Thermochimica Acta, 77 (1984) 87–93
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

TORSION EFFUSION MEASUREMENTS OF Hg PRESSURE OVER CONDENSED Hg–Te

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(Received 10 January 1984)

ABSTRACT

The sublimation of HgTe occurs according to the process

$HgTe(s) \rightarrow Te(s) + Hg(g)$

The mercury pressures were measured by the torsion–effusion method in the temperature range 478–576 K. From comparison with the literature data, the temperature dependence of the mercury pressure can be expressed by the equation

$\log P(\text{kPa}) = 8.18 - 5700/T$

Treating the results by second (and third) law the average $\Delta H^0_{298} = 105 \pm 4$ kJ mol^{-1} associated with the vaporization process was derived. Comparison of the ΔH^0_{298} values obtained by the two laws showed that until the first step of the vaporization the solid tellurium residue can be considered to be near unit activity. The standard heat of formation of HgTe, $\Delta H^0_{f,298} = -4.4$ kJ mol^{-1}, was also derived.

INTRODUCTION

Previous works on the condensed mercurium monotelluride give pressure data based on the assumption that this compound vaporizes congruently as HgTe(g) or as Hg(g) and Te_2(g) [1,2]. Goldfinger and Jeunehomme [3] found, by mass-spectrometric analysis of the vapour, that Hg(g) is the predominant species and reported pressure values of this element in the temperature range 442–553 K. Brebrick and Strauss [4] and Levitskaya et al. [5] studied the system Hg–Te at high pressure and temperature conditions by the optical adsorbtion method and found that, in addition to Hg(g), Te_2(g), is also present in the vapour, but in very small amounts ($P_{Hg}/P_{Te_2} \approx 10^2$).

An electron microprobe investigation [6] carried out in the temperature range 300–400°C reveals the existence of a transitory layer between the superficial layer and the interior of the crystal. Due to the considerable difference between Hg(g) and $Te_2(g)$ pressures, the predominant vaporization of mercury from the surface occurs in the first step of vaporization forming a tellurium-rich layer with parallel ducts through which mercury escapes from the interior of the crystal. During heating, changes in composition and structure of the superficial layer were observed so that the literature vapour pressure data measured after the first step of vaporization or obtained by the dynamic method, cannot be reliable considering the probable variation of the composition of the sample surface during the measurements. On this basis and considering that, at present, apparently no other pressure data have been reported in the literature, we thought it useful to carry out new measurements of the vapour pressure of solid HgTe employing the torsion–effusion technique.

EXPERIMENTAL AND RESULTS

Mercurium monotelluride was supplied by Koch Light Laboratories (99.999%). The vapour pressure was measured utilizing essentially the torsion–effusion technique. The experimental assembly was as previously described [7]. At each experimental temperature the corresponding vapour pressure was derived from measurements of the torsion angle, α, of the effusion cell by the simple relationship $P = K\alpha$, where K represents the cell parameters and the torsion constant of the wire (tungsten 30 μm in diameter) by which the cell is suspended. Temperatures were measured with a calibrated chromel alumel thermocouple inserted in a second cell placed below the torsion cell. In order to test the reliability of the employed cell constants, the temperature measurements, and that a thermodynamic equilibrium condition existed in the effusion cell, the absolute pressures of the pure standard elements lead and zinc are measured and compared with Hultgren's selected data [8]. Using a conventional pyrophillite cell, the vapour pressure of HgTe was measured in four vaporization runs. Analyzing the effusion vapour seen condensing in the first step of the vaporization, small amounts of mercury as impurity or derived from the narrow homogeneity range (1–2% of the original weight) are found. With increasing temperature the first pressure values are reproducible; the reproducibility decreasing slowly with the continuing vaporization.

The EDS X-ray pattern of the condensed vapour showed that its constitution is almost totally mercury, it is concluded, therefore, that HgTe vaporizes prevalently according to the reaction

$$\mathrm{HgTe(s)} \rightarrow \mathrm{Te(s)} + \mathrm{Hg(g)} \qquad (1)$$

On continuing the vaporization, the superficial layer of the HgTe sample becomes rich in tellurium as observed by Mikulko and Szummer [6] with a consequent decrease of the mercury activity.

Taking into account only the pressure values measured in the first step of the vaporization, the following pressure–temperature equation was selected

$$\log P(\text{kPa}) = (8.30 \pm 0.4) - (5700 \pm 200)/T$$

weighing proportionally to the number of points the slopes and intercepts of the corresponding equations obtained by a least-squares treatment of the data of each run as reported in Table 1. The associated errors are estimated. This equation is plotted in Fig. 1 together with the experimental points. From its slope the second-law standard vaporization enthalpy change $\Delta H^0_{298} = 107 \pm 4$ kJ mol^{-1}, corrected at 298 K by heat contents reported in the literature [8–10], was obtained. In Table 1 at each experimental temperature the corresponding standard vaporization enthalpies calculated by a third-law treatment of the vapour pressure are also reported. The free-energy function change used for these calculations, $\Delta[(G^0_T - H^0_{298})/T]$ equal to 110.5, 110.2 and 109.9 J K^{-1} mol^{-1} at 500, 550 and 600 K, respectively, were obtained from the corresponding values reported by Mills [10] for HgTe(s) and

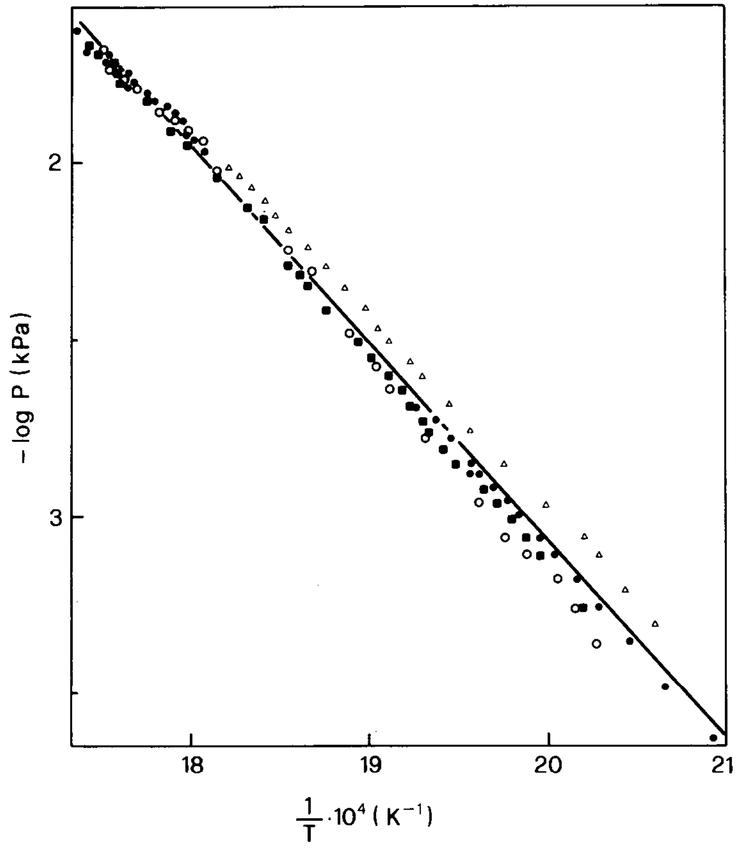

Fig. 1. Experimental vapour pressure of condensed HgTe measured by the torsion–effusion method. (△) run 3.703, (●) run 3.246, (○) run 3.276, (■) run 3.701.

TABLE 1

Experimental points, vapour pressures and third-law vaporization enthalpy, ΔH^0_{298}, of solid HgTe

T (K)	α (degrees)	P (kPa)	ΔH^0_{298} (kJ mol^{-1})	T (K)	α (degrees)	P (kPa)	ΔH^0_{298} (kJ mol^{-1})
Run 3.703				*Run 3.276*			
485	5	5.02×10^{-4}	102.7	493	4	5.01×10^{-4}	104.5
489	6	6.61×10^{-4}	102.5	496	5	6.02×10^{-4}	104.3
493	7	7.76×10^{-4}	102.7	499	6	7.08×10^{-4}	104.3
495	8	8.71×10^{-4}	102.7	503	7	8.33×10^{-4}	104.4
500	10	1.10×10^{-3}	102.6	506	8	9.33×10^{-4}	104.5
506	13	1.41×10^{-3}	102.7	510	10	1.15×10^{-3}	104.5
511	16	1.78×10^{-3}	102.8	518	15	1.70×10^{-3}	104.4
514	19	2.10×10^{-3}	102.8	523	21	2.34×10^{-3}	104.0
518	22	2.46×10^{-3}	102.7	525	24	2.69×10^{-3}	103.8
520	25	2.75×10^{-3}	102.7	529	30	3.31×10^{-3}	103.7
523	29	3.16×10^{-3}	102.8	535	46	5.13×10^{-3}	103.0
525	31	3.40×10^{-3}	102.7	539	51	5.62×10^{-3}	103.2
527	35	3.80×10^{-3}	102.5	551	88	9.55×10^{-3}	103.0
530	41	4.50×10^{-3}	102.5	553	104	1.15×10^{-2}	102.6
533	47	5.13×10^{-3}	102.5	556	112	1.23×10^{-2}	102.8
536	53	5.75×10^{-3}	102.5	558	119	1.32×10^{-2}	103.4
539	59	6.46×10^{-3}	102.6	561	126	1.38×10^{-2}	103.1
541	65	7.08×10^{-3}	102.5	565	150	1.66×10^{-2}	103.2
543	71	7.76×10^{-3}	102.5	567	156	1.70×10^{-2}	103.2
545	77	8.51×10^{-3}	102.5	569	173	1.91×10^{-2}	103.1
547	83	9.12×10^{-3}	102.5	571	190	2.09×10^{-2}	103.0
549	89	9.77×10^{-3}	102.6			Average	103.6 ± 0.6
		Average	120.6 ± 0.1				
$\log P(\mathrm{kPa}) = 7.74\pm0.04-(5352\pm22)/T$				$\log P(\mathrm{kPa}) = 8.80\pm0.10-(5972\pm49)/T$			
Run 3.246				*Run 3.701*			
478	2	2.19×10^{-4}	104.5	495	5	6.03×10^{-4}	104.1
484	3	3.31×10^{-4}	104.2	499	6	7.08×10^{-4}	104.2

489	4	4.36×10^{-4}	104.2
493	5	5.49×10^{-4}	104.7
496	6	6.61×10^{-4}	104.0
499	7	7.76×10^{-4}	104.0
502	8	8.71×10^{-4}	104.0
503	9	1.00×10^{-4}	103.6
506	10	1.10×10^{-4}	103.9
508	11	1.20×10^{-4}	103.9
510	12	1.32×10^{-4}	103.9
511	13	1.41×10^{-4}	103.8
514	15	1.66×10^{-4}	103.7
516	17	1.86×10^{-4}	103.6
520	19	2.09×10^{-4}	103.9
525	21	2.29×10^{-4}	104.5
553	103	1.10×10^{-2}	102.7
555	107	1.17×10^{-2}	102.8
556	113	1.23×10^{-2}	102.8
557	119	1.32×10^{-2}	102.7
558	125	1.38×10^{-2}	102.6
560	131	1.44×10^{-2}	102.7
562	137	1.51×10^{-2}	102.9
563	143	1.58×10^{-2}	102.9
566	155	1.70×10^{-2}	103.1
567	161	1.78×10^{-2}	103.0
568	167	1.82×10^{-2}	103.1
569	173	1.90×10^{-2}	103.1
572	185	2.04×10^{-2}	103.3
574	197	2.14×10^{-2}	103.4
576	209	2.29×10^{-2}	103.4

Average 103.5 ± 0.6

$\log P(\mathrm{kPa}) = 8.39\pm0.10-(5745\pm32)/T$

501	7	8.33×10^{-4}	104.1
503	8	0.33×10^{-4}	104.0
505	9	1.05×10^{-3}	103.9
507	10	1.15×10^{-3}	103.9
509	11	1.20×10^{-3}	104.1
511	12	1.32×10^{-3}	104.1
514	13	1.41×10^{-3}	104.3
516	14	1.55×10^{-3}	104.4
517	16	1.74×10^{-3}	104.5
519	17	1.86×10^{-3}	104.2
520	19	2.09×10^{-3}	103.9
521	21	2.34×10^{-3}	103.7
523	23	2.51×10^{-3}	103.7
526	25	2.75×10^{-3}	103.9
528	27	2.95×10^{-3}	103.9
533	35	3.89×10^{-3}	103.7
536	41	4.47×10^{-3}	103.7
537	44	4.79×10^{-3}	103.5
539	47	5.13×10^{-3}	103.5
543	63	6.92×10^{-3}	103.0
546	68	7.41×10^{-3}	103.2
551	84	9.33×10^{-3}	103.2
556	102	1.12×10^{-2}	103.2
559	113	1.23×10^{-2}	103.3
563	134	1.48×10^{-2}	103.2
566	156	1.70×10^{-2}	103.0
569	164	1.82×10^{-2}	103.0
573	193	2.14×10^{-2}	103.3

Average 103.7 ± 0.4

$\log P(\mathrm{kPa}) = 8.35\pm0.05-(5731\pm29)/T$

Hultgren [8] for Hg(g), and with solid tellurium considered at unit activity. The absence of evident temperature trends in the third-law ΔH^0_{298} and the agreement of the average value $\Delta H^0_{298} = 103.4 \pm 0.8$ kJ mol^{-1} with the corresponding second-law one, can be taken as evidence that the mercurium telluride vaporizes according to process (1) and that, the first step of the vaporization, the solid tellurium is at near unit activity. On this basis we propose as standard enthalpy change associated to the vaporization process of HgTe the average value 105 kJ mol^{-1} with an error that should not exceed 4–6 kJ mol^{-1}.

The pressure–temperature equation is reported for comparison in Fig. 2 with results of other authors, some of which are opportunally corrected according to vaporization process (1). Except for the data of Shakhtakh-

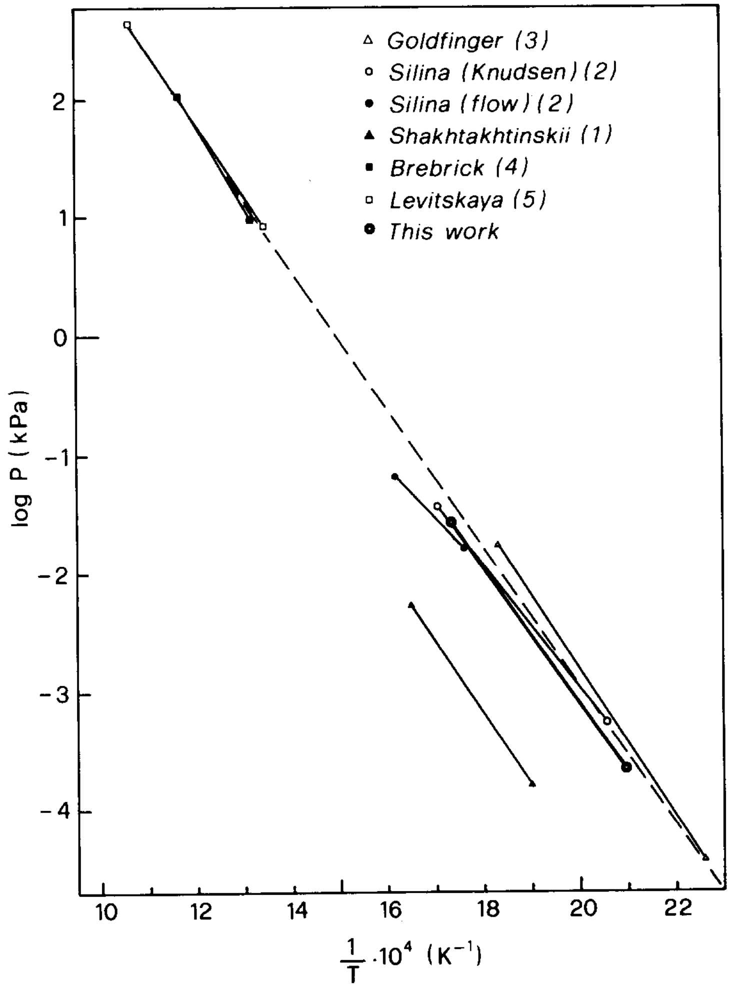

Fig. 2. Comparison of vapour pressure data over condensed HgTe. (– – –) Selected pressure–temperature equations.

tinskii [1] our results agree well with reported values, it is, therefore, concluded that the most probable equation of the mercury temperature pressure dependence is expressed by the following

$$\log P(\text{kPa}) = 8.18 - 5700/T$$

drawn as dotted line in Fig. 2.

Combining the standard mercury vaporization enthalpy [8] with that found for solid HgTe, the heat of formation for this compound $\Delta H^0_{f,298} = -4.4$ kJ mol^{-1} was derived. The value, within the estimated error of 6 kJ mol^{-1}, agrees well with the values derived from pressure data as reported by Mills [10] but is lower than that found by Ratajczak and Terpilowski [11] (-33 ± 2 kJ mol^{-1}) obtained by the FEM method.

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