in Fig. 1. Our selected value is shown by the curve and is represented by the equation:

$$C_p = 45.7478 + 0.0186236T - (6.07676E - 06)T^2 - 989644/T^2\,; 170 - 1563\text{K}$$

(7)

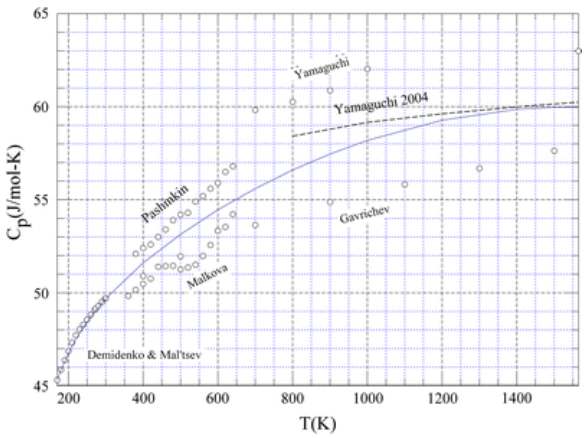

Fig. 1 Heat Capacity of ZnTe(s) as a function of temperature. Demidenko and Mal'tsev,[13] Malkova et al.,[14] Pashinkin et al.,[15] Gavrichev et al.,[16,17] Yamaguchi.[18] The solid curve is the fit to these data given by Eq 7 in the text. The dashed curve is from Yamaguchi[19]

Yamaguchi's[19] later results from 2004 are given by an equation for the 750-1573 K range and are shown by the dashed curve which is seen to agree closely with ours near the melting point. The points shown from Gavrichev et al.[16,17] are their extrapolation of measurements extending only to 983 K. Earlier equations by Mills[8] and by us[7] gave heat capacities of, respectively, 73 and 63.4 J/mol K at the melting point compared to the value of 60 from Eq 7.

At low temperatures the measured heat capacities from Irwin and LaCombe[23] covering 15-140 K and those from Demidenko and Mal'tsev[13] covering 56-300 K are in excellent agreement. Those from Gavrichev covering 15-925 K are given in a small figure. A table gives low temperature values only at 100, 200, and 298. From the first two sources we obtain a value of 81.25 J/mol for $S^\circ_{298} - S^\circ_{15}$.. Approximating the heat capacity between 0 and 15 by a T^3 term gives another 2.14 J/mol so $S^\circ_{298} = 83.89$ J/mol. Gavrichev et al.[16] calculate 81.94 for the same quantity. Mills[8] selected 77.82 ± 2/mol K based on the 56-300 K heat capacity available at that time and on emf measurements.

Values for the standard enthalpy of formation are −123 ± 6 kJ/mol from synthesis calorimetry,[20] −119 ± 2 from tin solution calorimetry,[21] −119.8 ± 5.6 from synthesis calorimetry at 800, 1173, and 1373 K,[19] and −119 ± 2 by DTA.[22]

Experimental Data

Partial Pressure Data

Partial pressures of Zn and Te_2 have been obtained[7] from optical absorbance measurements between 199 and 700 nm. Those for near congruently subliming ZnTe(s) from cell ZT-10 are given in Table 2 of Ref 7 while smoothed values of P_2 for ZnTe at its Te rich limit of stability from cells ZT-8 and ZT-1-55 are given in Table 1 of that reference. Beers law constants have been redetermined from the original measurements with pure Te and the Te vapor pressure given by Eq 4 and 5 and the partial pressures over ZnTe(s) recalculated. The values of P_2 given in Table 2 of Ref 7 must be decreased by about 20% near 1000 K and slightly less at higher temperatures. The new values are the average of those calculated from the optical absorbance at the 199.5, 202.5, and 205.6 nm vibration peaks. The measurements are at 20 temperatures between 833 and 1191 K, cover the range between 1.E−5 and 2E−3 bar, and are shown in Fig. 2 along with the partial pressure of Zn. The latter was calculated from the optical absorbance at the 213.8 nm peak after the Te_2 contribution was subtracted out as discussed earlier.[7] A least squares fit to the common logarithm of P_2 gives a standard deviation of 5.5E−5 and the equation:

$$\log_{10} P_2(\text{bar}) = -12561/T + 7.8195$$

(8)

Table 1 Corrected partial pressures and Gibbs energies of formation from optical absorbance measurements with cell ZT-5. The cell had a 9.92 cm optical path at 1273 K and contained a 20 mg crystal ground to 125-175 micron

T, K	P_{Zn}, bar	P_2, bar	$-\Delta G_f^\circ$ J/mol From gaseous elements	$-\Delta G_f^\circ$ J/mol From solid or liquid elements	*T*, K	P_{Zn}, bar	P_2, bar	$-\Delta G_f^\circ$, J/mol From gaseous elements	$-\Delta G_f^\circ$, J/mol From solid or liquid elements
1041.2	1.75E−4	5.71E−5	117,170	93,224	1136.4	1.21E−4	5.89E−4	98,623	88,252
1050.2	2.31E−4	7.28E−5	114,699	92,042	1139.5	1.29E−3	6.32E−4	97,946	88,016
1060.2	2.88E−4	1.01E−4	112,407	91,182	1147.8	1.46E−3	7.30E−4	96,778	88,034
1069.8	3.30E−4	1.26E−4	111,196	91,338	1158.2	1.77E−3	9.14E−4	94,696	87,414
1079.3	4.02E−4	1.62E−4	109,314	90,827	1165.8	2.09E−3	1.07E−3	92,952	86,733
1088.8	4.68E−4	2.04E−4	107,853	90,723	1174.4	2.41E−3	1.25E−3	91,465	86,459
1098.8	5.73E−4	2.57E−4	105,941	90,222	1174.0	2.33E−3	1.37E−3	91,351	86,286
1108.6	6.82E−4	3.21E−4	104,269	89,962	1178.3	2.49E−3	1.47E−3	90,676	86,214
1117.7	8.34E−4	4.35E−4	101,838	88,812	1182.7	2.70E−3	1.56E−3	89,917	86,082
1127.1	9.99E−4	4.94E−4	100,406	88,730	1187.5	2.89E−3	1.73E−3	89,120	85,955

Table 2 Corrected partial pressures and Gibbs energies of formation for Te saturated ZnTe(s). Zinc pressure from activities in Ref 26. Tellurium pressure is from a reanalysis of data in Ref 7

T, K	P_{Zn}, bar	P_2, bar Eq 9	$-\Delta G_f^\circ$, J/mol, from gaseous elements	$-\Delta G_f^\circ$ J/mol from solid or liquid elements
769.2	8.27E−11	7.15E−04	171,634	107,820
799.0	3.90E−10	1.47E−03	165,579	106,260
833.0	1.90E−09	3.10E−03	159,054	104,770
869.5	9.23E−09	6.41E−03	151,988	103,110
909.0	4.43E−08	1.31E−02	144,361	101,290
952.3	2.10E−07	2.63E−02	136,095	99,332
1000.0	1.10E−06	5.25E−02	127,057	97,189

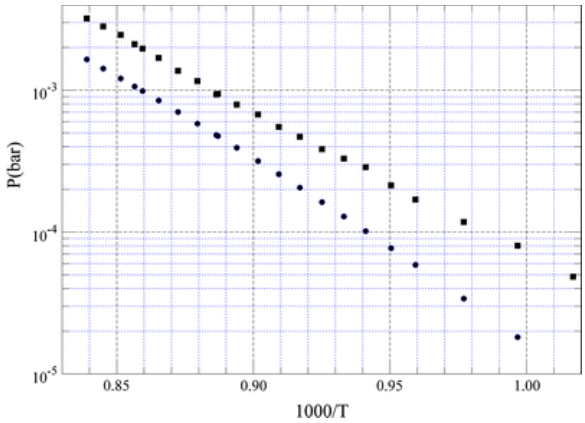

Fig. 2 Corrected partial pressures from optical absorbance measurements[7] with cell ZT-10. That for zinc is shown by squares and that for diatomic tellurium as circles. The sample is initially zinc rich and attains congruent sublimation at high temperature

Figure 3 shows the ratio of P_{Zn}/P_2 as a function of reciprocal temperature for the corrected values of P_2. The sample was a 2.1 mg crystal originally annealed in liquid Zn at 1043 K. Correspondingly the vapor is initially Zn rich but with increasing temperature the ratio approaches and then holds at a value of 2. As pointed out in Ref 7 the ratio reaches a value of 1.8 with the original values of P_2. In both Ref 7 and here the vapor pressure of Zn from the 1963 publication of Hultgren et al is used to establish the Zn pressure. If the vapor pressure from the 1973 publication is used the high temperature value of the ratio is about 2.1. A similar behavior is seen with cell ZT-5 containing a small, initially Zn saturated crystal which was not commented on in Ref 7. The partial pressures are given in Table 1. The calculation of the Gibbs energies shown are discussed in sections 6 and 7.

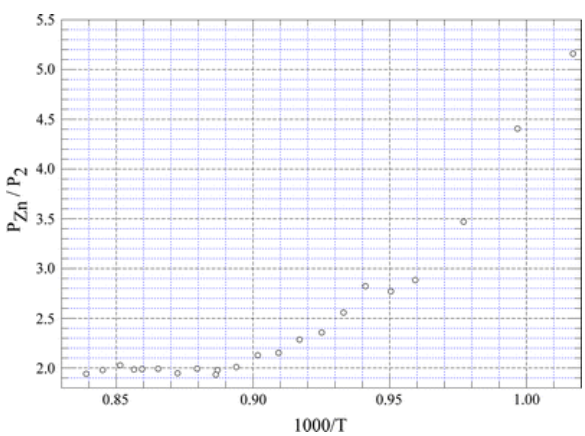

Fig. 3 The ratio of zinc pressure to that for diatomic tellurium for cell ZT-10[7] showing the attainment of congruent sublimation at high temperature

The values of P_2 for Te rich ZnTe(s) in Table 1 of Ref 7 are smoothed values and were determined from optical absorbance at 199.5, 202.5, and 205.6 nm vibration peaks at the lowest temperatures and the 435.7 peak and 500, and 550 nm continuum at higher temperatures. The data are from two optical cells. One, ZT-1-55, had an optical path length of 2.29 cm and contained about 3 g of a 55 at% Te sample. The second, ZT-8, had a path length of 9.65 cm. It contained about 0.5 g of a crystal initially held 136 hr at 1169 K in Te vapor, ground to less than 177 microns, and put into a small carbon coated

tube and weighed. The tube was then put into the carbon coated sidearm of the optical cell. The corrected values of P_2 agree with the original values to within 2% above 800 K. They are increasingly smaller with decreasing temperature, 5.2% at 769 K, 8.7% at 741, and 10% at 714 K. The corrected pressures from both cells are shown along with the vapor pressure in Fig. 4. The values from the two cells or from the optical absorbance at different wavelengths are not distinguished but are in good agreement. As can be seen the value of P_2 over ZnTe(s) that is as Te rich as possible is almost parallel to and about 10 % below that for pure Te. This is true even below the melting point of Te where one would expect the two to coincide assuming the ZnTe-Te eutectic is degenerate as reported.[24] This difference is present in the original values and even in the optical absorbances themselves and is not understood. Least squares fit to log (P_2) as a function of reciprocal temperature give:

$$\begin{aligned} \log_{10} P_2(\text{bar}) &= -5618.87/T - 21.7125 + 9.043\log(T)\; 641 < T < 722.65\text{K} \\ \log_{10} P_2(\text{bar}) &= -7686.30/T + 19.0297 + 4.2071\log(T)\; 722.65 < T < 1190K \end{aligned}$$

(9)

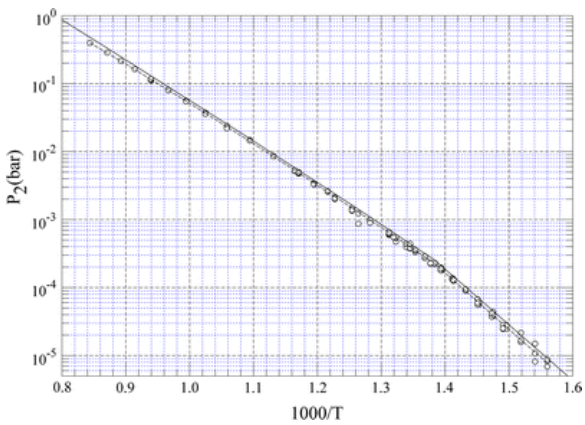

Fig. 4 Corrected partial pressure of diatomic tellurium over ZnTe(s) in equilibrium with its Te rich liquidus. Measurements[7] are from optical cells ZT-8 and ZT-1-55. The dashed line is a least squares fit given by Eq 9 in the text. The upper solid line is the vapor pressure of tellurium

The latter equation was obtained under the constraint that it gives the same value of 2.321E−4 for P_2 at 722.65 K as the first equation.

A later study[25] extends the measurement of P_2 over Te saturated ZnTe and P_{Zn} over Zn saturated ZnTe to higher temperature but does not include the simultaneous measurement of both partial pressures necessary to calculate a Gibbs energy and so is not discussed here..

Combination emf and Partial Pressure Data

Katayama et al.[26] have used solid electrolyte and fused salt cells to obtain the activity of zinc in Te saturated ZnTe(s) between 750 and 988 K. The zinc activity is given by the equation:

$$\log_{10} a_{\text{Zn}} = 2.365 - 7499.4/T$$

(10)

The zinc activity can be combined with P_2 over Te saturated ZnTe given by Eq 9 to obtain the Gibbs energy of formation of ZnTe. The activities along with the Gibbs energies of formation from the gaseous elements and from the condensed phase elements are given in our Table 2. The calculation of the Gibbs energies is discussed later.

Knudsen Cell Measurements

Bardi and Trionfetti[6] determined the total pressure over ZnTe as a function of temperature between 1025 and 1288 K from the weight loss of two Knudsen cells. The vapor pressures of metals from Hultgren et al.[11] were used to fix the product of the effusion hole area and the Clausing factor. Unfortunately, the metals and temperature range used were not identified. They give a table of the average weight loss per second at a given T as well as various calculated quantities such as the total pressure. An equation for temperature dependence of the total pressure is also given. Their equation for the total pressure as a function of the rate of weight loss is taken from one given by McCabe[27] and in our opinion is in error. It appears the total pressure calculated is that which holds when $P_{Zn} = 2P_2$, a condition that does not hold during steady state effusion. The proper condition is that the number of atoms of zinc effusing per second must be twice the number of molecules of diatomic tellurium. This implies that $P_{Zn} = 1.012P_2$ as now shown. It is assumed that diatomic tellurium and monatomic zinc are the only vapor species. The total pressure is then

$$P_{\text{Zn}} + P_2 = P_{\text{Tot}}$$

(11)

We assume an effusion steady state holds in which the number of zinc atoms leaving the Knudsen cell per sec is equal to twice the number of tellurium molecules. Each flux is proportional to the partial pressure of that species inside the cell and to the velocity of that species. In turn the velocity is inversely proportional to the square root of the species mass so that

$$P_{\text{Zn}} = 2(M_{\text{Zn}}/M_2)^{1/2}P_2 = 2(65.37/255.2)^{1/2}P_2 = 1.012P_2$$

(12)

Combining Eq 11 and 12 one obtains the partial pressures as

$$P_2 = 0.497P_{\text{Tot}}; P_{\text{Zn}} = 0.503P_{\text{Tot}}$$

(13)

Then taking account of the temperature dependence of the fluxes one can obtain the total pressure as a function of the rate of mass loss as

$$\begin{aligned} P_{\text{Tot}}(\text{kPa}) &= 0.02255\frac{\left(2\sqrt{M_{\text{Zn}}}+\sqrt{M_2}\right)}{(2M_{\text{Zn}}+M_2)}\sqrt{T}(dm/dt)/SK \\ &= 0.19029\sqrt{T}(dm/dt)/\text{SK} \end{aligned}$$

(14)

Here *dm*/*dt* is the weight loss in gm per second, SK is the product of the area of the effusion hole and the Clausing factor, and M_2 is the molecular weight of diatomic tellurium. The equation used by Bardi and Trionfetti reduces to the last form of Eq 14 but with a numerical factor of 0.1797 instead of 0.19029. Thus we find that P_{Tot} should be larger than calculated by Bardi and Trionfetti by a factor of 1.059. The error in ΔG_f° that is made by Bardi and Trionfetti by using the factor 0.1797 in Eq 14 rather than 0.19029 is −0.7034*T* J/mol. This gives a correction of 721 J/mol at 1025 K and 906 J/mol at 1288 K the highest temperature of measurement. We have calculated the total pressure using the tabulated values for (*dm*/*dt*) in Eq 14 and then the Gibbs energy of formation of ZnTe(s) from its gaseous elements. The result is

$$\Delta G_f^\circ(\text{J/mol}) = 8.317T\ln\left(P_{Zn}P_2^{1/2}\right) = 8.317T\ln\left(0.3546P_{Tot}^{3/2}\right)$$

(15)

A more exact calculation allowing for a nonideal vapor and changing the unit of pressure to bar is described in section 6.

Goldfinger and Jeunehomme[28] used Knudsen cell and mass spectrographic measurements to study the vaporization of ZnTe(s). They find the vapor consists of Zn(g) and Te_2(g). We scale their Fig. 5 showing 12 points of $\log_{10} K = \log_{10}\left(P_{Zn}^2 P_2\right)$ versus 1000/*T* Between 862 and 1102 K and calculate the individual partial pressures and the Gibbs energy of formation.

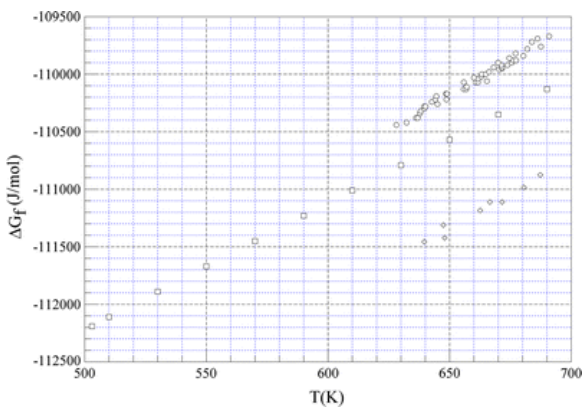

Fig. 5 Gibbs energy of formation from emf measurements. Circles from Ref 29. Squares are taken from an equation given in Ref 30. Diamonds are from Ref 31. Measurements from Ref 31 continue above the melting point of tellurium

Emf Measurements

The Gibbs energy of formation of Te saturated ZnTe(s) has been determined from emf measurements in three studies in all of which liquid salt electrolyte was used. We have scaled Fig. 1 from McAteer and Seltz[29] to obtain 47 points of emf versus *T* between 628 and 691 K.

Zabdyr[30] made similar measurements between 503 and 692 but gives only the equation,

$$\Delta G_f^\circ(\text{J/mol}) = -117725.9(\pm 573) + 11.012(\pm 0.88)T$$

(16)

Using Mills[8] heat capacity of ZnTe(s) he obtains

$$\Delta H^{\circ}_{\mathrm{f},298} = -116.61\mathrm{kJ/mol and} S^{\circ}_{298}(\mathrm{ZnTe(c)}) = 82.34 \pm 1.3\mathrm{J/molK}$$

(17)

For the purposes of our analysis we calculate eleven values of the Gibbs energy between 503 and 690 K using Eq 16.

Nasar and Shamsuddin[31] made similar measurements from 648 to 845.5 K, beyond the 722.65 K melting point of tellurium. They give equations for the Gibbs energy of formation for three temperature ranges. We scale their Fig. 1 to get 28 points of emf versus *T*. Above 722.65 ZnTe(s) is in equilibrium with a Te rich liquid rather than pure Te liquid. In order to get the Gibbs energy of formation from its elements one must add the term $0.5RT\ln(P_2/P_2^{\circ})$ where P_2° is the partial pressure of Te_2 over pure Te liquid and P_2 is that over the Te rich liquidus of ZnTe(s). Figure 4 shows P_2/P_2° is roughly constant so that the maximum value for this term appears to be at the maximum temperature of measurement, 845.5 K, where it is only 281 J/mol. This correction is neglected.

The Gibbs energies from these three studies are shown in Fig. 5 where it is seen they fall on nearly parallel lines as a function of temperature but spread over about 1 kJ/mol at a given temperature.

Gibbs Energy of Formation from the Gaseous Elements

The Gibbs energy of formation for the reaction,

$$\mathrm{Zn(g)} + 0.5\mathrm{Te_2(g)} \rightarrow \mathrm{ZnTe(c)}$$

(18)

is given by:

$$\Delta G^{\circ}_{\mathrm{f}} = RT\ln(f_{\mathrm{Zn}}P_{\mathrm{Zn}}f_2^{1/2}P_2^{1/2})$$

(19)

where f_j is the fugacity coefficient of gaseous species *j* which can be expressed in terms of the 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[32]:

$$\begin{aligned} \ln f_{\mathrm{Zn}} &= P_{\mathrm{Zn}}(1 + P_2/P_{\mathrm{T}})B_{\mathrm{Zn\text{-}Zn}} + (P_2^2/P_{\mathrm{T}})(2B_{\mathrm{Zn}-2} - B_{2-2}) \\ \ln f_2 &= P_2(1 + P_{\mathrm{Zn}}/P_{\mathrm{T}})B_{2-2} + (P_{\mathrm{Zn}}^2/P_{\mathrm{T}})(2B_{\mathrm{Zn}-2} - B_{\mathrm{Zn}-\mathrm{Zn}}) \end{aligned}$$

(20)

where $P_{\mathrm{T}} = P_{\mathrm{Zn}} + P_2$ and the subscript 2 stands for Te_2. Studies of tellurium vapor[33] have given its second virial coefficient as,

$$B_{2-2}(\mathrm{bar}^{-1}) = -434.672/T + 0.26549; T > 900\ \mathrm{K}$$

(21)

Hultgren et al.[11] have given an expression for the equation of state of tellurium vapor derived from an analysis of the vapor pressure. This leads to an equation for $RT \ln (f_2)$ that is increasingly more negative than that adopted by us by 100 J/mol at 1200 K where the vapor pressure is 0.57 bar and 5200 J/mol at 1400 K and 9.3 bar. Thus there is close agreement up to 1200 K, the highest temperature of the pressure measurements considered here. The second virial coefficient for Zn(g) is calculated here assuming a Leonard-Jones 6-12 potential. Optical absorbance measurements for a number of optical path temperatures and Zn pressures[34] give an energy minimum of −0.56 eV and a separation of 0.33 nm at zero potential energy for the Zn-Zn interaction. A published[35] series solution for the 2nd virial coefficient for the 6-12 potential was evaluated numerically to generate the virial coefficient as a function of temperature. The numerical result was fit with a standard deviation of 8.8E−05 for $300 < T < 1900K$ by the equation:

$$B_{\text{Zn-Zn}} = 0.987(24.366/T^{5/4} - 1831.1/T^{7/4} + 44800/T^{9/4} - 475570/T^{11/4})$$

(22)

The fractional powers of T in Eq 22 are similar to those that appear in the series solution for the virial coefficient. The virial coefficient for the Zn-Te_2 interaction was assumed to be the average of those for Zn-Zn and Te_2-Te_2,

$$B_{\text{Zn}-2} = (1/2)(B_{\text{Zn - Zn}} + B_{2-2})$$

(23)

The largest correction for non-ideality is for the tellurium partial pressures combined with the zinc activity data from Katayama and is −37 J/mol and is neglected.

The Gibbs energies are shown as a function of T in Fig. 6. Six points from Goldfinger and Jeunehomme below 960 K agree with those from Bardi (squares) and Katayama (diamonds). However, the points at higher temperature are more negative by 2000 J/mol. Data from Reynolds et al.[24] are significantly lower and not shown. The Gibbs energies from the emf measurements of Nasar were converted to Gibbs energies of formation from the gaseous elements using the properties of Zn and Te given in sections 2 and 3. These are shown as crosses and are in excellent agreement with those from Katayama. The data from the optical absorbance measurements are in good agreement among themselves, falling close to a straight line. The data from Bardi, Katayama, and Nasar, shown as squares, diamonds, and crosses, also fall close to their own straight line. This line is almost parallel to that from the optical absorbance measurements but is about 1000 J/mol more negative.

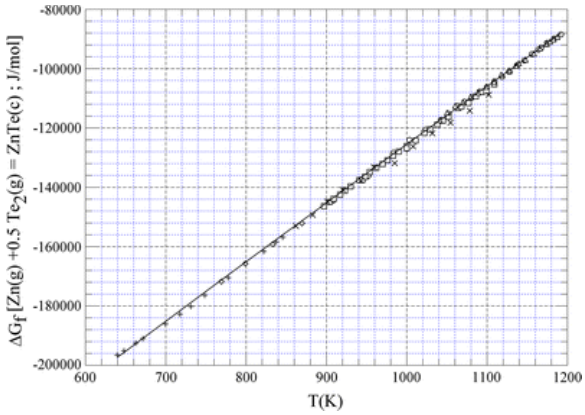

Fig. 6 Standard Gibbs energy of formation of ZnTe(s) from Zn(g) and ½ Te_2(g). Values from optical absorbance measurements[7] are shown as circles for cell ZT-10 and triangles for cell ZT-5. Squares are for Knudsen cell measurements,[6] diamonds for emf measurement[26] of zinc activity in Te saturated ZnTe(s) combined with partial pressure of diatomic tellurium.[7] Xs are from Knudsen cell measurements.[28] Crosses are for emf measurements.[31] Solid line is from a third law analysis using $\Delta H^{\circ}_{\mathrm{f},298} = -331246$ J/mol and S°_{298}[ZnTe(c)] = 78.23 J/mol K

The Gibbs energies from Bardi and Trionfetti can be brought into almost exact agreement with those from the optical absorbance measurements if the product of the effusion hole area and the Klausing factor used by Bardi is divided by a factor 1.058. Then by Eq 14 the total pressure must be multiplied by the same factor and the Gibbs energy corrected by the term 0.7034T. Interestingly, this is the same factor and correction already used by us to correct for the error in their basic equation as discussed in section 5.3. However, there appears to be no other basis for this change and the agreement of Bardi and Trionfetti's Gibbs energies with those which we calculate with Katayama's zinc activity and with the data from Nasar and Shamsuddin rules against making it. On the other hand a decrease by 5.6% in both the partial pressure of zinc and that of the tellurium molecule from the optical absorbance measurements would leave the partial pressure ratio unchanged and give a correction term of −0.7034*T* J/mol. This results in almost exact agreement between the Gibbs energies from Bardi and those from the congruently subliming ZnTe(s).

A least squares fit to the 92 points in Fig. 6, omitting those from Goldfinger and Jeunehomme, gives

$$\Delta G^{\circ}_{\mathrm{f}} = -324223 + 198.364T \text{J/mol} \sigma = 508$$

(24)

Now the partial pressure of tellurium, P_2, in the stoichiometric vapor can be calculated. This is also called the partial pressure over congruently subliming ZnTe(s). As discussed after Eq 23 the vapor is essentially ideal up to the highest temperature of measurement at 1200 K so Eq 19 holds with the fugacity coefficients set to unity. Secondly one assumes the homogeneity range is narrow enough that the variation of the Gibbs energy across it at constant temperature is negligible. This point is addressed again in section 9. Finally, one takes $P_{Zn} = 2P_2$. Combining these assumptions with Eq 24 gives P_2 in the stoichiometric vapor as,

$$\log_{10}\ P_2(\text{bar}) = -112867/T + 6.7048$$

(25)

This equation gives values for P_2 below those from total pressure measurements[36] by 40, 22, and 11% at 980, 100, and 1200 K, respectively.

A third law analysis is deferred until the Gibbs energy of formation from the condensed phase elements is considered.

Gibbs Energy of Formation from the Condensed Phase Elements

For the reaction,

$$\mathrm{Zn(c,L)} + \mathrm{Te(c,L)} \rightarrow \mathrm{ZnTe(c)}$$

(26)

the Gibbs energy of formation is given by,

$$\Delta G_{\mathrm{f}}^{\circ} = RT\ln\left(P_{\mathrm{Zn}} f_{\mathrm{Zn}} / P_{\mathrm{Zn}}^{\circ} f_{\mathrm{Zn}}^{\circ}\right) + (1/2)RT\ln\left(P_2 f_2 / P_2^{\circ} f_{\mathrm{Zn}}^{\circ}\right)$$

(27)

where the superscript circle indicates a partial pressure or fugacity in the vapor over the pure element. The necessary properties have been given in sections 2 and 3 and in section 6 for the fugacities. The corrections introduced by the fugacity coefficients are small but have been made. For the data of Bardi and Trionfetti[6] they range from less than 1 J/mol at 897 K to 132 J/mol at 1109 K. For the data from optical cell ZT-10 with eventually congruently subliming ZnTe(s) the corrections increase from 34 J/mol at 983 K to 260 J/mol at 1190 K. The corrections are less than 1 J/mol for tellurium partial pressures from optical cell ZT-8 which are used along with Katayama's zinc activity.

The Gibbs energies of formation from the various sources as a function of T are shown in Fig. 7. As seen there the highest temperature data from Katayama, shown as diamonds, are about 2 kJ/mol too negative compared to the other data. Generally, the Gibbs energies are in fair to good agreement. However, those from the different sources do present distinct differences. Further discussion is deferred until the next section where it is combined with the discussion of the results from a third law analysis.

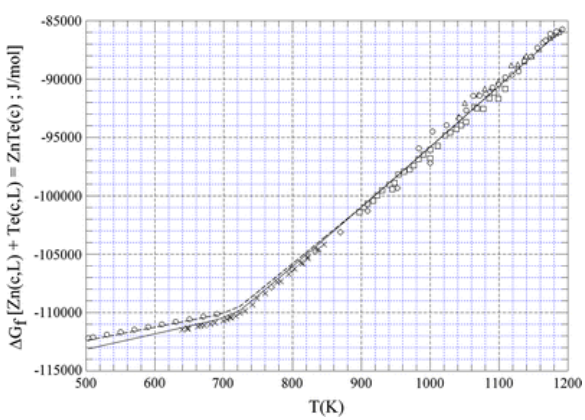

Fig. 7 Standard Gibbs energy of formation of ZnTe(s) from its liquid or solid elements as a function of temperature. Corrected data from Ref 7 are shown as circles for optical cell ZT-10 and triangles for cell ZT-5.

Squares are from Knudsen cell measurements.[6] Diamonds are from combination of optical cell measurements[7] with cell ZT-8 and emf measurements of zinc activity.[26] Crosses[31] and circles below 700 K[30] are from emf measurements. Dashed line is third law fit with $\Delta H^{\circ}_{\mathrm{f},298} = -117825$ J/mol and $S^{\circ}_{298}[\mathrm{ZnTe(c)}] = 80$ J/mol K. Solid line is third law fit with $\Delta H^{\circ}_{\mathrm{f},298} = -119486$ J/mol and $\Delta H^{\circ}_{\mathrm{f},298} = -119486$ J/mol K

Third Law Analysis

We first consider the Gibbs energy of formation from the solid or liquid elements according to Eq 26 using Eq 21 of Ref 3. The Simplex trial and error method[37,38] is used to obtain a least squares fit to the measured Gibbs energies using $\Delta H^{\circ}_{\mathrm{f},298}$ and $\Delta S^{\circ}_{\mathrm{f},298}$ as adjustable parameters. Additional fits are obtained for which the standard entropy is fixed. As is generally the case in fitting the Gibbs energy as a function of temperature, the enthalpy so obtained is a linear function of the entropy. Along this enthalpy-entropy straight line the standard deviation between measured and calculated Gibbs energies varies relatively slowly. In contrast the standard deviation increases relatively rapidly when the entropy-enthalpy point is moved away from this best fit line. With these calculations one can assess to what extent various Gibbs energy data sets are consistent with one another or with the calorimetric values for $\Delta H^{\circ}_{\mathrm{f},298}$ and $\Delta S^{\circ}_{\mathrm{f},298}$. The results of the various fits are shown in Table 3. The standard entropy of ZnTe(s) at 298 K, $S^{\circ}_{298}[\mathrm{ZnTe(s)}]$, is shown rather than the standard entropy of formation, $\Delta S^{\circ}_{\mathrm{f},298}$. The two quantities are related through the thermodynamic properties assumed for the elements by

$$S^{\circ}_{298}[\mathrm{ZnTe(c)}] = \Delta S^{\circ}_{\mathrm{f},298}[\mathrm{from\backslash;solid\backslash;elements}] + 90.73$$

(28)

Table 3 The standard enthalpy of formation and the standard entropy of ZnTe(s) giving the best fits to various data groups

Data group	Nbr Pts	σ, J/mol	$-\Delta H^{\circ}_{f,298}$,kJ/mol	S°_{298}(ZnTe(c)), J/mol K
McAteer and Seltz[29]	35	27	117.51	79.7
Zabdyr (Pts calculated from his equation)[30]	37	…	117.37	80.5
Nasar and Shamsuddin[31]	29	78	118.89	79.4
Bardi and Trionfetti[6]	30	258	118.23	79.84
Bardi + Katayama + Nasar	66	245	119.27	78.80
		493	116.50	82**
ZT-10 Optical absorbance corrected data from Ref 7	22	288	115.17	81.8
	22	295	117.17	80**
ZT-10 + ZT-5 optical absorbance	42	265	114.96	81.93
ZT-10 + Katayama[7,26]	29	534	121.3	76.4
ZT-10-Zabdyr	33	274	118.17	79.1
ZT-10 + ZT-5 + Bardi + Katayama + Zabdyr + Nasar	126	507	119.486	78.23
	126	604	117.825	80**

The superscript double asterisk indicates the entropy was held fixed at the value shown while the enthalpy of formation was allowed to vary

As seen in the first three rows of Table3 the emf measurements all give a standard entropy of ZnTe(s) that is within ±1 of 80 J/mol K, distinctly different than the value of 82-83 J/mol K from heat capacity measurements. As mentioned earlier, Fig. 5 shows that the three sets of emf measurements give Gibbs energies which do not overlap and which at a given temperature spread over about 1 kJ/mol. The Gibbs energies from the Knudsen cell measurements of Bardi and Trionfetti, those from Katayama, and those from Nasar and Shamsuddin all fall close to the same straight line. The standard deviation of a least squares fit to these data is only 245 J/mol as shown in Table 3. The table also shows that the best fit to the data of Bardi et al. alone occurs with a standard entropy for ZnTe(s) at 298 K of about 80 J/mol K and a standard enthalpy of formation of about −118.2 kJ/mol. In contrast the best fit to the Gibbs energies from ZT-10 occurs with standard entropy of ZnTe(s) of about 82 J/mol K and a standard enthalpy of about −115 kJ/mol. A common feature of the fits to various data groups is that the closer S°_{298}[ZnTe(c)] approaches 82 from below, the less negative is the corresponding $\Delta H^{\circ}_{\mathrm{f},298}$ relative to −119 kJ/mol.

As a compromise we have chosen the parameters in the next to last row of Table 3. For the data groups listed this is the best fit and is obtained with S°_{298}[ZnTe(c)] equal to 78.23 J/mol K and $\Delta H^{\circ}_{\mathrm{f},298}$ equal to −119.49 kJ/mol. The solid line in Fig. 7 shows the Gibbs energy of formation obtained with these parameters. Using the parameters in the last row the Gibbs energy shown by the dashed line results. The Gibbs energies obtained with these two sets of standard enthalpy and entropy agree at high temperatures but differ increasingly with decreasing temperature below 860 K.

Analytical formulae for the Gibbs energy of formation from the condensed phase elements in different temperature ranges are given in Table 4. Those for the formation from the gaseous elements discussed next are given in the last row. The standard enthalpy and entropy of formation of ZnTe(s) from Zn(g) and ½ Te_2(g) are related to the corresponding quantities for the formation from the solid elements. Using Eq 3 and 6 the relations as well as one involving the standard entropy of ZnTe(s) are

$$\begin{aligned}
\Delta H^{\circ}_{\mathrm{f},298}(\text{from gases}) &= \Delta H^{\circ}_{\mathrm{f},298}(\text{from solid elements}) - 211760 \\
\Delta S^{\circ}_{\mathrm{f},298}(\text{from gases}) &= \Delta S^{\circ}_{\mathrm{f},298}(\text{from solid elements}) - 199.63 \\
S^{\circ}_{298}[\text{ZnTe(s)}] &= \Delta S^{\circ}_{\mathrm{f},298}(\text{from gases}) + 290.36
\end{aligned}$$

(29)

Table 4 Analytical formulae for the Gibbs energy of formation of ZnTe(s) from its condensed phase elements with $\Delta H^{\circ}_{\mathrm{f},298} = -119486$ J/mol, $\Delta S^{\circ}_{\mathrm{f},298} = -12.50$ J/mol K

Temp. range, K	*A*	*B*	*C*	*D*	*E*	*F*
298-692.65	−119241	0.0193705	−3.25325E−03	1.29243E−06	−2.14250	25978.5
692.65-722.65	−122676	−49.4851	−7.70325E−03	1.29243E−06	−10.9362	493,220
722.65-833	−94801	−748.678	6.85768E−02	1.01279E−06	117.994	49,322
833-1565	−135917	−84.7442	−9.31180E−03	1.01279E−06	19.2672	49,322
298-1565	−337908	289.125	−2.69921E−03	5.57936E−08	−10.4266	494,819

The last row shows the coefficients for the formation from Zn (g, 1 bar) and ½ Te2 (g, 1 bar) with $\Delta H^{\circ}_{\mathrm{f},298} = -331246$ J/mol, S°_{298}[ZnTe(c)] $= 78.23$ J/mol K. $\Delta G^{\circ}_{\mathrm{f}}$(J/mol) $= A + BT + CT^2 + DT^3 + ET\ln(T) + F/T$

Then corresponding to the next to last row in Table 3, which we have selected as the best fit, the quantities for formation from Zn(g) and 0.5 Te_2(g) are

$$\Delta H^{\circ}_{\mathrm{f},298}(\text{from gases}) = -331.246\text{kJ/mol}; \Delta S^{\circ}_{\mathrm{f},298}(\text{from gases}) = -212.13$$

(30)

Then with Eq 10 of Ref 3 these parameters give a standard deviation between observed and calculated Gibbs energies of formation of 510 J/mol which is considered satisfactory.

Composition Dependence of the Gibbs Energy of Formation from Gaseous Elements

We wish to consider the composition dependence of the Gibbs energy of formation and show that it most likely can not account for the 1000 J/mol difference observed between the values obtained from the optical absorbance measurements and those from the other sources.

The Gibbs energy can be written in terms of the atom fractions of the zinc and tellurium components and the corresponding chemical potentials. The chemical potential of tellurium can be replaced by one half that of diatomic tellurium. Then since equilibrium with the vapor phase requires the chemical potential of each species must be the same in the vapor and solid phase the chemical potentials of the vapor species can be used to replace those of the solid components. The result is

$$G = X_{\mathrm{Zn}}RT\ln\left(f_{\mathrm{Zn}}P_{\mathrm{Zn}}\right) + X_{\mathrm{Zn}}\mu^{\circ}_{\mathrm{Zn(g)}} + (1/2)X_{\mathrm{Te}}RT\ln\left(f_{\mathrm{Te}_2}P_2\right) + (1/2)X_{\mathrm{Te}}\mu^{\circ}_{2(\mathrm{g})}$$

(31)

where the f_k are the fugacity coefficients described in section 6. If the terms for the gases at one bar pressure are transferred to the left side one has the difference in the Gibbs energy of the solid phase and that of the gas phase:

$$\Delta G = G - X_{\mathrm{Zn}}\mu^{\circ}_{\mathrm{Zn}} - (1/2)X_{\mathrm{Te}}\mu^{\circ}_2 = X_{\mathrm{Zn}}RT\ln\left(f_{\mathrm{Zn}}P_{\mathrm{Zn}}\right) + (1/2)X_{\mathrm{Te}}RT\ln\left(f_2P_2\right)$$

(32)

Equation 32 is multiplied by two to get the Gibbs energy for an Avogadro number of $\mathrm{Zn}_{0.5-\delta}\mathrm{Te}_{0.5+\delta}$ units and the atom fraction of tellurium in the solid phase is eliminated in favor of the deviation from stoichiometry, δ, where

$$X_{\mathrm{Te}} = 1/2 + \delta$$

(33)

The standard Gibbs energy of formation can be then be written as

$$\Delta G^{\circ}_{\mathrm{f}} = RT\ln\left(f_{\mathrm{Zn}}P_{\mathrm{Zn}}f_2^{1/2}P_2\right) + \delta RT\ln\left(f_2^{1/2}P_2^{1/2}/f_{\mathrm{Zn}}P_{\mathrm{Zn}}\right)$$

(34)

The second term on the right is further discussed later. The first term with the fugacity coefficients set to unity is usually taken as the Gibbs energy of formation. The last term is usually neglected since zinc telluride is assumed to be a narrow homogeneity range or line compound. We temporarily denote this approximation for the Gibbs energy of formation as $\Delta G''$,

$$\Delta G''(T,P) = RT\ln\left(f_{\mathrm{Zn}}P_{\mathrm{Zn}}f_2^{1/2}P_2^{1/2}\right)$$

(35)

We wish to consider the variation of this term when the ZnTe(s) is at constant temperature and under its own vapor pressure. We start with the differential for the Gibbs energy of the ZnTe(s) phase which contains the terms *VdP* and *SdT*. The last term of course vanishes under the isothermal condition considered. Using the room temperature molar volume of 6.8 cm^3/mol as an approximation the VP term is less than 1.0 J/mol for a 20 bar pressure change and negligible. In section 6 the non-ideality of the vapor phase was found to lead to generally small changes in the Gibbs energy of formation so the fugacity coefficients are set to unity. Thus the Gibbs-Duhem relation is a good approximation for ZnTe(s) at constant temperature and under its own vapor pressure and we have:

$$X_{\mathrm{Zn}}RTd\ln\ P_{\mathrm{Zn}} + \frac{1}{2}X_2RTd\ln\ P_2 = 0\mathrm{constant}T$$

(36)

The chemical potentials of the gaseous species at one bar are functions of temperature only and vanish in the differentiation. Solving for the differential of the zinc pressure gives

$$\ln\left(P_{\mathrm{Zn,L}}/P_{\mathrm{Zn,H}}\right) = \frac{1}{2}\int_{\mathrm{L}}^{\mathrm{H}}\left(X_{\mathrm{Te}}/X_{\mathrm{Zn}}\right)d\ln\ P_2$$

(37)

The L corresponds to a more zinc rich composition and higher zinc pressure than the letter H. The integrand increases monotonically with the tellurium atom fraction and partial pressure. Therefore replacing it by its value at the highest atom fraction of tellurium gives an upper limit for the integral and for the left side while replacing the integrand by its value at the lower atom fraction of tellurium gives a lower limit. Replacing X_{Te} by δ from Eq 33 the integrand in Eq 37 can be written accurate to the first power of δ as $4\delta + 1$. Upon rearranging one arrives at the result,

$$2\delta_{\mathrm{L}}RT\ln\left(P_{2\mathrm{H}}/P_{2\mathrm{L}}\right) \le \Delta G_{\mathrm{f}}''(T,P_{2\mathrm{L}}) - \Delta G_{\mathrm{f}}''(T,P_{2\mathrm{H}}) \le 2\delta_{\mathrm{H}}RT\ln\left(P_{2\mathrm{H}}/P_{2\mathrm{L}}\right)$$

(38)

Thus upper and lower limits for the difference in the approximate Gibbs energy of formation are determined by the compositions and by the partial pressures of diatomic tellurium at those compositions.

The dependence of the Gibbs energy of formation for ZnTe(s) on composition can now be assessed. The last term of Eq 34 is considered first. Both conductivity measurements on ZnTe(s) under controlled Zn pressure[39] and total pressure measurements with a Bourdon gauge[36] show the homogeneity range lies entirely on the Te rich side of 50 at.%. The latter measurements give the much larger values for δ at 1000 K, about 4.7E−05 at zinc saturation and 6E−05 at Te saturation. This is the highest temperature at which the Zn pressure for Te saturated ZnTe(s) is known from activity measurements. It is 1.0E−06 bar while the tellurium pressure from optical absorbance measurements and given by Eq 9 is 0.053 bar. Thus the last term of Eq 34 is (1E+05)δ or 6 J/mol. It would take a deviation from stoichiometry one hundred times larger at Te saturation to give a correction of 500 J/mol. The maximum deviation from stoichiometry occurs at Te saturation and is δ = 1.8E−04 at 1333 K. The 1.72 bar vapor pressure of Te at 1333 K is used as an upper limit for the corresponding tellurium pressure. An approximate value of 0.0046 bar for the zinc pressure is calculated from Eq 35 and the Gibbs energy of formation calculated from the parameters in the next to last row of Table 4. The correction term is then 11 J/mol. We conclude that most likely the Gibbs energy of formation given by Eq 34 is approximated by Eq 35 to better than 20 J/mol.

The remaining question then is how much the right side of Eq 35 varies with composition. We first compare Te saturated material at 1000 K, characterized above with δ = 6E−05 and P_2 = 0.053 bar, with the ZT-10 sample from optical absorbance measurements. From Eq 8 we have P_2 = 1.7E−04. Using the deviation from stoichiometry for zinc saturation, 4.7E−05, will over estimate the difference. The result is that the difference in the approximate Gibbs energy defined by Eq 35 lies between 6 and 7.5 J/mol. For a second comparison we consider 1333 K where as mentioned above the Te rich solidus attains a maximum value of 1.8E−04 for δ and a value of 4.6E−05 for the zinc solidus. For P_{2H} we take the 0.08 bar over Te saturated ZnTe(s) shown in Fig. 6 of Ref 7. For P_{2L} we want a low estimate for P_2 over zinc saturated ZnTe(s) at 1333 K. To calculate this we first get an approximate value for the corresponding zinc pressure at zinc saturation, taking the 3.73 bar vapor pressure of zinc from Eq 6. Figure 7 of Ref 7 shows the partial pressure of zinc over zinc saturated ZnTe(s) to equal the vapor pressure up to the 1200 K maximum temperature of measurement so this approximation is probably not in much error. In any event our use of a high value for the zinc pressure will result in a low value for P_{2L} and a high value for the Gibbs energy difference we wish to determine. Secondly, we obtain the value for $\Delta G''$ of Eq 35 at 1333 K with the parameters in the next to last row of Table 4 and calculate a value for P_2 using 3.73 bar for P_{Zn}. The result is 2.55E−06 bar which is taken as an approximation for P_{2L} in Eq 38. The final result is that the difference in $\Delta G''$ for congruently subliming and Te saturated ZnTe(s) lies between 14 and 53 J/mol. In conclusion the Gibbs energy of formation of ZnTe(s) from Zn(g) and 0.5 Te_2(g) is approximated by $\Delta G''$ as given by Eq 35 up to 1333 K and probably up to the melting point with an accuracy of better than 53 J/mol.

Summary

We have examined the partial pressure and emf data allowing calculation of the Gibbs energy of formation of ZnTe(s). An equation for the heat capacity from room temperature to the melting point has been constructed from published values. Published partial pressure data from optical absorbance measurements[7] are adjusted to be consistent with measurements on tellurium and a subsequent third law analysis of the tellurium crystal-liquid-vapor equilibrium.[5] These lead to a 15% decrease in

the vapor pressure of tellurium near its melting point. In addition the selected vapor pressure of zinc published in 1963[12] is used rather than a slightly higher value selected[11] in 1973. As a consequence the ratio P_{Zn}/P_2 attains the value of two expected for small samples of ZnTe(s) with no or minimal second phase. A small 5% increase to the total pressures obtained from extensive Knudsen cell measurements has been made because of an error in equation used to obtain the total pressure from the observed rate of mass loss.[6] This results in a temperature dependent increase in the Gibbs energy of about 700 J/mol. Finally, measurements of the zinc activity[26] in Te saturated ZnTe(s) have been combined with the partial pressure of diatomic tellurium[7] over Te saturated ZnTe(s) to obtain additional Gibbs energies. The Gibbs energy of formation from these sources and that from emf measurements are all in good agreement although those from the optical absorbance measurements are about 500-1000 J/mol high. Good fits to the Gibbs energies in third law analyses cannot be obtained that agree with both the standard entropy for ZnTe(s) and the standard enthalpy of formation obtained from calorimetric measurements. Because there are more concordant calorimetric measurements for the enthalpy of formation we choose fits that match that value more closely. Thus for the formation from the solid or liquid elements we get $\Delta H^{\circ}_{\mathrm{f},298} = -119.486$kJ/mol and $\Delta S^{\circ}_{f,298} = -12.505$J/molK.. The standard entropy of ZnTe(s) is then 78.23 J/mol K while heat capacity measurements lead to 80-82 J/mol K. The corresponding standard enthalpy and entropy of formation from Zn (g, 1 bar) and 0.5 Te_2 (g, 1 bar) are −331246 J/mol and −212.13 J/mol K.

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