Vapor Pressure of Liquid Copper

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The Knudsen effusion technique was used to determine the equilibrium vapor pressure of liquid oxygen-free–high-conductivity (OFHC) copper (99.98% Cu) in the temperature range 1475° to 1707° K. The vapor pressure in the above temperature range can be expressed as ln $P = -39129/T + 14.203$. The accommodation coefficient of copper was assumed to be unity. The average value of the heat of sublimation at absolute zero was calculated to be 80,807 ± 190 cal. per mole.

THE vapor pressure of pure liquid copper previously has been investigated by Jones, Langmuir, and McKay (*4*) using the surface evaporation method; by Harteck (*2*) over a limited temperature range using the Knudsen effusion technique; by Marshall, Dornte, and Norton (*6*) using the Langmuir free evaporation method (1356° to 1466° K.); by Hersh (*3*) using the Knudsen effusion technique (1356° to 1563° K.); and by Morris and Zellars (*7*) using the carrier gas method (1605° to 1879° K.). The present work is the first Knudsen effusion data to be reported above 1563° K.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The Knudsen method, developed by means of statistical thermodynamics and kinetic theory, postulates that the rate of effusion of a gas through an orifice into a high vacuum is related to the vapor pressure above the metal. The rate of effusion is related to the vapor pressure of the metal by the expression:

$$P = \frac{W}{At}\left(\frac{2\pi RT}{M}\right)^{1/2} = 2.258\,\dot{m} \times 10^{-2}\left(\frac{T}{M}\right)^{1/2} \qquad (1)$$

In these expressions, P is the vapor pressure in atmospheres, W is weight loss in grams during the effusion time interval, A is orifice area in square centimeters, t is effusion time in seconds, R is the universal gas constant, T is absolute temperature in degrees Kelvin, M is the molecular weight of the metal, and $\dot{m}$ is the effusion rate in grams/sec./sq. cm.

It is assumed in the above expressions that the orifice is ideal—i.e., infinite thinness. In actual practice, the orifice does have measurable thickness and approximates a short tube or channel. Speiser (*9*) has given equations to correct for this condition. The need for correction factors was avoided in this work by reaming the orifice to a knife-edge of 30° included angle. Calculations based on Balson's (*1*) derivation showed the orifice to be nearly ideal.

The vacuum chamber used was fabricated from a 7-inch diameter brass cylinder which measured 13 inches high. Copper tubing was used to circulate coolant water around the chamber and through hollow electrode leads to the resistance furnace. A mechanical forepump and an oil diffusion pump were used to create an operating vacuum of at least 1×10^{-5} mm. of Hg. A liquid-nitrogen trap prevented water and oil vapor in the diffusion pump from reaching the vacuum chamber. Operating temperatures were obtained with a wound, resistance-type, molybdenum wire furnace surrounded by three cylindrical tantalum heat shields. Power was supplied to the furnace by a constant voltage transformer.

The Knudsen cells which contained the alumina crucibles in which the samples were placed were fabricated from seamless tantalum tubing of 1-inch outside diameter and 0.020-inch wall thickness; cell bases and covers were formed from 0.010-inch thick tantalum sheet and welded in an argon atmosphere to the cells. A Leeds and Northrup disappearing filament-type optical pyrometer, calibrated against a Bureau of Standards pyrometer by means of a standard tungsten ribbon filament lamp, was used to determine temperatures. The calibration was performed with the glass viewport in place to avoid corrections for window transmissibility. A magnetically operated shutter was provided to prevent the deposition of metallic vapors on the borosilicate glass sighting window. All temperature measurements were made by sighting through the orifice into the interior of the cell, which is effectively a "hohlraum," so that corrections for emissivity of the sample are unnecessary (*9*). The manually controlled constant voltage transformer provided excellent temperature control (within the error of an optical pyrometer) and consequently minimized the temperature readings required.

Effective times at temperature were calculated to compensate for heating and cooling periods. The effective time was calculated from the following equation:

$$t_{\text{eff.}} = \sum \Delta t_i \left[e^{-\Delta H_v/RT_A + \Delta H_v/RT_R}\right] \qquad (2)$$

where Δt_i is the time interval between any two temperatures, T_A is the average temperature during that interval, T_R is the temperature of the test, and ΔH_v is the heat of vaporization of copper in calories per mole (*8*). This value was assumed initially to be 77,000 cal. per mole, but experi-

Table I. Copper Specimen Analysis

Element	Wt. %
Cu	99.98
Ni	0.001
Fe	0.005
Si	0.002
Al	<0.001
Zn	<0.001
Pb	<0.001
Sn	<0.001

Table II. Vapor Pressure of Pure Liquid Copper

Test	Temp., ° K.	Time, Sec.	Wt. Loss, Gram	Pressure, Atm.	Pressure,[a] Atm.
5	1514	7390	0.0166	9.452×10^{-6}	8.676×10^{-6}
6	1525	6876	0.0174	1.069×10^{-5}	1.045×10^{-5}
7	1475	8174	0.0086	4.371×10^{-6}	4.374×10^{-6}
8	1567	5940	0.0276	1.937×10^{-5}	2.081×10^{-5}
9	1593	4941	0.0370	3.144×10^{-5}	3.128×10^{-5}
10	1640	4077	0.0644	6.712×10^{-5}	6.328×10^{-5}
11	1684	2642	0.0695	1.132×10^{-4}	1.182×10^{-5}
12	1707	2517	0.0992	1.706×10^{-4}	1.617×10^{-4}

[a] Calculated from the empirical expression ln $P = -39130/T + 14.203$.

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Table III. Heat of Sublimation of Copper at Absolute Zero

Temp., ° K.	$-R \ln P$, Cal./ Mole-Deg.	$-\left[\frac{F^\circ - H_0^\circ}{T}\right]_{\text{Solid}}$	$-\left[\frac{F^\circ - H_0^\circ}{T}\right]_{\text{Gas}}$	ΔH_0°, Cal./Mole
1707	17.2426	13.577	43.490	80495
1684	18.0567	13.466	43.421	80852
1640	19.0963	13.246	43.298	80603
1593	20.6038	13.007	43.147	80835
1567	21.5655	12.874	43.069	81109
1525	22.7462	12.652	42.932	80865
1514	22.9924	12.594	42.895	80686
1475	24.5249	12.374	42.771	81010
			Average value	80807
			Standard dev.	±190

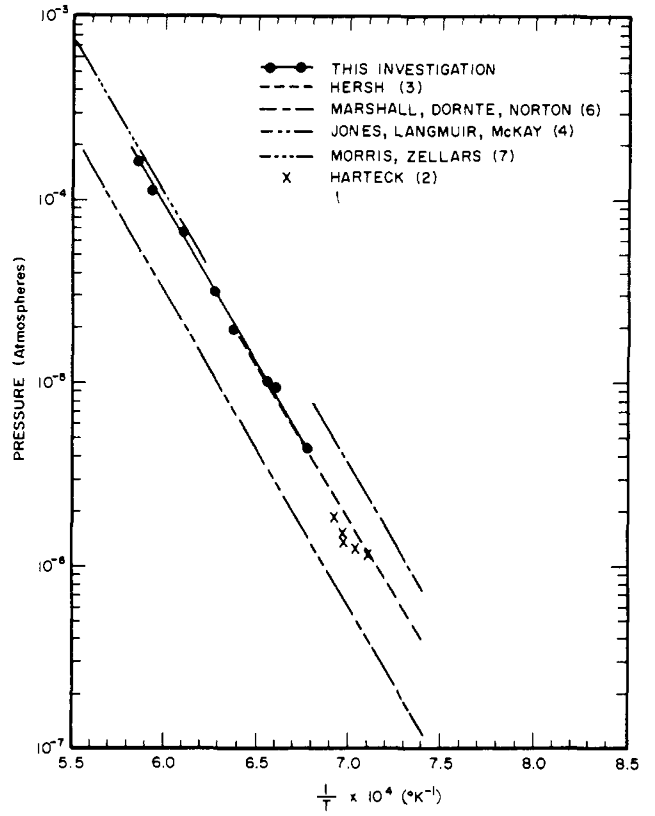

Figure 1. Vapor pressure of liquid copper

mentally determined to be 77.749 cal. per mole. Slight deviations in ΔH_v created negligible differences in the effective time calculations.

Orifice dimensions were corrected to account for the thermal expansion of the tantalum cell cover (*9*). Experimental data were determined to the following accuracy: weight loss, ±0.05 mg.; time, ±60 seconds; temperature, ±4° C.; and orifice area, ±0.001 sq. cm.

The orifice diameter was made small, and its ratio to the area of the evaporating surface was sufficiently less than unity, that the efflux of vapor did not appreciably upset the equilibrium pressure within the cell. Calibration tests performed at 1600° K. demonstrated that steady-state conditions were maintained within the cell; the ratios of the orifice area to the surface area were varied from 0.01 to 0.04 and the resulting rates of evaporation per unit area did not vary more than 5%. In addition, the value of the vapor pressure computed at 1707° K. from the best line established from the four lowest pressure readings (pressures on the order of 10^{-2} mm. of Hg or less – pressures accepted by some authors as the upper limit for the Knudsen method) was 1.65×10^{-4} atm. This value is within 3% of the measured value at 1707° K. adding further credence to the higher pressure data obtained.

Table IV. Comparison of Liquid Copper Vaporization Data

Observer	ΔH_0°, Cal./Mole	P at 1600° K., Atm.
This investigation	80807 ± 190	3.52×10^{-5}
Hersh (*3*)	81080	3.24×10^{-5}
Morris and Zellars (*7*)	80220 ± 137	4.24×10^{-5}

EXPERIMENTAL RESULTS AND DISCUSSION

The oxygen-free-high-conductivity copper (OFHC) used during this study assayed 99.98% copper (Table I). Experiments were conducted at eight selected temperatures in the liquid region, ranging from 1475° to 1707° K. at time intervals ranging from 20 minutes to 2 hours. The data for each test are given in Table II.

A plot of the vapor pressure of liquid copper is given in Figure 1. The line was obtained by the method of least squares. The temperature-pressure relationship can be expressed as:

$$\ln P = -39129/T + 14.203$$

Calculations were made to estimate the deviations of the individual values of the measured vapor pressures from those predicted from the above empirical equation. These values are given in Table II. Deviations were found to range from 8.9 to 0.7% with a mean deviation of 5%. These experimental results revealed a larger measure of scatter than would have been expected from experimental error. The heat of vaporization was calculated from the slope of the log plot in accordance with the Clausius-Clapeyron equation and determined to be 77,749 cal. per mole. The results of this work agree within 5% of the data reported by Hersh (*3*), and Morris and Zellars (*7*). The data obtained during this investigation and the data obtained by Morris and Zellars are the most recent and the only data available above 1563° K. The lower temperature Knudsen cell data previously reported by Hersh (*3*) are in excellent agreement with the higher temperature Knudsen cell data obtained during this investigation. The data reported by Harteck (*2*), which were obtained using platinum Knudsen cells, covered only a range of approximately 44° and made comparison difficult. The data reported by Marshall, Dornte, and Norton (*6*) appear to be low.

The reliability of the vapor pressure data for pure copper can best be established by the constancy and temperature dependence of ΔH_0°. The values of ΔH_0°, the heat of sublimation at absolute zero, were calculated from experimentally determined vapor pressures by means of the equation:

$$R \ln P = \left[\frac{F^\circ - H_0^\circ}{T}\right]_{\text{Solid}} - \left[\frac{F^\circ - H_0^\circ}{T}\right]_{\text{Gas}} - \frac{\Delta H_0^\circ}{T} \qquad (3)$$

in which the parenthetical terms are the free energy functions of solid and gaseous copper. The free energy functions were obtained from the spectroscopic and calorimetric data by Kelley (5). Values for ΔH_0° were calculated at each temperature and averaged to obtain a value of 80,807 cal. per mole (Table III). The values of ΔH_0° were consistent within the accuracy of this experiment, and an absence of any trend toward increasing or decreasing values indicates that there were no serious systematic errors. Further validity of data obtained in this investigation may be made by calculating the theoretical vapor pressure at some constant temperature using Equation 3 and the values of ΔH_0° reported by previous investigators (Table IV).

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Vapor Pressure of Sodium from 0.5 to 120 Atmospheres

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The vapor pressure of sodium was measured by a static capsule method from 0.5 to 120 atm. An equation, log p = 4.51961 − (5202.12/T), where p is pressure in atmospheres and T is temperature in degrees Kelvin, was fitted to the data with a standard deviation in p of 3.2°. This equation was pooled with equations determined in three previous independent studies. The pooled equation, log p_p = 4.54025 − (5242.11/T), probably offers the most accurate representation of the vapor pressure of sodium from 0.5 to 120 atm.

VAPOR-PRESSURE CURVES for sodium in various ranges above 1 atm. have been obtained by several investigators, each using a different experimental method: Makansi, Muendel, and Selke, 0.047 to 6.489 atm. (*5*); Kirillov and Grachev, 0.2 to 15.4 atm. (*4*); Ewing *et al.*, 1 to 25 atm. (*3*); Sowa, 1 to 25 atm. (*6*). Up to about 6 atm., there is good agreement within experimental error among the data of Ewing, Sowa, and Makansi; above 6 atm.,

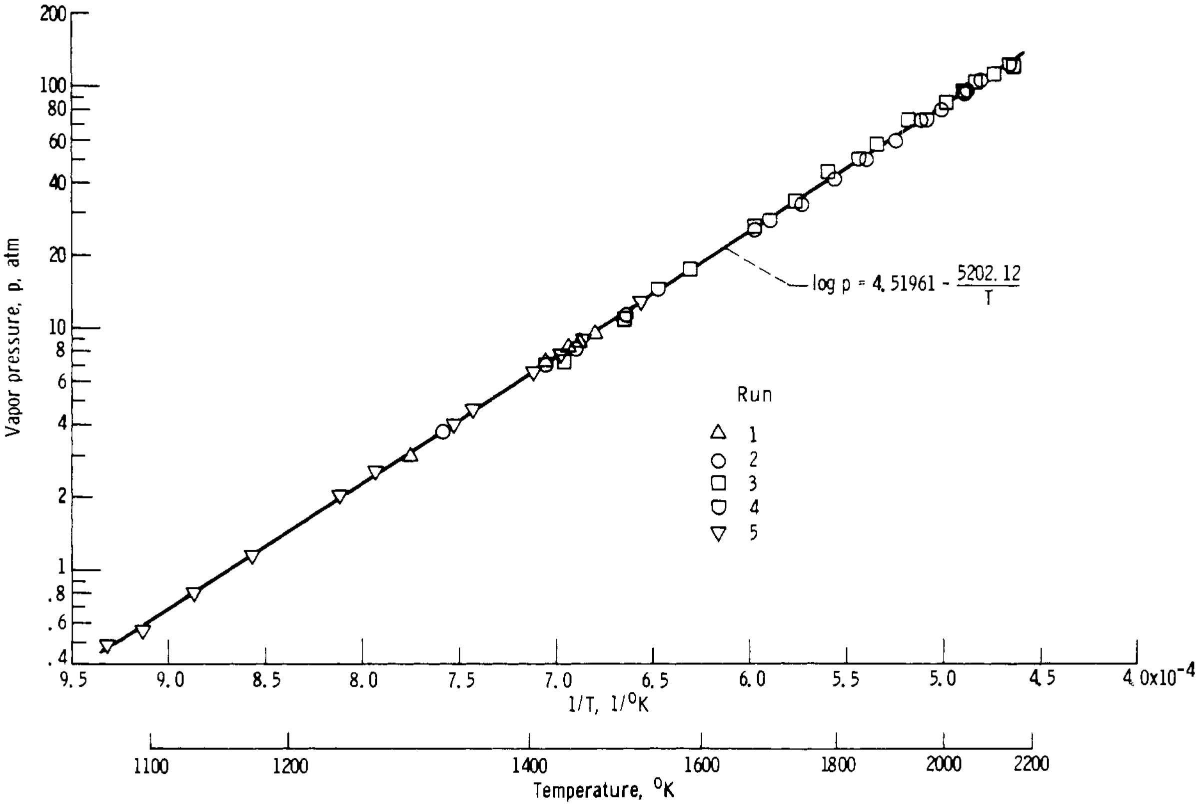

Figure 1. Vapor pressure of sodium