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Vapor Pressure of Tantalum Pentachloride

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The gas transpiration method was used to measure the equilibrium vapor pressure of tantalum pentachloride over the range 431–73°K. The second law enthalpy of sublimation was calculated to be $\Delta H_T° = 21.1 + 0.2$ kcal/g-mol. Third-law estimates of the enthalpy and entropy of sublimation at 298°K are $\Delta H_{298}° = 22.1$ kcal/g-mol and $\Delta S_{298}° = 44.8$ eu, respectively, based on estimated heat capacities. The data were fit by $\log_{10} P_{mm} = (12.03 \pm 1.86) - (4604 \pm 40)/T$.

Reported vapor pressures of tantalum pentachloride (*1*, *3*, *4*, *7*, *8*) differ appreciably at temperatures below the melting point (216.5°C). Data were obtained in this work using the gas transpiration method under carefully controlled anhydrous conditions. The vapor pressure data obtained compared favorably with the literature values of Saeki et al. (*4*), whereas the heat of sublimation is more consistent with the calculated values reported by Schafer and Kahlenberg (*5*) as obtained from prior published data.

EXPERIMENTAL

The apparatus used in this experimental work consisted of a pyrex sublimation chamber which was maintained isothermal by a fused salt bath, a connecting hot line, and a condenser which was connected to the hot line by a ball and socket joint. The equipment and experimental technique are essentially the same as those used and described by Joung and Stevenson (*2*). Resublimed tantalum pentachloride was obtained in sealed ampuls from Alfa Inorganics, Inc. (lot No. 06871) and contained no detectable quantities of niobium according to spectroscopic analysis. Other impurities were less than 0.02%. The $TaCl_5$ was loaded into the sublimation chamber within an inert atmosphere dry box having fewer than 0.5 ppm H_2O content. The sublimer was sealed (fused) into the system under dry inert gas purged to prevent any contamination by atmospheric moisture.

Measurements were made after the helium carrier gas flow rate and salt bath temperatures had stabilized. The sublimed $TaCl_5$ was condensed from the gas phase for a measured period of time and weighed to determine the gas composition. Flow rates were measured before and after each run using a soap film flow meter and appropriately corrected to standard conditions. Flow rates could be determined to within about 0.002 cc/sec in this way. Temperatures were measured by a calibrated chromel-alumel thermocouple placed in the salt bath next to the sublimer. The temperature of the salt bath in the vicinity of the sublimer was thus established to within approximately ±0.2°C.

Vapor pressures were calculated from the expression

$$P_{TaCl_5} = P/(1 + Mvt/22{,}400\, w)$$

where

P_{TaCl_5} = vapor pressure of $TaCl_5$ in mm Hg
P = system pressure, mm Hg
M = mol wt of $TaCl_5$
v = flow rate of the carrier gas, std. cc/sec
t = time, sec
w = weight of $TaCl_5$ condensed in grams

Partial pressures of $TaCl_5$ were calculated from the above equation for flow rates between 0.15 and 0.9 std cc/sec to

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establish the range of flow rates in which the gas was saturated and where diffusional errors could be neglected. Figure 1 shows the variation of the partial pressure of $TaCl_5$ as a function of the carrier gas flow rate and sublimation temperature. Flow rates of 0.3 to 0.6 std cc/sec were considered adequate to ensure gas saturation.

RESULTS

The vapor pressure data obtained in this work are tabulated in Table I and plotted (log P vs. $1/T$) in Figure 2. The calculated vapor pressures by Schafer and Kahlenberg (*5*) summarizing results prior to 1960, and the more recent results of Shchukarev and Kurbanov (*7*) and Saeki et al. (*4*) are also represented for comparison.

The heat of sublimation was calculated by the second law method to be $\Delta H_T^\circ = 21.1 \pm 0.2$ kcal/g-mol. Third-law

Table I. Vapor Pressure of Solid $TaCl_5$

Temp, °K	Vap. press., mm Hg	He flow rate, std cc/sec	Time, sec	$TaCl_5$ Condensed, g
473.2	192.64	0.4445	600	1.5124
472.8	192.68	0.4447	600	1.5127
471.2	183.10	0.4438	600	1.4090
471.2	181.57	0.4450	600	1.3966
469.5	169.70	0.4399	600	1.2631
469.4	170.48	0.4399	600	1.2707
465.5	140.56	0.4498	900	1.5194
465.3	132.98	0.4471	900	1.4110
460.7	107.18	0.4483	900	1.0946
460.6	107.81	0.4427	900	1.0883
460.4	103.58	0.4112	300	0.3228
455.3	82.36	0.4430	1200	1.0672
455.2	81.16	0.4426	1200	1.0491
453.3	73.05	0.5420	300	0.2862
453.1	74.43	0.3064	300	0.1652
448.6	58.23	0.4434	1020	0.6194
448.3	53.57	0.4449	1020	0.5676
446.9	55.88	0.5717	420	0.3152
442.9	42.52	0.4355	1200	0.5107
442.1	41.66	0.4332	1500	0.6216
441.6	42.33	0.3127	600	0.1829
441.6	43.44	0.5416	600	0.3256
436.8	31.72	0.5543	900	0.3602
436.5	30.30	0.3017	1200	0.2492
434.2	24.85	0.4358	1500	0.3643
434.2	25.75	0.4392	1500	0.3754
434.0	25.54	0.4326	1500	0.3719
431.4	22.96	0.5445	900	0.2531

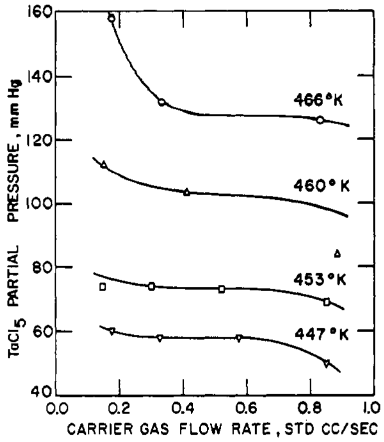

Figure 1. Effect of carrier gas flow rate on gas saturation

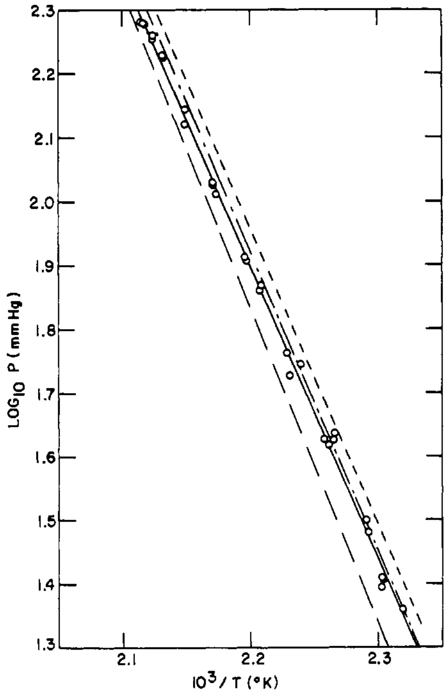

Figure 2. Vapor pressure of $TaCl_5$ (solid phase)

— — — Shchukarev and Kurbanov (*7*)
— — — Saeki et al. (*4*)
- - - - Schafer and Kahlenberg (*5*)
—○— This work

Table II. Comparison of Vapor-Pressure Equations[a] and Sublimation Enthalpies

Authors	A	B	ΔH_T°	ΔS_T°	ΔH_{298}°	ΔS_{298}°	Temp range	Method
Opikhtina & Fleischer (*3*) 1937	12.75	4900	22.4[b]	45.2[b]	23.4[b]	47.9[b]	393–mp	Transpiration
Tarasenkov & Komandin (*8*) 1949	11.73	4460	20.4[b]	40.5[b]	21.5[b]	43.6[b]	301–476	Static
Alexander & Fairbrother (*1*) 1949	12.57	4890	22.4[b]	44.3[b]	23.5[b]	47.3[b]	412–mp	Static
Schafer & Kahlenberg (*5*)	12.197[c]	4654[c]	21.3[c]	42.6[c]	22.3[c]	44[c]	—	—
Shchukarev & Kurbanov (*7*) 1962	12.774	4959	22.7	45.2	23.8	48.3	425–mp	Static
Saeki et al. (*4*) 1968	12.323	4729	21.63	43.19	—	—	363–mp	Static
This work 1971	12.03 ±1.86	4604 ±40	21.1 ±0.2	41.9	22.1	44.8	431–473	Transpiration

[a] $\log_{10} P_{mm} = A - B/T(°K)$. [b] Calculated by Schafer and Polert (*6*). [c] Calculated by Schafer and Kahlenberg (*5*) from previous data.

calculations were made using the estimated heat capacities of Schafer and Kahlenberg (*5*), viz., $C_p(g) = 31.6 - 3.7 \times 10^5/T^2$ and $C_p(s) = 38 - 3 \times 10^5/T^2$. The standard enthalpy and entropy of sublimation values at 298 were calculated to be $\Delta H_{298}° = 22.1$ kcal/g-mol and $\Delta S_{298}° = 44.8$ eu, respectively. The equation, $\log_{10} P_{\text{mm}} = (12.03 \pm 1.86) - (4604 \pm 40)/T$ was obtained by a least-squares fit of the experimental data and is shown in Table II along with enthalpies and entropies of vaporization at the mean temperature and at 298 for comparison with similar values of previous investigators.

DISCUSSION

The heat of sublimation obtained in this work compares favorably with the values reported by both Saeki et al. (*4*) and Schafer and Kahlenberg (*5*) as noted in Table II while the vapor-pressure values are in reasonably close agreement only with Saeki's (less than 5% difference at the mean temperature). The vapor pressure of Shchukarev and Kurbanov (*7*) is 14% lower than reported in this paper while the vapor pressure calculated from the equation of Schafer and Kahlenberg is approximately 15% higher.

No experimental heat capacity data were found in the literature; consequently, only estimates of the standard enthalpy and entropy at 298 could be made. The uncertainties of the estimated heat capacities of Schafer and Kahlenberg is probably greater than the experimental uncertainty as given for $\Delta H_T°$. The true values of $\Delta H_{298}°$ and $\Delta S_{298}°$ are estimated to be within 3–5% of those reported.

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Surface Properties of Nine Liquids

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The surface energy, the surface entropy, and the latent heat of surface formation, all per unit area, have been calculated for nine pure liquid-air systems from information on surface tension as a linear function of temperature. For seven of the liquids—water, benzene, *n*-butanol, methyl propyl ketone, isooctane, diisopropyl ether, diisobutyl ketone—experimental surface tension measurements are presented at 20, 30, 40, and 50°C. This information has been augmented by selected values from the literature and by equations derived to express surface tension as a function of temperature. For toluene and carbon tetrachloride, all the information was taken from the literature. To about 1 part in 1000 at least, the surface energies per unit area of the reported liquids are constant over a range of about 100°C. Two new equations are derived to predict the surface tension of benzene over its normal liquid range. These equations, representing a consensus of much work, predict for benzene at 20°C that $\sigma = 28.88$ dyn/cm, thus confirming the accepted standard value proposed by Harkins in 1945.

If data are available on the surface tension of a liquid-gas system over an appreciable range of temperature, it is possible to calculate several significant surface properties, such as the latent heat and the entropy of formation of a fresh unit of surface. Unfortunately, rarely is surface tension measured over a significant temperature range. Accordingly, when suitable experimental data became available on seven liquids, the thermodynamic properties were derived by conventional surface thermodynamics. At the same time, an assessment of literature data on two additional liquids made it possible to raise the number of substances thus evaluated to nine.

EXPERIMENTAL

Seven liquids—water, benzene, isooctane, *n*-butyl alcohol, methyl propyl ketone, diisopropyl ether, and diisobutyl

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