Thermochimica Acta, 157 (1990) 287–294
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

VAPOUR PRESSURE AND SUBLIMATION ENTHALPY OF ZINC SELENIDE AND ZINC TELLURIDE BY THERMOGRAVIMETRIC KNUDSEN–EFFUSION METHOD

G. BARDI

Centro per la Termodinamica Chimica alle Alte Temperature, C.N.R., Rome (Italy)

G. TRIONFETTI

Dipartimento di Chimica, Università di Roma "La Sapienza", P. le Aldo Moro 5, 00185 Rome (Italy)

(Received 12 June 1989)

ABSTRACT

The total vapour pressure of solid ZnSe and ZnTe was measured by using the thermogravimetric Knudsen–effusion method. The results obtained can be expressed (in kPa) by the equations

$$\log p_{tot}(\mathrm{ZnSe}) = (9.15 \pm 0.06) - (12798 \pm 73)/T$$

$$\log p_{tot}(\mathrm{ZnTe}) = (9.10 \pm 0.08) - (11215 \pm 75)/T$$

in the temperature ranges 1025–1288 K and 897–1109 K, respectively. The standard sublimation enthalpies were derived by second- and third-law treatment of the data, and the values $\Delta H^{\ominus}_{298}$ (ZnSe) = 377 ± 4 kJ mol^{-1} and $\Delta H^{\ominus}_{298}$ (ZnTe) = 332 ± 4 kJ mol^{-1} are proposed.

INTRODUCTION

Zinc selenide and zinc telluride have been studied by several authors. The vapour pressure of the zinc selenide has been measured over a higher temperature range (1100–1400 K) by the transpiration method [1–3] and at lower temperatures by Korneeva et al. [4] and by Goldfinger and Jeunehomme [5] by using the Knudsen–effusion method. As concerns the zinc telluride, Brebrick [6] measured its vapour pressure at higher temperatures by optical absorption and other sets of vapour pressure of this compound have been measured at lower temperatures by the Knudsen–effusion [5–8] and the torsion–effusion [9] methods. In addition, an equation of the vapour pressure has been found by using the mass-spectrometric technique [10]. Apart from two papers which are not generally available [11,12] no other vapour-pressure data for zinc selenide and zinc telluride are apparently reported in the literature. The vapour-pressure data of both compounds, as

0040-6031/90/$03.50

well as the values of their sublimation enthalpy, are not in excellent agreement, so that, as part of our research program on the vaporization of chalcogenides [13,14] we have studied these compounds determining new values of their vapour pressure and sublimation enthalpy.

METHODS AND RESULTS

The experimental apparatus used consists of an Ugine–Eyraud B 60 model thermobalance, a vertical furnace, a silica glass coaxial reaction chamber and temperature- and weight-recording systems. The assembly was recently improved in the vacuum system: two diffstak diffusion pumps were placed at the two extremities of the reaction chamber, so that the operative vacuum is not less than about 1×10^{-7} kPa, and a calibrated opposition device allows the temperature always to be measured at the same highest sensitivity of ± 0.01 mV of the temperature recorder. The samples used were supplied by Koch–Light; 99.998% purity. Conventional graphite effusion cells were used, calibrated for the effusion hole by vaporizing pure metals having well-known vapour pressure [15], suspended from the balance beam and located at the centre of the previously determined isothermal zone of the reaction chamber. The temperatures were measured by a Pt–Pt/Rh10% previously calibrated thermocouple placed immediately beneath the effusion cells.

Mass spectrometric experiments have shown that the sublimation of ZnSe and ZnTe occur congruently. Since the contribution of the Te(g) species in the gas phase [16] is negligible in the temperature and pressure range investigated, the sublimation process was assumed to be

$$\mathrm{ZnX(s)} = \mathrm{Zn(g)} + 1/2\mathrm{X}_2\mathrm{(g)} \qquad (\mathrm{X} = \mathrm{Se, Te}) \tag{1}$$

In this Knudsen–effusion study, taking into consideration the vaporization with dissociation of these compounds by using the correction factor reported by McCabe [17], the total vapour pressure was measured from the total mass-loss rate of the samples by means of the Knudsen equation

$$p_{\mathrm{tot}} = (2.279/SK)(T/M_{\mathrm{ZnX}})^{1/2}3/2\left(M_{\mathrm{Zn}}^{1/3}M_{\mathrm{X}_2}^{1/6}/M_{\mathrm{ZnX}}^{1/2}\right)(\mathrm{d}m/\mathrm{d}t) \qquad (\mathrm{kPa}) \tag{2}$$

where S is the area of the effusion hole (cm^2), K is Clausing's correction factor, M_{Zn} is the atomic weight of zinc, M_{X_2} is the molecular weight of the chalcogen, M_{ZnX} is the molecular weight of the chalcogenide, $(\mathrm{d}m/\mathrm{d}t)$ is the total mass-loss rate (g s^{-1}) and T is the absolute temperature.

Two vaporization runs were carried out for ZnSe and for ZnTe, by using two cells of different diameter and thickness of effusion hole. The experimental data and the values of the total vapour pressures are given in Tables 1 and 2.

TABLE 1

The total vapour pressure and third-law sublimation enthalpy of ZnSe according to process (1)

T (K)	$\mathrm{d}m/\mathrm{d}t$ (g s^{-1})	p_{tot} (kPa)	$-\log K_p$ $(kPa)^{3/2}$	$-\Delta(G_T^\ominus - H_{298}^\ominus)/T$ (J K^{-1} mol^{-1})	$\Delta H_{298}^\ominus$ (kJ mol^{-1})
Run 1 (cell 1, $SK = 7.53\times10^{-3}$ cm^2)					
1025	4.541×10^{-7}	4.28×10^{-4}	5.47	206.4	378.1
1031	5.223×10^{-7}	4.94×10^{-4}	5.38	206.4	378.1
1040	6.679×10^{-7}	6.34×10^{-4}	5.22	206.3	378.2
1043	7.232×10^{-7}	6.88×10^{-4}	5.16	206.3	378.3
1056	1.046×10^{-6}	1.00×10^{-3}	4.91	206.1	377.6
1064	1.294×10^{-6}	1.24×10^{-3}	4.78	206.1	377.8
1075	1.629×10^{-6}	1.57×10^{-3}	4.63	206.0	378.4
1078	1.808×10^{-6}	1.75×10^{-3}	4.56	206.0	378.1
1087	2.375×10^{-6}	2.30×10^{-3}	4.37	205.9	378.0
1093	2.601×10^{-6}	2.53×10^{-3}	4.32	205.9	378.0
1102	3.254×10^{-6}	3.18×10^{-3}	4.17	205.8	378.0
1118	4.813×10^{-6}	4.73×10^{-3}	3.91	205.6	377.8
1123	5.252×10^{-6}	5.18×10^{-3}	3.85	205.4	377.9
1131	6.277×10^{-6}	6.22×10^{-3}	3.73	205.5	378.1
1136	7.174×10^{-6}	7.12×10^{-3}	3.64	205.5	377.8
				Average [a]	378.0 ± 0.2
Run 2 (cell 2, $SK = 1.11\times10^{-3}$ cm^2)					
1147	1.529×10^{-6}	1.03×10^{-2}	3.40	205.4	376.1
1156	1.908×10^{-6}	1.30×10^{-2}	3.25	205.3	375.7
1161	2.045×10^{-6}	1.39×10^{-2}	3.21	205.3	376.4
1170	2.501×10^{-6}	1.71×10^{-2}	3.07	205.2	376.0
1175	2.687×10^{-6}	1.84×10^{-2}	3.02	205.1	376.4
1189	3.779×10^{-6}	2.60×10^{-2}	2.80	205.1	375.8
1196	4.210×10^{-6}	2.91×10^{-2}	3.73	205.0	376.4
1200	4.838×10^{-6}	3.35×10^{-2}	3.63	205.0	375.3
1216	6.305×10^{-6}	4.39×10^{-2}	3.46	204.9	376.2
1231	8.631×10^{-6}	6.05×10^{-2}	3.25	204.7	375.8
1242	1.007×10^{-5}	7.09×10^{-2}	3.14	204.6	376.4
1251	1.275×10^{-5}	9.01×10^{-2}	1.99	204.6	375.4
1263	1.522×10^{-5}	1.08×10^{-1}	1.87	204.5	376.0
1273	1.773×10^{-5}	1.26×10^{-1}	1.77	204.4	376.5
1288	2.463×10^{-5}	1.77×10^{-1}	1.55	204.3	375.3
				Average [a]	376.0 ± 0.4

[a] The associated errors are standard deviations.

The least-squares treatment of the total-vapour-pressure data yielded the $\log p_{tot}$ vs. $1/T$ equations for ZnSe and ZnTe reported in Tables 3 and 4, respectively, together with the results of the other authors, where the associated errors are standard deviations. The total-vapour-pressure equations derived from the two vaporization runs are in excellent agreement for ZnSe and ZnTe, so that the following average equations for the overall

TABLE 2

The total vapour pressure and third-law sublimation enthalpy of ZnTe according to process (1)

T (K)	$\mathrm{d}m/\mathrm{d}t$ ($\mathrm{g\ s^{-1}}$)	p_{tot} (kPa)	$-\log K_p$ $(\mathrm{kPa})^{3/2}$	$-\Delta(G_T^{\ominus} - H_{298}^{\ominus})/T$ ($\mathrm{J\ K^{-1}\ mol^{-1}}$)	$\Delta H_{298}^{\ominus}$ ($\mathrm{kJ\ mol^{-1}}$)
Run 1 (cell 1, $SK = 7.53\times10^{-3}\ \mathrm{cm^2}$)					
897	5.548×10^{-7}	3.97×10^{-4}	5.52	206.8	331.8
904	6.943×10^{-7}	4.98×10^{-4}	5.37	206.7	331.8
909	8.152×10^{-7}	5.87×10^{-4}	5.27	206.6	331.7
917	1.026×10^{-6}	7.42×10^{-4}	5.11	206.5	331.7
923	1.246×10^{-6}	9.04×10^{-4}	4.99	206.5	331.7
930	1.543×10^{-6}	1.12×10^{-3}	4.84	206.4	331.5
941	2.110×10^{-6}	1.55×10^{-3}	4.64	206.3	331.7
945	2.248×10^{-6}	1.65×10^{-3}	4.59	206.2	332.2
948	2.530×10^{-6}	1.86×10^{-3}	4.52	206.2	332.0
954	3.098×10^{-6}	2.29×10^{-3}	4.38	206.1	331.5
962	3.809×10^{-6}	2.82×10^{-3}	4.24	206.0	331.5
970	4.641×10^{-6}	3.45×10^{-3}	4.11	205.9	331.9
976	5.469×10^{-6}	4.08×10^{-3}	4.00	205.9	331.7
983	6.677×10^{-6}	5.00×10^{-3}	3.87	205.8	331.6
990	8.032×10^{-6}	6.03×10^{-3}	3.75	205.7	331.6
1000	1.029×10^{-5}	7.77×10^{-3}	3.58	205.6	331.6
				Average [a]	331.7 ± 0.2
Run 2 (cell 2, $SK = 1.11\times10^{-3}\ \mathrm{cm^2}$)					
1000	1.416×10^{-6}	7.25×10^{-3}	3.63	205.6	332.5
1011	1.940×10^{-6}	1.01×10^{-2}	3.42	205.5	332.0
1022	2.609×10^{-6}	1.35×10^{-2}	3.22	205.4	331.6
1029	3.055×10^{-6}	1.59×10^{-2}	3.12	205.3	331.8
1038	3.734×10^{-6}	1.95×10^{-2}	2.99	205.2	332.0
1045	4.382×10^{-6}	2.29×10^{-2}	2.88	205.1	332.0
1052	5.117×10^{-6}	2.69×10^{-2}	2.77	205.0	331.9
1064	7.042×10^{-6}	3.72×10^{-2}	2.56	204.9	331.3
1068	7.513×10^{-6}	3.97×10^{-2}	2.52	204.9	331.7
1077	8.812×10^{-6}	4.68×10^{-2}	2.41	204.7	332.0
1086	1.104×10^{-5}	5.90×10^{-2}	2.26	204.6	331.6
1093	1.294×10^{-5}	6.93×10^{-2}	2.16	204.5	331.5
1099	1.379×10^{-5}	7.41×10^{-2}	2.12	204.4	332.5
1109	1.736×10^{-5}	9.37×10^{-2}	1.96	204.3	331.9
				Average [a]	331.9 ± 0.3

[a] The associated errors are standard deviations.

temperature ranges were obtained

$$1025\text{–}1288\ \mathrm{K}:\ \log p_{\mathrm{tot}}(\mathrm{ZnSe}) = (9.15 \pm 0.06) - (12798 \pm 73)/T \qquad (\mathrm{kPa}) \tag{3}$$

$$897\text{–}1009\ \mathrm{K}:\ \log p_{\mathrm{tot}}(\mathrm{ZnTe}) = (9.10 \pm 0.08) - (11215 \pm 75)/T \qquad (\mathrm{kPa}) \tag{4}$$

TABLE 3

Comparison of the total vapour pressure and equilibrium constant equations and of the standard sublimation enthalpy according to process (1) determined for ZnSe in the present and previous works

Author	Method	ΔT (K)	$\log p_{tot} = A - B/T$ (kPa)		$\log K_p = A - B/T$ (kPa)$^{3/2}$		$\Delta H^{\ominus}_{298}$ (kJ mol^{-1})	
			A [a]	B [a]	A [a]	B [a]	Second law [a]	Third law [a]
Korneeva et al. [4]	Knudsen–effusion	916–1095	10.63 [b]	14202	15.53	21303	416.4	
Goldfinger and Jeunehomme [5]	Knudsen–effusion	980–1190	8.715 [b]	14320	12.66	18510	364.1	
Wosten and Geers [1]	Transpiration	1060–1393	9.528 ± 0.170 [b]	13492 ± 204	13.88 ± 0.17	20238 ± 204	399.4 ± 3.9	
Boev et al. [2]	Transpiration	1123–1473	9.306 ± 0.067	13199 ± 86	13.54 ± 0.07	19799 ± 86	392.1 ± 1.6	
Flogel [3]	Transpiration	1173–1413	9.733	13326	14.19	19989	395.7	
This work	Knudsen–effusion Run 1	1025–1136	9.15 ± 0.04	12825 ± 46	13.30 ± 0.04	19238 ± 46	377.9 ± 0.9	378.0 ± 0.2
	Knudsen–effusion Run 2	1147–1288	9.15 ± 0.08	12770 ± 100	13.30 ± 0.08	19155 ± 100	376.9 ± 1.9	376.0 ± 0.4
	Average value	1025–1288	9.15 ± 0.06	12798 ± 73	13.30 ± 0.06	19197 ± 73	377.4 ± 1.4	377.0 ± 0.3

[a] The associated errors are standard deviations.

[b] Value corrected by using the factor of McCabe [17].

TABLE 4

Comparison of the total vapour pressure and equilibrium constant equations and of the standard sublimation enthalpy according to process (1) determined for ZnTe in the present and previous works

Author	Method	ΔT (K)	$\log p_{\mathrm{tot}} = A - B/T$ (kPa)		$\log K_p = A - B/T$ $(\mathrm{kPa})^{3/2}$		$\Delta H^{\ominus}_{298}$ (kJ mol^{-1})	
			A [a]	B [a]	A [a]	B [a]	Second law [a]	Third law [a]
Korneeva et al. [7]	Knudsen–effusion	791– 888	8.70 [b]	10627	12.64	15941	314.2	
Goldfinger and Jeunehomme [5]	Knudsen–effusion	860–1090	8.393 [b]	10730	12.18	16045	318.9	
Lee and Munir [9]	Torsion–effusion	888–1142	8.18	10650	11.82 [d]	15975	317.4	327 ± 13
Reynolds et al. [8]	Knudsen–effusion	918–1095	8.86 [c]	11513	12.84	17270	342.0	
Brebrick [6]	Optical absorption	961–1190	8.85 ± 0.06	10900 ± 68	12.86 ± 0.06	16350 ± 68	326.0 ± 1.3	
Ivanov [10]	Mass spectrometry	873–1300	9.00	11030	13.05 [d]	16545	330.0	
This work	Knudsen–effusion Run 1	897–1000	9.13 ± 0.05	11237 ± 48	13.28 ± 0.05	16856 ± 48	332.8 ± 0.9	331.7 ± 0.2
	Knudsen–effusion Run 2	1000–1109	9.06 ± 0.10	11193 ± 101	13.19 ± 0.10	16790 ± 101	332.5 ± 1.9	331.9 ± 0.3
	Average value	897–1109	9.10 ± 0.08	11215 ± 75	13.24 ± 0.08	16873 ± 75	332.6 ± 1.4	331.8 ± 0.3

[a] The associated errors are standard deviations.

[b] Value corrected by the factor of McCabe [17].

[c] Value derived from the log K_p vs. $1/T$ equation reported by the present authors considering $P_{\mathrm{Zn}}/P_{\mathrm{Te}_2} = 2(M_{\mathrm{Zn}}/M_{\mathrm{Te}_2})^{1/2}$.

[d] Value derived from the log p_{tot} vs. $1/T$ equation reported by the present authors considering $P_{\mathrm{Zn}}/P_{\mathrm{Te}_2} = 2(M_{\mathrm{Zn}}/M_{\mathrm{Te}_2})^{1/2}$.

Our tensimetric data for ZnSe are in agreement with those of Goldfinger and Jeunehomme [5], while those for ZnTe agree with Brebrick's results [6] even if the slope of our equation is slightly larger.

The log K_p vs. $1/T$ equations relative to the sublimation process (1) of ZnSe and ZnTe determined in the present and previous works are reported in Tables 3 and 4, respectively. From the slopes of these equations we have derived, also for the results of the other authors, the second-law values of the standard sublimation enthalpy of ZnSe and ZnTe (also reported in Tables 3 and 4). The necessary enthalpic functions were taken from Hultgren et al. [15] for Zn(g) and from Mills [16] for Se_2(g), Te_2(g), ZnSe(s) and ZnTe(s). The standard second-law sublimation enthalpy values relative to reaction (1) obtained as an average from the two vaporization runs for ZnSe and ZnTe are $\Delta H^\ominus_{298}$(ZnSe) = 377.4 ± 1.4 kJ mol^{-1} and $\Delta H^\ominus_{298}$(ZnTe) = 332.6 ± 1.4 kJ mol^{-1}, where the associated errors are standard deviations.

The evaluation of the standard enthalpy change for sublimation process (1) was also effected for ZnSe and ZnTe by a third-law treatment of the K_p values obtained at each experimental temperature from the tensimetric data. The necessary free-energy functions were taken from Hultgren et al. [15] for Zn(g) and from Mills [16] for ZnSe(s), ZnTe(s), Se_2(g) and Te_2(g). Tables 1 and 2 report this treatment and the average third-law values of the standard sublimation enthalpy of ZnSe and ZnTe obtained in each run, with the associated standard deviations. In none of the four vaporization runs was any temperature-related trend of the $\Delta H^\ominus_{298}$ values observed, and this fact can be considered as a check of the reliability of the experimental tensimetric data and of the free-energy functions used.

The results obtained in the two pairs of vaporization runs are in excellent agreement for both compounds; thus we report as third-law values of the sublimation enthalpy, the corresponding average values $\Delta H^\ominus_{298}$(ZnSe) = 377.0 ± 0.3 kJ mol^{-1} and $\Delta H^\ominus_{298}$ (ZnTe) = 331.8 ± 0.3 kJ mol^{-1}, where the associated errors are standard deviations. Our third-law values of the standard sublimation enthalpy of ZnSe and ZnTe are reported in Tables 3 and 4, respectively, in comparison with the corresponding second-law data. The agreement between the second- and third-law results is excellent for both compounds, and we report as the standard sublimation enthalpy of ZnSe and ZnTe, according to reaction (1), the following values, with an estimated error not exceeding ±4 kJ mol^{-1}: $\Delta H^\ominus_{298}$(ZnSe) = 377 ± 4 kJ mol^{-1} and $\Delta H^\ominus_{298}$(ZnTe) = 332 ± 4 kJ mol^{-1}. The value of 377 kJ mol^{-1} proposed for ZnSe agree with the second-law values obtained from the log K_p vs. $1/T$ equations of Boev et al. [2] and of Goldfinger and Jeunehomme [5]. As concerns ZnTe, the value of 332 kJ mol^{-1} agrees with the values obtained from the equations of Brebrick [6] and of Ivanov [10], with the third-law value reported by Lee and Munir [9], and is almost the same as value of 330 kJ mol^{-1} selected by Mills [16].

REFERENCES

1 W.J. Wosten and M.G. Geers, J. Phys. Chem., 25 (1962) 1252.
2 E.I. Boev, L.A. Benderskii and G.A. Milkov, Zhur. Fiz. Khim., 43 (1969) 1393.
3 P. Flogel, Z. Anorg. Chem., 370 (1969) 16.
4 I.V. Korneeva, V.V. Sokolov and A.V. Novoselova, Zhur. Neorg. Khim., 5 (1960) 241.
5 P. Goldfinger and N. Jeunehomme, Trans. Faraday Soc., 59 (1963) 2851.
6 R.F. Brebrick, J. Electrochem. Soc., 116 (1969) 1274.
7 I.V. Korneeva, A.V. Belyaev and A.V. Novoselova, Zhur. Neorg. Khim., 5 (1960) 1.
8 R.A. Reynolds, D.G. Stroud and D.A. Stevenson, J. Electrochem. Soc., 114 (1967) 1281.
9 W.T. Lee and Z.A. Munir, J. Electrochem. Soc., 114 (1967) 1236.
10 Yu.M. Ivanov, Zhur. Fiz. Khim., 47 (1973) 1602.
11 L.R. Shiozawa, R. Lebo and J.M. Jost, Clearinghouse Fed. Sci. Tech. Inform., AD 1969, AD 694533.
12 Yu.M. Ivanov, Izd. Metallurgiya, 73 (1973) 47.
13 G. Bardi, K. Ieronimakis and G. Trionfetti, Thermochim. Acta, 129 (1988) 341.
14 G. Bardi and G. Trionfetti, Thermochim. Acta, 136 (1988) 313.
15 R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley and D.D. Wagman, Selected Values of the Thermodynamic Properties of the Elements, American Society for Metals, Metal Park, OH, 1973.
16 K.C. Mills, Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides, Butterworths, London, 1974.
17 C.L. McCabe, J. Metals, 200 (1954) 969.