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Note

VAPORIZATION ENTHALPY OF CADMIUM SELENIDE AND TELLURIDE OBTAINED BY VAPOUR PRESSURE MEASUREMENTS

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The vapour pressures of cadmium selenide and telluride and their vaporization enthalpies have been determined by several authors. Mills [1] has made a critical review of thermodynamic data reported in literature and, concerning the vapour pressures of these compounds, has suggested the more reliable results are those of Flogel [2] obtained by transpiration method for CdSe, and those obtained by Brebrick and Strauss [3] with the optical absorption for CdTe. Continuing the systematic investigation of the vaporization behaviour of calcogenides, we have studied these compounds are the results obtained are reported in this note. Sets of their vapour pressure values were obtained by the Knudsen method, and also by this method coupled with the torsion one. Techniques and details of the assemblies used have been reported in previous works [4,5]. Conventional graphite

TABLE 1

Instrument constants used for the pressure measurements by the Knudsen and Knudsen–torsion methods

Method	Cell	Nominal effusion diameter (mm)	K_k [a] Knudsen (kPa s(TM)$^{-1/2}$)	K_t [a] torsion (kPa deg^{-1})
Knudsen	1	1.0	8.99×10^{-4}	
	2	0.6	2.71×10^{-3}	
	3	2.0	2.33×10^{-4}	
Knudsen–torsion	A	1.0	5.58×10^{-4}	1.51×10^{-4}
	B	1.2	4.90×10^{-4}	1.91×10^{-4}

[a] $K_k = p^0(dt/dm)(m_0/T)^{1/2}$; $K_t = p^0/\alpha$, where p^0 and m_0 are the vapour pressure and the molecular weight of the standard, (dt/dm) the reciprocal of the rate of mass loss, T the absolute temperature and α the torsion angle of the cell in the torsion method.

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TABLE 2

Vapour pressure and standard vaporization enthalpies of CdSe and CdTe

Cell	Run	Number of points	T (K)	$\log p_{\text{tot}} = A - B/T$		$\log K_p^{3/2} = A - B/T$		$\Delta H^{\ominus}_{298}$ (kJ mol^{-1})	
				A [a]	B [a]	A [a]	B [a]	Second law [a]	Third law [a]
CdSe									
Knudsen									
1	0.12	13	895–1045	8.76±0.03	10998±31	12.73±0.05	16497± 47	323.2±0.9	330.6±0.3
	0.12_{bis}	16	893–1039	8.79±0.04	11054±38	12.77±0.06	16581± 57	324.7±1.1	331.6±0.3
2	0.18	20	950–1109	8.81±0.02	11029±23	12.80±0.03	16544± 35	325.3±0.7	330.5±0.2
	0.18_{bis}	12	953–1115	8.96±0.05	11188±51	13.03±0.08	16782± 77	329.9±1.5	330.7±0.3
3	0.17	18	831– 975	8.73±0.03	11018±24	12.68±0.05	16527± 36	322.8±0.7	331.5±0.4
	0.17_{bis}	13	830– 943	8.65±0.06	10903±55	12.56±0.09	16355± 82	319.3±1.6	330.2±0.5
								324.2±1.0 [b]	330.9±0.3 [b]
Knudsen–torsion									
A	A.02	11	873–1042	8.82±0.04	10952±39	12.82±0.06	16428± 59	321.7±1.1	327.6±0.4
CdTe									
Knudsen									
1	0.10	15	806– 935	8.61±0.05	9791±39	12.50±0.08	14687± 59	292.7±1.1	292.8±0.3
	0.10_{bis}	8	775– 874	8.65±0.11	9855±97	12.56±0.16	14783±145	292.5±2.7	293.7±0.5
2	0.16	11	836–1009	8.72±0.01	9903±12	12.67±0.15	14855± 18	297.0±0.3	293.0±0.2
	0.16_{bis}	7	893– 993	8.74±0.04	9923±41	12.70±0.06	14885± 62	298.2±1.2	292.9±0.3
3	0.15	8	721– 871	8.68±0.04	9870±29	12.61±0.06	14805± 43	290.1±0.8	293.3±0.3
	0.15_{bis}	12	730– 865	8.52±0.04	9737±31	12.37±0.06	14606± 47	288.8±0.9	293.1±0.3
								293.0±1.1 [b]	293.1±0.3 [b]
Knudsen–torsion									
B	B.04	17	772– 920	8.96±0.06	10021±47	13.03±0.09	15032± 71	298.2±1.4	290.8±0.5
B	B.06	11	766– 909	8.76±0.07	9852±61	12.73±0.11	14778± 92	293.1±1.8	290.8±0.5
								296.2±1.6 [b]	290.8±0.5 [b]

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[a] The associated errors are standard deviations.

[b] Average value obtained weighting the single values proportionally to the number of the experimental points.

effusion cells with different diameters (and size of their effusion holes) were employed in both procedures. The instrument constants (reported in Table 1) were determined experimentally by vaporizing standard pure elements (cadmium, lead and zinc) having well known vapour pressures [6].

The compounds CdSe and CdTe vaporize according to the reaction [7]

$$CdX_{(s)} = Cd_{(g)} + \tfrac{1}{2}X_{2(g)} \qquad (X = Se, Te) \tag{1}$$

In Table 2 the temperature dependence of the total vapour pressures of these compounds obtained by least-squares treatment of the experimental data are reported. The two values obtained by the simultaneous torsion and Knudsen method at each experimental temperature are in agreement within 10% and their average value was used for the calculation of the log p_{tot} vs. $1/T$ equations. The pressure–temperature equations obtained with both procedures are in very good agreement. The equilibrium constants K_p of reaction (1) were derived from the total vapour pressures. The constants of the log K_p vs. $1/T$ equations calculated for each run are reported in Table 2. Treating the K_p values by second- and third-law methods, the standard vaporization enthalpies of CdSe and CdTe were derived. The thermodynamic functions necessary for calculations were taken from Mills [1] for $CdSe_{(2)}$, $CdTe_{(s)}$, $Se_{2(g)}$ and $Te_{2(g)}$, while those for gaseous cadmium were Hultgren's values [6]. The third-law $\Delta H^{\ominus}_{298}$ values do not show temperature trends and agree well with the values obtained from the second-law treatment of the K_p data. On this basis, the average standard sublimation enthalpies values $\Delta H^{\ominus}_{298} = 326$ kJ mol^{-1} and $\Delta H^{\ominus}_{298} = 293$ kJ mol^{-1} for CdSe and CdTe, respectively, were selected as the associated error does not exceed an estimated value of ± 4 kJ mol^{-1}. These values agree well with that proposed for CdSe by Mills [1] (327.2 ± 4.2 kJ mol^{-1}) and with the value 292.8 kJ mol^{-1} obtained for CdTe combining the selected standard heat of formation of solid compound [1], with the standard sublimation enthalpies of cadmium and tellurium.

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