found at three days in a solution 0.073 *f* in the potassium salt of the complex, 4 *f* in sulfuric acid and 0.5 *f* in hydrochloric acid.

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LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Vapor Pressure of Liquid Tellurium

BY ROBERT E. MACHOL AND EDGAR F. WESTRUM, JR.

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The vapor pressure of liquid tellurium was measured with a silica Bourdon gage and can be represented by $\log_{10}P_{\text{mm}} = -10{,}663.14/T + 64.73140 - 18.61687 \log_{10}T + 0.00341783T$ from the triple point to 855°C. The magnitudes of these parameters indicate that the van der Waals constants of tellurium vapor must be unusually large. The extrapolated boiling point is 994 ± 3° and the heat of vaporization is $33.8 - 0.009t$(°C.) kcal. mole^{-1}.

Introduction

The vapor pressure of liquid tellurium has been reported by four investigators. The two earliest sets of measurements[1,2] were by dynamic methods and were discordant and apparently quite inaccurate. A static method, involving a Bourdon gage, was employed in the third.[3] The fourth,[4] also static, was based on measurement of vapor density by means of tracer quantities of radioactive tellurium and calculation of the pressure. In addition, measurements of the sublimation pressure of solid tellurium over the temperature range 320 to 410°[5] permit extrapolation to 449.7°, the triple point,[6] to obtain one additional datum. The present measurements utilize a vitreous silica Bourdon gage similar to that of Brooks,[3] with certain refinements which are described elsewhere.[7]

Experimental

Two series of measurements were made. For the first, tellurium (semiconductor grade, 99.999+% pure) procured from American Smelting and Refining Company was used. For the second, tellurium which had been zone refined and repeatedly sublimed to an impurity content less than one part per hundred million was used (this impurity content was determined electrically and does not take account of possible surface contamination by tellurium dioxide). This tellurium was further purified by distilling it out of the silica vapor pressure apparatus into a narrow vertical silica tube where it refluxed repeatedly. After the apparatus had been degassed for 24 hr. at 800° and 10^{-6} mm. pressure, the lower portion of the tellurium was melted gently at a temperature below that at which TeO_2 is volatile[8] and allowed to run back into the apparatus, which was then sealed off. The two series of measurements used different gages and different thermocouples.

Both sets of thermocouples (Pt–Pt–10% Rh) were repeatedly calibrated *in situ*[7] at the melting points of zinc (419.50°), aluminum (660.15°) and copper–silver eutectic (779.2°). The temperatures are considered to accord with the international temperature scale within 0.2° on the second series of measurements and 0.3° on the first series. The pressure measurements are believed accurate within 0.1 mm., except at the highest temperatures where the probable temperature error is equivalent to a larger pressure error.

The first series consisted of 30 measurements, from 484 to 782°; five of the measurements were at temperatures below 600° and were of little significance because the 0.1 mm. error was a large fraction of the total pressure. The second series consisted of 17 measurements, from 507 to 855°, of which four were below 600°. Each "measurement" consisted of the average of two to five observations, spaced by several minutes, at a single temperature.

Results and Discussion

The vapor pressure data are presented in chronological sequence in Table I. The observations are represented by the formula

$$\log_{10}P = -10{,}663.14/T + 64.73140 - 18.61687 \log_{10} T + 0.00341783T \quad (1)$$

where P is pressure in mm. at 0° and standard gravity, T is temperature in degrees Kelvin. For the triple point this expression predicts 0.17 mm. Linear extrapolation of Niwa's data[5] yields 0.187 mm.; however, as noted below, the extrapolation should not be linear, and 0.17 mm. is the best estimate from the reported observations. The validity of this expression in representing the observations may be judged from Fig. 1. The deviations of literature data also are shown.

A Clausius–Clapeyron-like equation for the vaporization process can be rigorously derived[9] in the form

$$d \log_e P/d(1/T) = -C_1C_2\Delta H/R \quad (2)$$

where ΔH is the molar heat of vaporization, R is the gas constant and C_1 and C_2 are correction factors for the non-zero volume of the liquid and the non ideal behavior of the gas, respectively. These correction factors are given by

$$C_1 = 1/(1 - V_l/V_g) \text{ and } C_2 = 1/(1 + B/V_g)$$

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[2] A. Schneider and K. Schupp, *Z. Elektrochem.*, **50**, 163 (1944).

[3] L. S. Brooks, THIS JOURNAL, **74**, 227 (1952); reported in greater detail in AECD 2546 (1948).

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[5] K. Niwa, *J. Faculty Sci., Hokkaido Imp. Univ.*, III, **3**, 75 (1940).

[6] R. E. Machol and E. F. Westrum, Jr., *J. Phys. Chem.*, **62**, 361 (1958).

[7] R. E. Machol and E. F. Westrum, Jr., to be published.

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TABLE I

MEASURED VAPOR PRESSURE OF TELLURIUM

T, °C.	P(mm.)	T, °C.	P(mm.)	T, °C.	P(mm.)
Series I					
Run I		735.7	48.67	660.2	16.09
		723.5	41.32	649.9	13.57
483.8	0.52	716.8	37.64	639.9	11.41
553.1	2.18	706.8	32.58	615.9	7.51
666.1	17.68	698.8	28.97	604.4	5.98
723.5	41.39	690.4	25.60	604.4	5.99
782.1	88.25	683.3	22.97	587.3	4.26
782.1	88.53	683.3	22.85	553.1	2.10
723.5	41.59	673.2	19.47		
666.1	17.76			Run IV	
553.1	2.27	Run III			
				803.9	114.16
Run II		673.2	19.56	786.7	93.77
		673.2	19.55	786.7	94.39
742.3	52.99	673.2	19.79	768.5	75.78
Series II					
Run I		688.1	24.79	719.6	39.02
		649.7	13.52	748.9	58.21
506.7	0.68	609.9	6.77	778.4	84.45
548.8	1.93	569.9	3.34	805.7	117.09
587.2	4.28			831.2	157.78
629.1	9.46	Run II		855.0	204.21
667.6	18.16				
705.6	32.00	694.7	27.16		

where V_1 is the molar volume of the liquid, V_g is the molar volume of the gas and B is the second virial coefficient. The first of these expressions is rigorous and the second is accurate except for terms of higher order than B/V_g. Each of these factors is unity at 0°K. and increases monotonically up to the critical temperature. At the highest temperature of the present measurements, $V_1 \approx 50$ cc. and $V_g \approx 400{,}000$ cc., so that C_1 may be neglected. If the second virial coefficient of tellurium vapor were the same as that of more familiar gases, C_2 could also be neglected, but this turns out not to be the case.

If (2) is integrated on the assumptions that C_1 and C_2 are constant and ΔH is linear with T, an expression similar to (1) results in which the final term is zero. Over the present temperature range, ΔH does vary linearly with T, since

$$\mathrm{d}\,\Delta H/\mathrm{d}T = C_p(\text{gas}) - C_p(\text{liquid}) \qquad (3)$$

within factors comparable to C_1 and C_2,[10] and the C_p values for the liquid and gas probably do not vary appreciably from 18.00 and 8.92, respectively.[11] Hence, $\mathrm{d}\Delta H/\mathrm{d}T$ should be about -9.08 cal. mole^{-1} deg.$^{-1}$. However, if ΔH is computed from (1) assuming $\Delta H = R\,\mathrm{d}\ln P/\mathrm{d}(1/T)$, then $\mathrm{d}\Delta H/\mathrm{d}T$ varies from about -12 cal. mole^{-1} deg.$^{-1}$ at 450° to -9 at 600° and to 0 at 910°. This variation in the curvature of the log P *vs.* $1/T$ plot may be an artifact at low temperatures, due to the use of the simple form—a linear term in T—to correct for it in fitting the data. For the same reason there appears a deviation in Fig. 1 of 0.6 mm. although none of the observations deviate from a smooth curve by more than 0.2 mm. However, the lack of curvature at higher temperatures is definitely not an artifact. The data leave no question that the plot is curved at low temperatures and nearly linear at higher temperatures. Such behavior is, indeed, found where accurate vapor pressure data exist over a wide temperature range, but the inflection typically occurs at 0.80–0.85 times the critical temperature,[12] never below the boiling point as in this case.

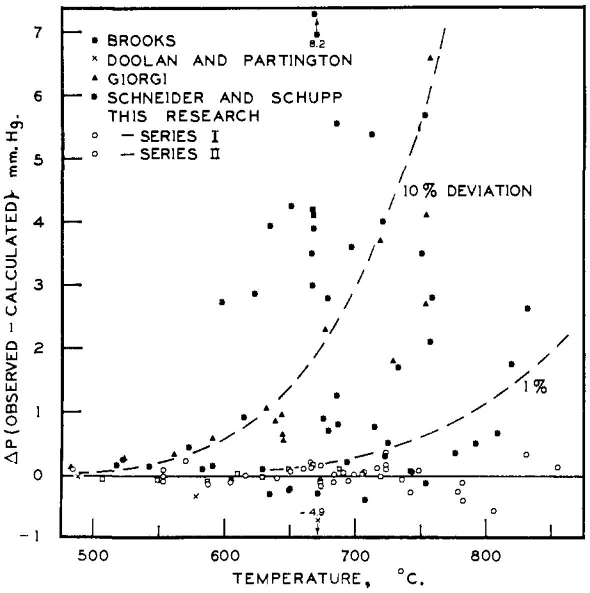

Fig. 1.—Deviation of observed vapor pressure from equation 1.

Three explanations of this behavior are possible: systematic errors exist in the data; the specific heat of the liquid varies; or the gas departs markedly from ideality.

The accuracy of the data is guaranteed not only by their internal consistency and the directness of the method, but also by the excellent agreement with Brooks' data[8] which, in spite of their somewhat lower precision, show independently that the curvature at high temperatures is smaller than predicted by (2) and (3) with C_2 constant. Conceivably both of the present samples of tellurium, as well as Brooks' sample, might have been contaminated by a volatile material which increased the observed pressure by an amount which increased with temperature, but the only imaginable contaminant, TeO_2, is insufficiently volatile.[8] The specific heat of the liquid might vary, in view of the chains of atoms in the liquid near the triple point,[13] but variation by a factor of two is inconceivable. Non-ideality of the gas cannot be due to dissociation or association of the molecules.[4,5] Hence, the absolute magnitude of the second (and higher) virial coefficients, or alternatively of the van der Waals constants, must be very much higher than for gases whose constants have been measured.

Extrapolation of (1) to 760 mm. gives 994 for the normal boiling point. Linear extrapolation from the highest temperatures measured gives a value

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(10) E. A. Guggenheim, "Thermodynamics," 3rd Ed., Amsterdam, 1957, p. 151.

(11) D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," Govt. Printing Office, Washington, D. C., 1956.

(12) W. Waring, *Ind. Eng. Chem.*, **46**, 762 (1954).

(13) A. S. Epstein, H. Fritzsche and K. Lark-Horovitz, *Phys. Rev.*, **107**, 412 (1957).

1.5° smaller, while if the observations were indeed in error due to contamination by TeO_2, the temperature should be 2° higher. Hence the boiling point of tellurium may be stated as 994 ±3°.

The use of (2) to compute the heat of vaporization is inaccurate at the lowest temperatures because of uncertainty of the data and inaccurate at the highest temperatures because of uncertainty in the value of C_2. At 600°, ΔH is computed from (1) and (2) to be 28.4 kcal. mole^{-1}; this value, together with $d\Delta H/dT = -9$ cal. mole^{-1} deg.$^{-1}$, probably gives heats of vaporization accurate within a few hundred calories per mole.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS AND CO., INC.]

Preparation and X-Ray Study of Some Tantalum Halides

BY ROBERT F. ROLSTEN

RECEIVED DECEMBER 3, 1957

Tantalum penta-iodide and -bromide crystallize in the orthorhombic system. The pentaiodide was found to have a pycnometric density of 5.80 g. cc.$^{-1}$ and an X-ray density of 5.809 g. cc.$^{-1}$ with eight formula weights per unit cell. The pentabromide was found to have a pycnometric density of 4.99 g. cc.$^{-1}$ and an X-ray density of 5.238 g. cc.$^{-1}$ with eight formula weights per unit cell. Tantalum pentachloride crystallizes in the monoclinic system with an X-ray density of 3.761 g. cc.$^{-1}$, with twelve formula weights per unit cell. This is an excellent agreement with the pycnometric density of 3.68 g. cc.$^{-1}$. A compound corresponding to TaI_4 was prepared and characterized.

Introduction

There have been numerous reports on the preparation of the tantalum pentahalides.[1,2] The vapor pressures[3–5] and structures[6] of the gaseous species have been determined, but the X-ray diffraction and subsequent structural studies of the pure solid phases have not been made. The compound corresponding to TaI_4 was probably first isolated, although not characterized, by Körösy.[7]

Results and Discussion

Pure tantalum pentaiodide was prepared in the same manner as pure niobium pentaiodide.[8] Pure "iodide" tantalum was suspended in a Pyrex flask which contained only the vapor of resublimed iodine. The tantalum reacted to yield pentaiodide at about 300°, more rapidly at 340–370° (the previously reported[2] minimum value was 700°) and was prevented from reducing the pentaiodide to a lower iodide by maintaining a high partial pressure of iodine. The excess iodine was easily sublimed from the iodide. Tantalum was determined on freshly prepared samples by precipitation of tantalum hydroxide with ammonium hydroxide and igniting to the pentoxide (Ta_2O_5). Halogen, in this case iodine, was determined by the modified[9] Volhard technique. The results of chemical analyses are: 22.55, 22.26, 22.34% Ta; 77.95, 78.89, 77.95, 77.95% I; the theoretical values are 22.18% Ta and 77.82% I.

Samples of the powdered and hygroscopic material were hermetically sealed in 0.3 mm. Lindemann glass capillary tubes and exposed 24 hr. to the K-alpha radiation of copper (λ = 1.5418 Å.). The film, in a Phillips 114.6 mm. diameter camera, was covered with two nickel screens. In addition, a single crystal of the pure pentaiodide was hermetically sealed in a 0.3 mm. Lindemann glass capillary tube. The 0 and 1 levels were obtained with copper radiation by precession of the crystal about both the b and c-axis, the 2 and 3 level with molybdenum radiation by precession about the b-axis. The crystal was rotated also about the a-axis. As a result of this the crystal appears to be orthorhombic, D_{2h}^{16}-$P2_1/b\ 2_1/n\ 2_1/m$, with the lattice parameters of a_0 = 6.65Å., b_0 = 13.95 Å. and c_0 = 20.10 Å. The observed and calculated d-spacings (Å.) with the indices assignment and visually observed intensities determined as a result of this investigation were reported recently.[10]

The pycnometric density was determined at 26° by evacuating the pycnometer bulb containing the pure pentaiodide and then distilling, under vacuum, absolute carbon tetrachloride onto the solid sample. Values for three different samples were 5.791, 5.798 and 5.807 g. cc.$^{-1}$. The X-ray density was found to be 5.809 g. cc.$^{-1}$ as calculated with the above determined cell parameters and with eight formula weights per unit cell. It is interesting to observe that Körösy[2] found the density to be 4.68 g. cc.$^{-1}$ at 150° in carbon tetrachloride. This is obviously a misprint.

Tantalum pentaiodide is not isostructural with niobium pentaiodide.

Tantalum Pentachloride.—Tantalum pentachloride was prepared by the chlorination of a heated mixture of carbon and tantalum pentoxide and purified by sublimation in a current of purified chlorine. Results of chemical analyses are 50.88, 50.76, 50.68% Ta; 49.39, 48.97, 49.99% Cl; the theoretical values are 50.50% Ta and 49.50% Cl.

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[1] Georg Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, Germany, 1954, pp. 979, 982, 983.

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[8] R. F. Rolsten, *ibid.*, **79**, 5409 (1957).

[9] J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

[10] Copies of Document 5487 can be obtained at a cost of $1.25 from Chief, Photoduplication Service, ADI Auxiliary Publications Project, Library of Congress, Washington 25, D. C.