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Vapor Pressure of Titanium

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In view of the current interest in the use of titanium metal at high temperatures, it is important that vapor-pressure data be made available. The vapor pressure of titanium has been determined over the range from 1500 to 1800°K., using the method of Langmuir.[1]

The vapor pressure (p) was calculated from the measured rate of evaporation *in vacuo* (m) of an electrically heated titanium wire by the well-known Knudsen equation

$$\alpha p = m(2\pi RT/M)^{1/2} \qquad (1)$$

where m is in grams per square centimeter per second, and M is the molecular weight in the vapor phase. The *accommodation coefficient* (α) was assumed to be unity as has been found generally to be the case for metals.[2]

Measurement of the weight per unit length of the wire before (w_0) and after (w) a run of t seconds duration leads to the rate of evaporation by the relationship[1]

$$m = \left(\frac{\rho}{\pi}\right)^{1/2} \frac{w_0{}^{1/2} - w^{1/2}}{t} \qquad (2)$$

where ρ is the density. These average m values may be checked by following the resistance of the wire during the run. If one plots the square root of the ratio of the resistance (R_0) of the wire at $t = 0$ (extrapolated) to the resistance at time t against t, one should obtain in the case of constant m, a straight line of slope x which leads to the rate of evaporation by the relationship[1]

$$m = (\rho w_0/\pi)^{1/2}x \qquad (3)$$

Experimental.—Titanium wire of 0.46-mm. diameter and of 99.7 to 99.9% purity was supplied by the U. S. Bureau of Mines. It was produced by the magnesium reduction of titanium tetrachloride.[3] Lengths of 8 to 9 cm. were mechanically cleaned and polished with fine emery paper. Contact with 1-mm. tungsten electrodes was made by placing the ends of the wire and of the electrodes into slotted copper blocks (0.95 × 0.95 × 1.6 cm.), and then crimping the assembly in a vise.

The filament assemblies were sealed in turn into a 1-liter Pyrex round-bottom flask, being oriented along the large diameter perpendicular to the axis of the neck. A plane Pyrex window was sealed into the neck of the flask through which the temperature measurements were made. In order to prevent clouding of the window between temperature readings by the condensed titanium, a magnetically operated shutter was provided between the window and the filament. The effectiveness of the shutter in preventing the progressive formation of appreciable optically absorbing film was evident from the constancy during each run of the product of the filament voltage and the cube-root of the current[1] together with the constancy of the observed optical temperature. The bulb was evacuated to 10^{-6} mm. of mercury by means of a vacuum system consisting of a Cenco-Hyvac mechanical pump followed by a single-stage mercury condensation pump and a liquid air-trap.

Prior to the run, the bulb was alternately outgassed by flaming, and flushed with pure dry helium. A glow discharge from a Tesla coil was played on the wire during the next to the last pump-down in an effort to clean off small particles of abrasive, etc.

A battery-stabilized direct-current supply was used to heat the filament wire, the resistance of which was derived from current and voltage. The heating current was determined by measuring with a potentiometer the voltage developed across a standard resistance in series with the filament. A voltage divider was provided to measure with the potentiometer, the voltage across the filament. Corrections were made for lead resistance determined at the end of the run by passing a current equal to the average of that used during the run through the lead assembly with the copper terminal blocks soldered together.

Filament temperatures were determined with a Leeds and Northrup optical pyrometer calibrated with window *in situ* against a N.B.S. standard tungsten-ribbon lamp. The observed temperatures were corrected for the emissivity of titanium.[4] It is fortunate that the heat conductivity of titanium is relatively low. This led to an observed constant temperature (±10°) over 95% of the length of the wire.

Approximately one-tenth of the filament was allowed to evaporate during each run. The rates of evaporation as determined by resistance change were quite constant throughout the runs, except for short periods at the start when the wire was becoming stabilized (evaporation of small magnesium content, transition from α- to β-titanium, etc.)

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[1] I. Langmuir, *Phys. Rev.*, **2**, 329 (1913).

[2] H. L. Johnston and A. L. Marshall, THIS JOURNAL, **62**, 1382 (1940).

[3] R. S. Dean, J. R. Long, F. S. Wartman, E. L. Anderson and E. T. Hayes, *Trans. Am. Inst. Mining Met. Engrs., Inst. Metals Div.*, **166**, 369 (1946). The titanium powder produced by the reduction was compacted and then sintered *in vacuo* at 1000° for sixteen hours, volatilizing the impurities, hydrogen and magnesium. The remaining principal impurities are Fe < 0.1%, Si < 0.1% and O + N, < 0.1%.

[4] Van Arkel, "Reine Metalle," J. Springer, Berlin, 1939, p. 187. The emissivity was checked in the neighborhood of 1400°K., $\epsilon_{0.65\mu} = 0.49$ by temperature observations on the surface of and on a hole in an induction-heated titanium block. The results checked to within ±10° (the uncertainty in the reading of the temperature of the filament wire).

Data.—The experimental results are given in Table I. A "high-temperature density" of 4.35 (as compared to the room-temperature value of 4.5) was determined from the observed sag in in the filaments upon heating.[5] This value was used for ρ in Equations (2) and (3).

TABLE I

RATE OF EVAPORATION OF TITANIUM

Temp., °K.	Time of run, sec.	Rate of evaporation,[a] g./sq. cm./sec.	
1510	144,000	1.62×10^{-8}	1.80×10^{-8}
1613	39,300	1.60×10^{-7}	1.86×10^{-7}
1636	21,120	2.9×10^{-7}	3.1×10^{-7}
1727	4,800	1.33×10^{-6}	1.37×10^{-6}
1822	1,050	9.2×10^{-6}	8.9×10^{-6}

[a] The first value was determined by resistance change, the second by weight loss.

One run was made at each of the recorded temperatures.

Thermodynamic Treatment.—The validity of the data can best be tested by determining the constancy of ΔH_0^0 in the relationship

$$R \ln p \text{ (atm.)} = \left(\frac{F^0 - H_0^0}{T}\right)_{\text{solid}} - \left(\frac{F^0 - H_0^0}{T}\right)_{\text{vapor}} - \frac{\Delta H_0^0}{T} \quad (4)$$

The free-energy function of the solid is related to the heat capacity as

$$\left(\frac{F^0 - H_0^0}{T}\right)_{\text{solid}} = \frac{1}{T}\int_0^T C_p \mathrm{d}T - \int_0^T C_p \mathrm{d} \ln T \quad (5)$$

The free-energy functions of the vapor can be determined accurately from spectroscopic data.[6]

The C_p data for solid titanium of Kelley[7] in the low-temperature range, and of Jaeger and others[8] from 200° to 1200° were used in evaluating Equation (5). Free-energy functions for titanium vapor were evaluated using spectroscopic data from Landolt–Börnstein.[9]

The values of ΔH_0^0 of sublimation as calculated from Equation (4) using the vapor-pressure data are given in the fifth column of Table II. The average value of ΔH_0^0, 111,064 cal., added to the difference between $(H^0 - H_0^0)$ of solid and vapor leads to the heat of sublimation at 298.2°K., $\Delta H_{298.2}$ = 111,720 cal.

The fact that there is no apparent trend of ΔH_0^0 with temperature, and that the maximum deviation from the mean is only 578 cal. speaks well for the validity of the data.

Carpenter and Reavell[10] have recently determined the rate of evaporation of titanium using the present technique. In an advance announcement of their results, they give no data, but present the following equation for the rate of evaporation of titanium

$$\log mT^{1/2} = 7.70 - (2.07 \times 10^4/T) \quad (6)$$

TABLE II

ΔH_0^0 OF SUBLIMATION OF TITANIUM

T, °K.	$-\left(\frac{F^0 - H_0^0}{T}\right)_{\text{vapor}}$	$-\left(\frac{F^0 - H_0^0}{T}\right)_{\text{solid}}$	Vapor pressure,[a] atm.	ΔH_0^0,[a] cal.	ΔH_0^0 (C. and R.),[b] cal.
1510	46.282	12.26	2.05×10^{-9}	111,393	110,094
			2.28×10^{-9}	111,076	
1613	46.637	12.73	2.08×10^{-8}	111,394	110,926
			2.42×10^{-8}	110,894	
1636	46.713	12.84	3.8×10^{-8}	110,937	111,101
			4.1×10^{-8}	110,724	
1727	47.005	13.23	1.79×10^{-7}	111,633	111,892
			1.86×10^{-7}	111,512	
1822	47.294	13.61	1.28×10^{-6}	110,486	112,636
			1.24×10^{-6}	110,595	

Av. ΔH_0^0 = 111,064 ± 578 cal.

[a] The upper value was determined by resistance change, the lower by weight loss. [b] Calculated using Equation (6) of Carpenter and Reavell.

The authors have calculated ΔH_0^0 at their own experimental temperatures using this equation. The resulting values given in the sixth column of Table II show a trend with temperature of roughly twice the maximum spread of the present data. Thus, Equation (6) is inconsistent with the C_p data. However, there is fair agreement with the C_p data and with the present vapor-pressure data at 1613 and 1636°K. The reason for the deviation at higher and lower temperatures may become apparent when the experimental data of Carpenter and Reavell are published.

If the average value of ΔH_0^0 from the present work be substituted in Equation (4) together with a linear expansion of $(F^0 - H_0^0/T)_{\text{sublimation}}$ as a function of the absolute temperature, one arrives at the equation

$$\log p \text{ (atm.)} = 7.782 - (24{,}275/T) - 0.230 \times 10^{-3}T \quad (7)$$

which is believed to represent the vapor pressure of titanium to within 10% over the range 1200–2000°K. This equation together with the experimental data is plotted in Fig. 1. The points in the squares are those obtained from weight loss, and those in the small circles from resistance change. The large circles are centered midway between the weight-loss and resistance-change points, and have radii of 10°. The dashed curve is from Equation (6).

The data may be extrapolated to give an equation for the vapor pressure of liquid titanium. A reasonable entropy of fusion of 2.5 e. u. at the melting point, 2000°K.[11] is assumed together with a constant heat capacity for the liquid of 8.0 cal./mol./°. These values, when combined with ΔH_0^0

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[5] Van Arkel, ref. 4, p. 185, gives 4.31 as the density of β-titanium at the transition temperature.

[6] W. F. Giauque, THIS JOURNAL, **52**, 4808 (1930).

[7] K. K. Kelley, *Ind. Eng. Chem.*, **36**, 865 (1944).

[8] F. M. Jaeger, E. Rosenbohm and R. Fonteyne, *Rec. trav. chim.*, **55**, 615 (1936).

[9] Landolt-Börnstein, "Tabellen," Pt. 3, III Suppl., p. 2346.

[10] L. G. Carpenter and F. R. Reavell, *Nature*, **163**, 527 (1949).

[11] Van Arkel, ref. 4, p. 186.

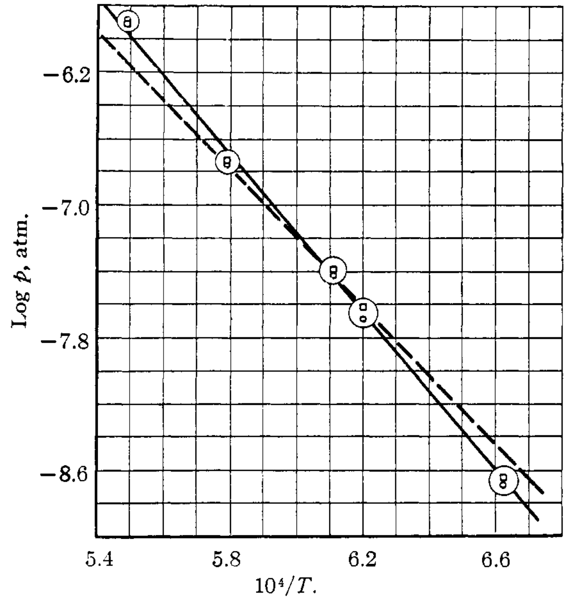

Fig. 1.—Vapor pressure of titanium: O, resistance change; □, weight loss; large circles, ±10° temperature. The full curve is that of Equation (7). The dashed curve is from Equation (6) of Carpenter and Reavell.

and the free-energy functions for titanium vapor as given by Latimer,[12] lead to vapor pressures which may be expressed to within 2.5% by the equation

$$\log p \text{ (atm.)} = 6.255 - (22{,}110/T)$$

The calculated boiling point is 3535°K.

It has been observed in this Laboratory that at the temperatures encountered in the present work, oxygen and nitrogen diffuse very rapidly into titanium, forming solid solutions. This fact greatly reduces the possibility of an error encountered with many metals using the Langmuir technique, *i. e.*, a lowering of the rate of evaporation by surface oxide or nitride films. The impurities in solid solution with the titanium used in the present work, a maximum of 0.005 mole-fraction, would reduce the vapor pressure of pure titanium, and might yield observed values roughly 99.5% of the true values. This difference is insignificant relative to experimental error.

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Summary

The vapor pressure of solid titanium has been determined in the range 1500–1800°K. by measuring the rates of evaporation of titanium wire using the Langmuir technique. The data fit the thermodynamic requirements quite well and yield heats of sublimation of 111,000 cal. at 0°K. and 111,700 at 298.2° K. The resulting equation for the vapor pressure of solid β-titanium, valid over the range 1200–2000°K., is $\log p$ (atm.) = 7.782 − (24,275/T) − 0.230 × 10^{-3} T.

The data may be extrapolated to yield an equation for the vapor pressure of the liquid: $\log p$ (atm.) = 6.255 − (22,110/T), leading to a normal boiling point of 3535°K.

The data agree over a limited range with the incomplete experimental results of Carpenter and Reavell. Their equation for the rate of evaporation of titanium has been shown to be inconsistent with other available thermodynamic data.

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[12] Wendell M. Latimer, "Tables of Free-Energy Functions for Elements and Compounds in the Temperature Range 2000–5000°K." MDDC-1462, U. S. Atomic Energy Commission, Sept. 10, 1947, p. 4.

[13] Deutsch and Loonam, Consultants, 70 E. 45th Street, New York 17, N. Y.

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[Contribution from the Department of Chemistry, The Johns Hopkins University]

The State of Oxidation of S^{35} Formed by Neutron Irradiation of Potassium Chloride

By W. S. Koski

When potassium chloride is irradiated with thermal neutrons the following is one of the reactions that takes place

$$\mathrm{Cl}^{35} + \mathrm{n} \longrightarrow \mathrm{S}^{35} + \mathrm{H}' + Q$$

The Q of this reaction as estimated from the masses is 0.63 mev. From simple considerations of conservation of energy and momentum, one can estimate the energy of the recoiling sulfur fragment as equal to 17.6 kev. Since it is believed[1,2] that ionization by a rapidly moving particle is probable only at velocities comparable to the effective velocities of free electrons, the recoiling sulfur fragment will produce no appreciable ionization by the process of electron ejection and capture. However, the irradiated chlorine is an ion in the crystal lattice, and the proton on leaving the compound nucleus will reduce the nuclear charge by +1 leaving the residual sulfur fragment with a double negative charge. This charge may be reduced by electron capture by the proton as it moves through the electronic field of the sulfur fragment. Such

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[1] H. A. Bethe, *Rev. Mod. Phys.*, **9**, 262–265 (1937).

[2] J. Knipp and E. Teller, *Phys. Rev.*, **59**, 659 (1941).