

The Boiling Point Relation for Tellurium at Elevated Pressures

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The Boiling Point Relation for Tellurium at Elevated Pressures

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The boiling points of tellurium at elevated pressures have been determined by means of an internally heated pressure-vessel with argon as the pressure medium. A vapour pressure-temperature relation has been derived for pressures and corresponding temperatures in the ranges 0.043–21 atm. and 708–1507°, respectively. By means of the tabulated free-energy functions, an approximate virial coefficient has been derived for the vapour, and has been used to evaluate ideal heats of vaporisation from the pressure-temperature relation up to 1400°K.

PREVIOUS measurements of the vapour pressure-temperature relations for liquid tellurium have apparently been restricted to pressures below 1 atm. (see refs. 1 and 6 for bibliography). The most comprehensive study has been that of Machol and Westrum,¹ who measured the vapour pressures with a quartz Bourdon gauge developed from that of Brooks.² Their measurements in the temperature range 484–855° are expressed by a relation involving four terms, which shows the plot of $\log P$ against $1/T$ to be curved at lower temperatures, but linear at temperatures near the normal boiling point; the latter is found to be 994°. This unusual behaviour of the plot is attributed to the second virial coefficient for the vapour being abnormally high; this is, in fact, the case.

Kudryavtsev and Ustyugov³ have measured the boiling points from 646 to 990°, the last temperature being that at 1 atm. Their results, which show fair agreement with those of Machol and Westrum, are expressed by a linear relation between $\log P$ and $1/T$,

from which an "apparent" heat of vaporisation of 27.26 kcal. mole⁻¹ is derived directly.

The aim was to extend measurements to much higher pressures, and to test the method by making some measurements at lower pressures for comparison with other data. The boiling-point method was employed and involves detection of the thermal arrest shown by the sample when its vapour pressure equals the applied pressure. The thermocouple for detection is immersed in the small (*ca.* 0.5 c.c.) sample; this minimises errors due to thermal gradients.

EXPERIMENTAL

Apparatus.—The high-pressure furnace and auxiliary equipment were essentially those used for studying the boiling-point relation of cadmium,⁴ except that a full-sized mercury manometer, which could be read to within *ca.* 0.2 mm., was incorporated for measurements below 1 atm.

For measurements up to 1440° a boiling-point tube of clear silica was employed. The portion containing the

¹ R. E. Machol and E. F. Westrum, *J. Amer. Chem. Soc.*, 1958, **80**, 2950.

² L. S. Brooks, *J. Amer. Chem. Soc.*, 1952, **74**, 227.

³ A. A. Kudryavtsev and G. P. Ustyugov, *Russian J. Inorg. Chem.*, 1961, **6**, 1227.

⁴ E. H. Baker, *J. Appl. Chem.*, 1966, **16**, 321.

sample was in the form of a cylindrical round-bottomed bulb, 0.8 cm. in bore and 2 cm. long. This was sealed to a tube 9 cm. long and 0.5 cm. in bore. The top of this tube just emerged from the top of the furnace-tube, in which it was fixed concentrically by means of a loose plug of asbestos fibre. To this silica tube was sealed a further length, 9 cm. long and 1 cm. in bore, which passed through a hole in the water-cooled lid of the pressure vessel⁴ and protruded for 2 cm. into a small water-cooled brass dome bolted to the lid. The dome functioned as an additional condenser, to remove any trace of tellurium vapour which might diffuse out owing to accidental overheating.

The clear silica thermocouple sheath, outer diameter 0.3 cm., was mounted concentrically in the boiling-point tube. Its lower end was drawn down for 1 cm., and the thermojunction was positioned in it so that it was 0.3 cm. below the surface of the tellurium; the depth of the latter was 0.7 cm., and its weight about 2.6 g.

For measurements to temperatures above 1440° a boiling-point tube of alumina 20 cm. long and 0.9 cm. bore was used. The thermocouple sheath, o.d. 0.3 cm., was also of alumina, and the weight of the sample was 3 g.

A new thermocouple (Pt-Pt + 13% Rh), which was checked at the gold point, and a new boiling-point tube, were used for each run.

Materials.—Tellurium of purity 99.99% was used; technical argon was the pressure medium.

Determination of the Boiling Points.—The procedure was similar to that used with cadmium,⁴ except that after being flushed with argon the pressure vessel was evacuated to the lowest pressure required for the run. A heating rate of 3° per min. was employed before each b. p., the latter being shown by a sharp arrest in the temperature plot of the thermocouple in the sample. With the present version of the boiling-point tube, evaporative loss from the sample was small, and ten measurements at different pressures could be made during a run.

A run was made with the alumina assembly over the temperature range 993–1507°; no significant discrepancy was observed between the results and those obtained with the silica assembly.

During a run, the power input to the top subsidiary winding of the furnace was adjusted so that the temperature at a point 2 cm. above the sample was about 2° lower than that of the sample. Under these conditions, the temperature above the hottest zone was known to fall sharply, so that the vapour pressure of any tellurium in the upper part of the tube would rapidly diminish along its length. This helped to prevent diffusion of tellurium vapour out of the tube.

RESULTS AND DISCUSSION

The boiling points at different pressures from five runs are given in Table 1; temperatures are given to the nearest 0.5° which is the average accuracy of the measurements. The b. p. of 993°/1 atm. falls in the range 990–994° obtained at this pressure from other relations.¹⁻³

The results are expressed satisfactorily by the relation

(1). In the derivation of this relation, a slight weighting has been applied to take account of the errors being

$$\log P_{(\text{atm})} = -6447.0/T - 1.0 \log T + 8.1945 \quad (1)$$

slightly higher at the two ends of the range. Pressures calculated from equation (1) at alternate temperatures are compared in Table 1 with those observed; the average discrepancy between the two sets is about 0.5%.

Heat capacities for diatomic tellurium,⁵ derived at lower temperatures, indicate that the value of ΔC_p for liquid vaporisation should be $-9 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, which implies a greater degree of curvature for the plot of $\log P$ against $1/T$ than is found from expression (1).

TABLE 1

Observed pressures (atm.), calculated pressures (atm.), and observed boiling points of tellurium (°C)

<i>P</i> (obs.)	<i>P</i> (calc.)	Temp.	<i>P</i> (obs.)	<i>P</i> (calc.)	Temp.
0.0434	0.0428	708°	3.17		1147°
0.0724		747	3.69	3.69	1169
0.100	0.0988	770	3.80		1174.5
0.121		786	4.20	4.19	1190
0.159	0.155	807	4.71		1210
0.176		818	5.00	5.04	1220
0.200	0.201	829	5.60		1239
0.262		852.5	6.20	6.23	1256.5
0.313	0.310	869	7.13		1281.5
0.316		870.5	8.16	8.23	1307
0.382	0.381	889	8.96		1324
0.474		912	9.88	9.92	1343
0.494	0.493	915	10.85		1361
0.626		941.5	11.22	11.24	1368
0.663	0.672	948	11.30		1369.5
0.801		970	12.02	12.06	1382.5
0.825	0.826	971	12.79		1396.5
1.00	0.998	993	13.82	13.86	1412
1.28		1024	14.17		1417
1.58	1.58	1050	15.10	14.98	1429
1.72		1060.5	16.12		1444
1.94	1.94	1077	16.45	16.46	1450
2.03		1083	17.00		1455.5
2.03	2.04	1083.5	18.02	17.96	1470
2.69		1122	18.95		1480
3.05	3.05	1141	21.00	21.00	1507

The near-linearity found here for this plot, however, is in accordance with the findings of the other authors, that the plot steepens at higher temperatures.^{1,3} Non-ideal behaviour of the vapour must be a major cause of this discrepancy of curvature.

If the system is regarded as one in which the vapour behaves as a non-ideal diatomic gas, a value of $\Delta H_{v, \text{st}}$, the heat of vaporisation at 298°K, can be obtained from the relation (2).⁶ Here, b/T^2 is an empirical virial

$$Q = \Delta H_{v, \text{st}} + bP_2/T^2 = -T\Delta(G_T - H_{\text{st}})/T - RT \ln P_2 \quad (2)$$

coefficient, and P_2 is the pressure of diatomic tellurium obtained from expression (1) after correction from the equilibrium data for the very small amount of monatomic gas present.⁶⁻⁸ If values of Q , obtained by means of

⁶ K. K. Kelley, *Bull. U.S. Bureau Mines*, Washington D.C., 1960, No. 584, p. 185.

⁷ R. Hultgren *et al.*, supplement on Te to ref. 9, Amer. Atomic Energy Commission, California University, Berkeley, 1964.

⁸ D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," *Amer. Chem. Soc.*, Washington D.C., 1956, p. 200.

⁹ J. Horau, "Nouveau Traité de Chimie Minérale," Masson et Cie, Paris, 1960, vol. XIII, p. 1937.

the free-energy functions at round temperatures⁶ up to the normal b. p., are plotted against P_2/T^2 , the slope yields a mean value for b of -670×10^6 cal. deg.² atm.⁻¹, whilst the intercept yields a value for $\Delta H_{v, \text{st}}$ of $40,230 \pm 25$ cal. mole⁻¹. These limits are based on the fact that the plot shows a deviation from linearity which cannot be ascribed merely to interpolation errors; b varies from about -700×10^6 near 1000°K to about -600×10^6 at the normal b. p. (1266°K). For evaluation of thermal quantities at higher temperatures, this variance should, at least approximately, be taken into account; a better virial coefficient, which is based on an approximate temperature relation for b , is $-(1100/T^2 - 0.4/T) \times 10^6$ cal. atm.⁻¹. These values show a fair agreement with those derived from all the available low-pressure data by Hultgren *et al.*,⁶ namely, $40,240 \pm 200$ cal. mole⁻¹ for $\Delta H_{v, \text{st}}$ and -796×10^6 cal. deg.² atm.⁻¹ for a mean value of b .

The free energy of vaporisation of diatomic tellurium⁹ will be given by equation (3). Values of ΔG_v

$$\Delta G_v = -RT \ln P_2 + (1100/T^2 - 0.4/T) \times 10^6 P_2 \quad (3)$$

derived from this expression are given in column (a) of Table 2. Values of ΔH_v , the heat of vaporisation, which have been derived graphically from this expression

TABLE 2
Free energies and heats of vaporisation

T (°K)	ΔG_v (cal. mole ⁻¹) (a)	ΔH_v (kcal. mole ⁻¹)		
		(b)	(c)	(d)
1000	5777	27.0	26.9	27.5
1100	3677	26.2	26.0	27.3
1200	1666	25.1	25.1	27.1
1266	392	24.4	24.5	27.0
1300	-243	23.9	24.2	26.9
1400	-2040	22.6	23.3	26.7

(a) and (b) from expression (3); (c) from heat-content data; (d) by differentiation of expression (1).

by means of the Gibbs-Helmholtz relation, are in column (b). The values in column (c) have been calculated from the value of $\Delta H_{v, \text{st}}$ derived here, in conjunction with tabulated heat-content data^{5,6} for diatomic tellurium; the fair agreement between the values in columns (b) and (c) shows that this virial coefficient applies reasonably well up to 1400°K.

"Apparent" values of ΔH_v obtained by differenti-

⁹ R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," Wiley and Sons, Inc., New York, 1963, p. 7.

ation of equation (1) are given in column (d) of Table 2. Each value includes the effect of the monatomic content of the vapour, but since the content only reaches 1.7% at 1400°K, its contribution is small; non-ideal behaviour of the vapour accounts principally for these values being so high.

Electrical measurements on the liquid near the m. p. indicate that much of the tellurium is present as chains of molecules, but that as the temperature is increased, these break up and the liquid becomes increasingly metallic in character.¹⁰ Any polymer content of the vapour must be exceedingly small, so that with increasing temperature the constitution of the vapour will alter little and, even then, mainly as a result of a slight dissociation of Te_2 molecules. In the liquid, however, the content of "free" tellurium must increase significantly. This effect could contribute to some extent to the steepening of the pressure-temperature curve at the lower temperatures. The values of ΔH_v in columns (b) and (c) of Table 2 are derived on the assumption that the value for the heat capacity of the liquid,^{5,11} 9 cal. deg.⁻¹ g.-atom⁻¹, remains constant with temperature. Since this value was obtained from measurements only up to 870°K, any changes in the constitution of the liquid with increasing temperature must impart some uncertainties to the accuracy of these values of ΔH_v , particularly those in column (b). For this reason, the free-energy functions were used only up to the normal b. p., and expression (3) only employed up to 1400°K. The evaluation of additional virial terms is consequently not justified. Despite the uncertainties, the values of ΔH_v in column (b) should be accurate within a few hundred calories.

At the boiling points, the gas layer in equilibrium with the liquid is solely tellurium vapour, so that the observed departures from ideal behaviour must be attributed solely to tellurium itself, and not to any molecular interaction between the vapour and the inert gas present. This conclusion is supported by the fact that results obtained with nitrogen, and also with helium, as the pressure medium showed no significant difference from those obtained with argon. As the thermal characteristics of the high-pressure furnace are somewhat better with argon, the use of the latter is preferred.

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¹⁰ A. S. Epstein, H. Fritsche, and K. Lark-Horovitz, *Phys. Rev.*, 1957, **107**, 412.

¹¹ O. Kubaschewski and F. E. Wittig, *Z. Elektrochem.*, 1941, **47**, 433.