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The Vapor Pressure of Copper

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The vapor pressure of copper has been determined by the Knudsen effusion method between 1240° and 1560°K. The vapor pressures (mm.) in the solid and liquid states are given by the equations: $\log p_s = -1{,}726 \times 10^4/T + 9.232$ and $\log p_l = -1.682 \times 10^4/T + 8.907$. The latent heats of sublimation and evaporation are 78.96 ± 0.1 and 76.96 ± 0.1 kilocalories per gram atom, respectively.

Introduction

The purpose of the present investigation was to establish as accurately as possible the vapor pressure of copper prior to studying the thermodynamic activities of copper alloys. By using the Knudsen effusion technique in its unmodified form it has been possible to measure the vapor pressures of copper between 1242° and 1563°K. with relatively high precision. A description of the theory employed in this study is given by Speiser and Johnston.[1]

Vapor pressures, p, were computed from the measured rates of evaporation, G, per unit area of orifice *in vacuo*, by means of the relation

$$p = G\sqrt{2\pi RT/M} = 2.325(\Delta m/t_{\text{eff}}\, a)T^{1/2} \quad (1)$$

where p is in mm., T is in degrees Kelvin, M is the molecular weight of copper, Δm is the evaporation loss in grams, t_{eff} is the time at temperature T and a is the orifice area.

A vapor pressure measurement consists of heating to some temperature a non-volatile, non-reactive Knudsen cell[1] containing the condensed substance under investigation, and determining the loss of mass of the cell per unit time and area. The direct microgravimetric method of determining the amount of material which effused through the orifice was used. This method is tedious but has the advantage of simplicity. The target technique,[2] in which many targets are loaded in the vapor cell at one time and successively exposed to the molecular beam without breaking the vacuum between runs, in contrast to the present method, is more convenient experimentally but involves the problem of geometry of the target and source.

The results of previous workers are not in complete agreement.[3-6] To minimize or avoid the possible sources of error present in those works, the following conditions were made to prevail in the present study: (1) The Knudsen method was used rather than the Langmuir method[1] in order to eliminate consideration of the accommodation coefficient as in the work of Marshall, *et al.*[5] (2) A molybdenum Knudsen cell was used which did not react with copper; Harteck's cell was made of platinum, and might have alloyed with copper.[7] (3) Knudsen's condition that the ratio of the mean free path to the orifice diameter be greater than ten was fulfilled. (4) The orifice diameter was made small, and its ratio to the area of the interior evaporating surface so much less than unity, that the efflux of vapor did not appreciably upset the equilibrium between the saturated vapor and the condensed copper, thereby lowering the steady-state pressure within the vessel; the ratios for three cells were 0.008, 0.002, 0.01; that the steady state was established at the highest pressure is shown by the fact that the use of orifices with ratios 0.008 and 0.05 did not affect the rates of evaporation per unit area; the value of the pressure at 1340°K. as computed from the best line of five points below 1357°K. (ratio 0.008) is 2.23×10^{-4} mm.; the experimental vapor pressure at this same temperature for a Knudsen cell with an orifice of three times the area was 2.25×10^{-4}. (5) The orifice was effectively knife-edged; it may be estimated using the equation given by Speiser and Johnston and the observed thickness of the "knife-edge" (less than 2×10^{-4} cm.) that $p \sim p_{\text{true}}$ to within less than 0.4%.

Apparatus

The quartz water-cooled vapor pressure cell is shown in Fig. 1 and contains the Knudsen cell filled with oxygen-free copper of 99.99% purity which is heated *in vacuo* by radiofrequency induction.

The Knudsen cell, in the form of a right circular cup one inch in diameter and $^3/_4$ inch high was made from 10-mil cross-rolled molybdenum sheet by deep drawing through three dies.[8]

The orifice was prepared by grinding out a smaller hole previously made at the center of the cup with a pointed carborundum grinding pencil having a 90° included angle while the cup was rotating at high speed in the opposite direction. It was then finished by hand lapping using a wooden tool laden with diamond abrasives. After thorough vacuum annealing, the diameter of the orifice was measured by means of a toolmakers' comparator and also a microscope with filar eyepiece. The diameter was rechecked after use.

The cell containing the copper was closed by means of a tightfitting lid of smaller diameter.[8] The seam was then electrically welded in a helium atmosphere in a closed glass system containing tubulations with ball joints, vacuum and gas connections and sylphon bellows for proper manipulation.

The effusion vessel was weighed on a modified Ainsworth 1812-C microbalance capable of a precision of ±3 micrograms. Three weighings were made and the results averaged to give the "true" mass. An effusion cell with orifice was used as a tare to minimize errors due to buoyancy.

The specimen was heated by a 20 kilowatt, 385 kilocycle oscillator.

Temperatures were determined optically at the orifice which served as a blackbody hole. A modified Leeds and Northrup 8622-C disappearing filament optical pyrometer was used. The optical path included an optical window and

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[1] R. Speiser and H. L. Johnston, *Trans. A.I.M.*, **42**, 283 (1950).

[2] T. E. Phipps, G. W. Sears, R. L. Seifert and O. C. Simpson, *J. Chem. Phys.*, **18**, 713 (1950).

[3] S. Dushman, "Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 778.

[4] P. Harteck, *Z. physik. Chem.*, **134**, 1 (1928).

[5] A. L. Marshall, R. W. Dornte and F. J. Norton, THIS JOURNAL, **59**, 1161 (1937).

[6] H. A. Jones, I. Langmuir and G. MacKay, *Phys. Rev.*, **30**, 201 (1927).

[7] A. Schneider and V. Esch, *Z. Elektrochem.*, **50**, 300 (1944).

[8] G. W. Ziegler, Jr., R. Speiser and H. L. Johnston, *Rev. Sci. Instruments*, **20**, 367 (1949); although molybdenum cold-works very readily it was possible to make all three draws without intermediate annealing by slight modifications in the dies.

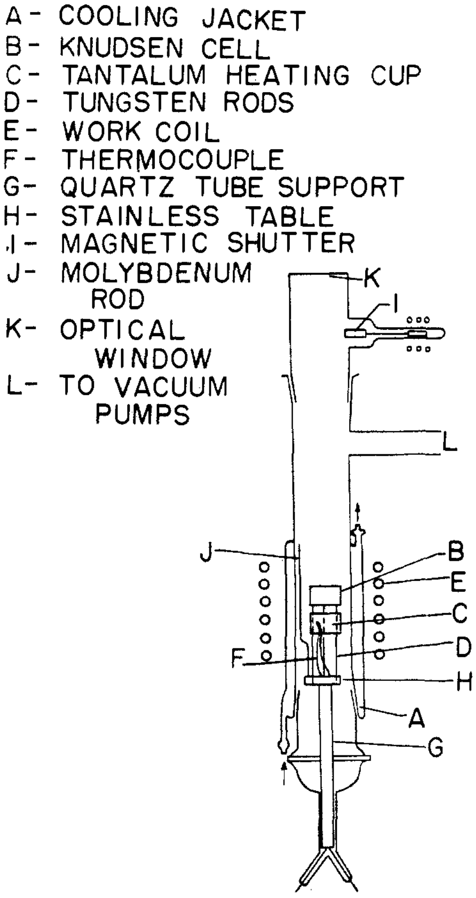

Fig. 1.—Quartz vapor pressure cell.

prism. By means of a standard tungsten-ribbon lamp certified by the National Bureau of Standards, a set of calibration curves were made from which it was possible to correct each temperature reading for the errors in the optical pyrometer itself and for the absorption of red light by the window and prism. After considerable practice it was possible to reproduce temperature readings to one degree.

Power level adjustment was achieved by varying the voltage to the grids of the oscillator tubes. An automatic controller maintained the power level against changes due to varying line voltage and thereby controlled the temperature. The detector, a Pt/Pt-13% Rh thermocouple (F), was enclosed in a dummy tantalum heating cell (C) which was of the same size and placed just below the Knudsen cell. The work coil (E) surrounded the whole assembly. The thermocouple e.m.f. was fed into the controller and also into a Brown recorder which traced the time–temperature curve of the thermocouple for recording purposes.

High vacuum was attained by the gettering action of the hot tantalum heating cup, as well as two liquid air traps, a glass three-stage oil-pump and a mechanical forepump.

Treatment of Data and Results

The treatment of data consisted of obtaining the mass loss of the Knudsen cell per unit time and area, and the average temperature at which effusion occurred. The mass loss per unit area was corrected for the thermal expansion of the orifice at high temperatures.[9] Temperature readings were corrected for the window and prism. The effective heating time, t_{eff}, including the initial heating and the final cooling time, and the average temperature, T_{ave}, was determined by a method of exponential averaging which makes use of the equation

$$\int_0^{t_{\text{eff}}} e^{-\frac{E}{RT}}\,\mathrm{d}t = t_{\text{eff}} \exp - E/RT_{\text{ave}} \qquad (2)$$

Using an approximate value of 80,000 calories for E, and graphical integration of the data to evaluate the left-hand member of (2), the equation was solved for T_{ave}.

The data were substituted in (1) and plotted as $-\log p$ *vs.* $1/T$. The results are given in Table I.

TABLE I

EVAPORATION OF COPPER

T, °K.	t_{eff}, sec.	Cm.^{2} × 10^1	Δm, g.	G g.-cm.$^{-2}$ sec.$^{-1}$	p, mm. × 10^3
1242	12,895	4.345	0.00159	0.2838	0.0215
1280	15,708	4.347	.00498	.7293	.561
1305	13,430	4.348	.00755	1.293	1.004
1328	4,420	2.749	.00266	2.189	.1715
1336	7,420	4.352	.00837	2.592	.2037
1340	6,151	13.53	.02375	2.854	.2245
1370	4,237	2.749	.00628	5.391	.4289
1380	5,645	2.749	.00996	6.418	.5125
1387	6,217	2.749	.01297	7.589	.6076
1432	4,163	2.751	.01996	17.43	1.417
1439	4,202	2.752	.02403	20.79	1.696
1477	4,253	2.755	.04595	39.22	3.239
1484	3,030	0.567	.00830	48.31	4.000
1513	3,217	.567	.01345	73.74	6.166
1522	3,120	.567	.01332	75.30	6.315
1533	3,079	.567	.01784	102.2	8.603
1563	3,520	.568	.03489	174.5	14.84

One line for the solid and one for the liquid were obtained by the method of least squares (see Fig. 2). The heats of sublimation and evaporation were then derived from the slopes in accordance with the Clausius–Clapeyron equation.

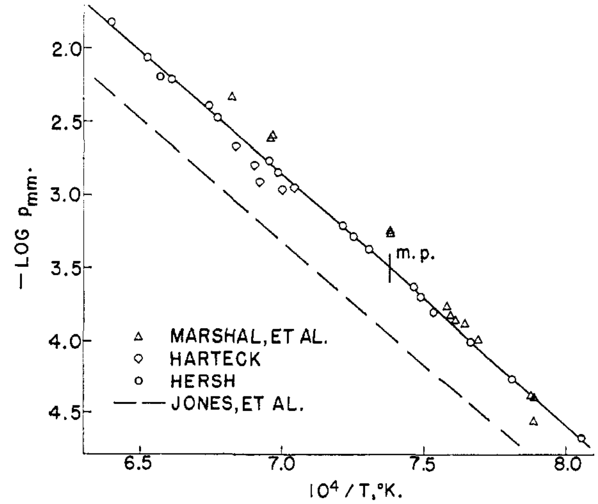

Fig. 2.—Vapor pressure of copper.

The vapor pressures, in mm., are given by the equations

$$\text{solid: } \log p_s = -1.726 \times 10^4/T + 9.232$$
$$\text{liquid: } \log p_l = -1.682 \times 10^4/T + 8.907$$

The latent heats of sublimation and evaporation are 78.96 ± 0.1 and 76.96 ± 0.1 kcal. per gram atom, respectively.

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[9] A. Worthing and D. Halliday, "Heat," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 12.

Discussion

The heat of sublimation at the absolute zero, as obtained from each point, was computed in accordance with the equation

$$\Delta H_0^0 = -RT \ln P + [(F^0 - H_0^0/T)_s - (F^0 - H_0^0/T)_l]T \quad (3)$$

The data for the free energy functions were obtained from calorimetric data[10] and the multiplicity of the ground state of copper.[11] Table II shows the value of ΔH_0^0 computed for each individual datum. The rather small deviations from the average demonstrate that the temperature coefficient of the vapor pressure is consistent with specific heat data. In addition, the relative constancy in the computed values of ΔH_0^0 imputes a certain reliability to the separate values obtained for the heat of sublimation and evaporation. The heat of fusion, which is the difference of these two numbers and therefore subject to a large percentage error, is about 2 kilocalories, as compared with Kelley's[12] best value of 3 kilocalories per gram-atom.

TABLE II

HEAT OF EVAPORATION OF COPPER

T, °K.	$-\log p$	$-R \ln P_{atm}$	$-(F^0 - H_0^0/T)$ condensed	$-(F^0 - H_0^0/T)$ gaseous	ΔH_0^0, cal. mole^{-1}
1242	4.668	34.54	11.13	41.87	81,078
1280	4.252	32.63	11.31	42.02	81,075
1305	3.998	31.47	11.45	42.12	81,092
1328	3.766	30.41	11.55	42.21	81,100
1336	3.691	30.07	11.60	42.24	81,109
1340	3.649	29.87	11.61	42.25	81,083
1370	3.368	28.59	11.77	42.36	81,077
1380	3.291	28.24	11.81	42.40	81,185
1387	3.217	27.90	11.86	42.42	81,084
1422	2.849	26.22	12.12	42.58	81,166
1439	2.771	25.86	12.15	42.60	81,030
1477	2.490	24.57	12.37	42.73	81,132
1484	2.398	24.15	12.41	42.75	80,864
1513	2.210	23.29	12.57	42.84	81,036
1522	2.200	23.24	12.62	42.87	81,412
1533	2.066	22.63	12.69	42.91	81,019
1563	1.829	21.55	12.84	43.00	80,823
				Mean ΔH_0^0,	81,080

The vapor pressure data of Jones, Langmuir and McKay[7] were obtained by the free vaporization of copper from an electrically heated wire. Their values have been generally recognized as being too low and may be excluded from comparison.

Marshall, Dornte and Norton[9] measured the vaporization rate from a large, freely evaporating surface of copper (Langmuir method) and give very precise data for both the solid and liquid state. However, upon calculation of ΔH_0^0 from the individual points the authors found a trend in their data which they state indicates a systematic error in their results which they were unable to explain. It is interesting to note that results below the melting point are closer to the present results which do not involve the accommodation coefficient or the emissivity of copper. Their values above the melting point seem suddenly to become much higher and are consistently somewhat higher than the values of Harteck[10] and the present author. The explanation for this may possibly be as follows: They measured the rate of free vaporization of liquid copper contained in a groove in one face of a molybdenum ring; our experience has been that liquid copper shows a tendency to creep as a thin film on molybdenum and thereby changes the effective evaporating area.

Harteck measured the rate of effusion from a platinum Knudsen cell. Our agreement with some of Harteck's data is taken to establish the absolute values of the pressures, a factor not involved in the above check for thermodynamic consistency of the data. His data cover a very small temperature range of 44° so that it is difficult to make a more detailed comparison.

The internal consistency and precision of the present data which cover a range of temperature of more than 300 degrees are considered adequate to establish the vapor pressure curve for copper with greater certainty than heretofore.

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[10] (a) W. F. Giauque and P. F. Meads, THIS JOURNAL, **63**, 1897 (1941); (b) K. K. Kelley, Bureau of Mines Bulletin 476 (1949), p. 62.

[11] A. G. Gaydon, "Dissociation Energies," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 217.

[12] K. K. Kelley, Bureau of Mines Bulletin 393 (1936), p. 41.