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Note

VAPORISATION THERMODYNAMICS OF THORIUM TETRABROMIDE

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The vapour pressure of solid and liquid $ThBr_4$ has been measure experimentally by Fischer et al. [1] using the evaporation temperature technique, and Rand [2] has given estimated vapour pressure values in a recent compilation. In the present study, the vapour pressure of solid and liquid $ThBr_4$ has been measured in the temperature range 821—970 K and 970—1089 K, using two independent techniques, namely, transpiration and evaporation temperature.

EXPERIMENTAL

Transpiration technique

The apparatus and procedure used for the vapour pressure measurements have been discussed in detail elsewhere [3]. Purified argon was used as carrier gas and the vapour pressure values at a constant temperature were found to be independent of carrier gas flow rates in the range 2×10^{-5}—7×10^{-5}

TABLE 1

Vapour pressure data for $ThBr_4$

$ThBr_4$ (s)				$ThBr_4$ (l)			
Transpiration		Evaporation temp.		Transpiration		Evaporation temp.	
T/K	10^2p/kPa	*T*/K	10^2p/kPa	*T*/K	$10p$/kPa	*T*/K	$10p$/kPa
821.5	5.97	842.5	12.79	974.0	86.78	982.0	100.1
842.5	13.79	859.5	25.17	976.5	88.39	998.0	137.3
860.0	24.48	875.5	43.09	992.0	124.0	1019.5	208.0
881.0	50.93	892.0	72.94	1012.5	170.4	1044.0	296.0
898.0	88.02	907.5	117.7	1013.0	171.9	1060.0	382.6
914.0	143.3	916.0	168.1	1031.5	227.0	1089.0	570.6
934.0	290.0	933.0	263.3	1048.0	308.1		
953.0	475.0	952.5	485.1	1068.0	412.9		
964.5	661.1	963.0	653.2				
		965.0	706.6				

$m^3\ min^{-1}$: all the experiments were carried out in this region of flow rate. The condensate was analysed in each experiment for its thorium and bromine content. In a few cases thorium tetrabromide remaining in the boat was also analysed for thorium and bromine. In all cases the mole ratio of thorium to bromine in the residue and the condensate was 1/4, indicating the absence of any thermal decomposition. Vapour pressure was measured both in heating and cooling cycles to detect any systematic errors. All the thermocouples used in these experiments were calibrated at the melting temperatures [4] of bismuth (544.5 K), antimony (904 K) and silver (1234 K). From the quantity of $ThBr_4$ transported, the mole fraction (x) was determined using monomeric molar mass and the vapour pressure of $ThBr_4$ (p) was then calculated using the relation $p = xP$, where P is the total pressure of the system. Vapour pressure data on solid and liquid $ThBr_4$ are given in Table 1.

Evaporation temperature technique

The experimental assembly and procedure adopted for the vapour pressure measurements have been described earlier [5]. Vapour pressure data obtained using this method are given in Table 1.

Materials

Thorium tetrabromide was prepared by the action of Analar bromine on the hydride of nuclear grade thorium at 650—700 K, and was purified by vacuum sublimation at 850 K. The material was stored in an argon atmosphere dry box, which has oxygen and moisture impurity levels of less than 20 ppm and 10 ppm, respectively. All the loading and assembling operations were carried out in the argon atmosphere box only. The chemical analysis of the sublimed product gave the thorium to bromine mole ratio as 1/4.

Chemical analysis

In the transpiration experiments, the material transported to the condenser was dissolved in chilled distilled water and analysed for thorium and bromine gravimetrically as ThO_2 and AgBr. The vapour pressures calculated on the basis of thorium and bromine masses were identical.

RESULTS

Least squares analysis of the vapour pressure data on $ThBr_4(s)$ was carried out and the vapour pressure equations obtained from transpiration and evaporation temperature techniques are given as

$$\log_{10}(p/\mathrm{kPa}) = (12.55 \pm 0.11) - (11319 \pm 95)(\mathrm{K}/T) \qquad (1)$$

$$\log_{10}(p/\mathrm{kPa}) = (12.66 \pm 0.13) - (11411 \pm 119)(\mathrm{K}/T) \qquad (2)$$

The vapour pressure values do not vary more than 4% throughout the temperature range of the present study and hence the data were combined to give

$$\log_{10}(p/\mathrm{kPa}) = (12.60 \pm 0.08) - (11357 \pm 69)(\mathrm{K}/T) \tag{3}$$

The vapour pressure equations for $ThBr_4(l)$ from transpiration and evaporation temperature data were obtained and are represented as

$$\log_{10}(p/\mathrm{kPa}) = (8.84 \pm 0.16) - (7709 \pm 160)(\mathrm{K}/T) \tag{4}$$

$$\log_{10}(p/\mathrm{kPa}) = (8.95 \pm 0.16) - (7814 \pm 163)(\mathrm{K}/T) \tag{5}$$

The values from the two techniques agreed within 1% throughout the temperature range and hence were combined to give

$$\log_{10}(p/\mathrm{kPa}) = (8.91 \pm 0.10) - (7779 \pm 110)(\mathrm{K}/T) \tag{6}$$

Using eqns. (3) and (6) the melting temperature and the normal boiling temperature were calculated to be 970 and 1127 K, respectively. The combined data were also used to calculate the enthalpy of vaporisation at 298.15 K by second- and third-law methods. For the second-law method ΔH^0(vap., 298.15 K) was calculated using the "sigma" method reported by Darken et al. [6]. Heat capacity data for solid, liquid and gaseous $ThBr_4$ were taken from a recent compilation by Wagman et al. [7]. The relation between sigma (Σ) and temperature can be represented by

$$\Sigma_s = -(89.81 \pm 0.37) + (57843 \pm 327)(\mathrm{K}/T)$$

$$\Sigma_l = -(153.3 \pm 0.5) + (51175 \pm 467)(\mathrm{K}/T)$$

where

$$\Sigma = [-R \ln(p/\mathrm{kPa}) + \Delta a(T/\mathrm{K}) + (T/\mathrm{K})(\Delta b/2) + (\mathrm{K}/T)^2(\Delta c/2)]/\mathrm{J\ K^{-1}\ mole^{-1}}$$

Constants Δa, Δb and Δc were obtained from heat capacity data. This analysis of the data gave ΔH^0 (vap., 298.15 K) as 233.2 ± 1.3 kJ $\mathrm{mole^{-1}}$, ΔS° (vap., 298.15 K) as 229.3 ± 8.2 J $\mathrm{K^{-1}}$ $\mathrm{mole^{-1}}$ and ΔH° (fus., 970 K) as 62.8 ± 2.4 kJ $\mathrm{mole^{-1}}$. Third-law analysis of the data was carried out using free energy functions reported by Wagman et al. [7] and the values of ΔH^0 (vap., 298.15 K) obtained using vapour pressure data for solid and liquid are 205.0 ± 1.7 and 201.2 ± 0.4 kJ $\mathrm{mole^{-1}}$, respectively.

DISCUSSION

The vapour pressure data for $ThBr_4(s)$ and $ThBr_4(l)$ obtained by transpiration and evaporation temperature methods in the present study agree within 4%. This confirms our assumption that $ThBr_4$ exists as a monomeric species in the vapour phase. The vapour pressure data from the combined

TABLE 2

Thermodynamic and vapour pressure data for $ThBr_4$ and comparison with published data

Ref.	Temp. range (K)	Method	ΔH° (vap., 298.15 K) (kJ mole^{-1})		ΔS° (vap., 298.15 K) (J K^{-1} mole^{-1})	p (kPa)			
						$ThBr_4$ (s)		$ThBr_4$ (l)	
			II law	III law		850 K	950 K	1000 K	1100 K
1	902– 952 952–1124	Evaporation temp.	205.4	202.4	201.2	0.350	5.41	13.98	67.79
Present study	821– 970 970–1089	Combined transpiration and evaporation temp.	232.2 ± 1.3	205.0 ± 0.7	229.3 ± 8.2	0.173	4.42	13.52	68.89 [a]

[a] Extrapolated.

equations are compared with the only available data of Fischer et al. [1] in Table 2. The vapour pressure values of $ThBr_4$(s) are much lower than those reported by Fischer et al. [1], but for $ThBr_4$(l) the two sets of data are in good agreement. For solid $ThBr_4$ Fischer et al. [1] have carried out the vapour pressure measurements in a very narrow temperature range; also, the value of ΔH^0 (fus., 952 K) reported by them is much lower than that of ΔH^0 (fus, 970 K) obtained in the present study. As the present sets of data obtained by using two independent techniques are in good agreement, eqns. (3) and (6) could be considered as the best representation of the vaporisation behaviour of solid and liquid $ThBr_4$.

The ΔH^0 (vap., 298.15 K) values obtained in the present study are also compared with the data of Fischer et al. [1] in Table 2. The enthalpy of vaporisation ΔH^0 (vap., 298.15 K) from combined vapour pressure data of the present study (233.2 ± 1.3 kJ mole^{-1}) is not in agreement with the value of Fischer et al. Third-law treatment of the vapour pressure data for solid and liquid $ThBr_4$ gave ΔH^0 (vap., 298.15 K) values of 205.0 ± 1.7 and 201.2 ± 0.4 kJ mole^{-1}, respectively. These values are in good agreement with the third-law value of Fischer et al. (202.4 kJ mole^{-1}). However, the large difference in the second- and third-law enthalpy data may be attributed to the fact that free energy functions available at present are not entirely based on experimental data and some errors in estimation are inevitable.

The value of entropy of vaporisation, ΔS^0 (vap., 298.15 K), obtained from the second-law treatment of the present data is not in agreement with the value of Fischer et al. [1]. The present values, based on two sets of experimental data, should be more reliable.

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