Vapor Pressure of Silver

MORTON B. PANISH
Physics Research Department, Research and Advanced Development Division, Avco Corp., Wilmington, Mass.

A COMBINATION of Knudsen effusion, radioactive tracer, and mass spectrometric techniques have been used in a study of the vaporization of silver. The equilibrium vapor pressure was determined by measuring the rate of effusion of silver from a Knudsen effusion cell, and the gaseous species were identified mass spectrometrically. The pressures within the Knudsen effusion cell were calculated by the use of the usual effusion equations and with the usual assumption that the accommodation coefficient of the silver is equal to unity. Third law calculations were used for the treatment of the data and calculation of heats of vaporization.

Detailed discussions of effusion techniques and restrictive conditions are available in standard texts (*2, 5, 11*).

EXPERIMENTAL

Condensed Sample Studies. In these studies, silver was caused to effuse from a tantalum effusion cell in such a manner that a small portion of the effusion beam normal to the axis of the effusion orifice of the cell passed through a collimator and struck a cooled copper target.

The apparatus which was used is similar to that used by other workers (*1, 8, 9*). Twelve copper target holders could be placed in a double-walled copper magazine which was cooled by liquid nitrogen. The targets were dry, chemically cleaned disks of copper 0.005 inch thick.

The effusion cell which is illustrated in Figure 1 was surrounded by tantalum radiation shields, except where it was necessary to have spaces for supports, electrical leads, the effusion hole, and for sighting with an optical pyrometer.

The top and bottom halves of the effusion cell were each heated by electron bombardment from separate filaments. The electrical circuit was arranged so that, while the total emission current from the filaments was automatically controlled, the ratio of emission current from the two filaments could be varied. In this manner, it was possible to keep the upper half of the effusion cell at a slightly higher temperature than that of the lower half. This heating arrangement, coupled with the effusion cell geometry which permits efficient heat conductivity to the thin edges of the effusion hole, prevents clogging and dimensional changes.

Oven temperatures were measured with a platinum, platinum–10% rhodium thermocouple press-fitted into a hole in the base of the effusion cell and also with an optical pyrometer by sighting into the black body hole drilled into the base of the cell. The usual corrections were made for absorption by the optical system. The thermocouple readings were calibrated for errors due to thermal conductivity in the leads by a determination of the temperature within the cell with another thermocouple inserted through the effusion hole. The thermocouples were generally used to measure temperatures below 950° C., and the optical pyrometer was used for measurements above this temperature. We have estimated the pyrometer temperature measurements to be accurate to ±5° C. or better. The temperatures measured with the thermocouple were accurate to ±2° C., or better.

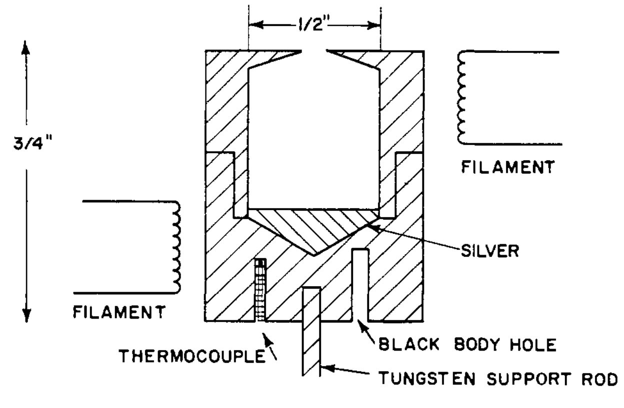

Figure 1. Effusion cell

The temperature was controlled by means of an automatic emission control system and manual control of the high voltage supply. Since only very small corrections to the voltage were necessary, it was possible to maintain the temperature within ±1° C.

The molecular beam was turned on and off with a magnetically operated shutter. After a target had been exposed to the beam for a specific amount of time, the shutter was closed and the target holder and target were ejected magnetically into the storage chamber. Exposure times were accurate to ±0.5 second. No total exposure times of less than 200 seconds were used.

During all measurements, the residual gas pressure, as determined by the ionization gage, was less than 5×10^{-6} mm.

The silver used for the condensed sample studies was prepared by precipitation of metallic silver from an aqueous solution of $AgNO_3$ by reduction with hydrazine. The amount of silver deposited on each target was determined by either of two methods. In some cases, the target was weighed before and after use. The change in weight was taken as the amount of silver deposited during exposure to the molecular beam. At the lower temperatures, radioactive silver (Ag^{110}) was used as a tracer, and a calibration was necessary to determine what fraction of the silver deposited was Ag^{110}. This was done by using targets upon which there was deposited over 100 μg. of silver containing the tracer. These targets were made into calibration standards by determining the counting rate for the Ag^{110} present and the absolute weight of silver deposited by weighing. It was then possible to analyze for very small amounts of silver deposited on other targets by counting.

Mass Spectrometric Studies. To determine what species emerged from the effusion cell, they were identified mass spectrometrically. This was done by effusing the silver beam across the electron beam of a Bendix time-of-flight mass spectrometer. The major species identified was monatomic silver. Polymeric species were not observed and were therefore not present in amounts greater than 1%. These observations are in agreement with those of Chupka and Inghram (*3*) and Drowart and Honig (*4*), but cannot be reconciled with those of Searcy, Freeman, and Mickel (*10*).

RESULTS AND DISCUSSION

In Table I, the experimental data for these runs are listed. Pressures were calculated from the usual effusion equation.

$$p = \frac{17.14(D^2 + 4L^2)\,W}{aD^2\tau}\left(\frac{T}{M}\right)^{1/2} \qquad (1)$$

where p is the pressure in millimeters of mercury, D the collimator diameter in centimeters, a the orifice to collimator distance in centimeters, M the molecular weight of the effusion species, W the weight in grams of silver depoisted, τ the deposition time in seconds, and T the temperature in ° K. These data have been plotted in Figure 2 along with those of Fischer (*6*) and McCabe and Birchenall (*7*).

Tables II and III show the results of third law calculations for the heat of vaporization of silver at 298° K. In these calculations, the heat of vaporization is obtained at each experimental point by the use of the equations:

Table I. Experimental Data and Calculated Vapor Pressures for Silver at a Number of Temperatures

T, ° K.	Time of Target Exposure, Sec.	Weight of Silver Condensed, μg.	p, Mm. Hg	Run No.[a]
958[b]	21,600	0.040	8.30×10^{-7}	4
979[b]	7,320	0.029	1.80×10^{-6}	2
1010[b]	3,197	0.044	6.50×10^{-6}	2
1065[b]	3,600	0.29	3.90×10^{-5}	2
1085[b]	5,400	0.70	6.20×10^{-5}	3
1115[b]	1,819	0.51	1.40×10^{-4}	2
1123[b]	3,600	1.35	1.80×10^{-4}	3
1152[b]	783	0.58	4.10×10^{-4}	2
1190[b]	2,260	4.06	9.00×10^{-4}	3
1228[b]	627	2.80	2.30×10^{-3}	2
1237[b]	1,200	6.56	2.80×10^{-3}	3
1265[b]	300	3.5	6.50×10^{-3}	2
1263[b]	1,800	22	7.20×10^{-3}	1
1287[b]	1,020	14.8	6.40×10^{-3}	3
1313	1,200	25	1.20×10^{-2}	1
1315	1,800	58	1.73×10^{-2}	2
1335	300	11.1	1.96×10^{-2}	3
1349	982	40	2.49×10^{-2}	1
1356	1,800	282	4.30×10^{-2}	2
1374	559	49	5.50×10^{-2}	1
1392	600	54	4.90×10^{-2}	3
1393	1,800	174	5.21×10^{-2}	3
1402	300	32	6.60×10^{-2}	1
1467	255	89	2.21×10^{-1}	1
1503	281	110	2.50×10^{-1}	1

[a] All runs $a = 6.95 \times 10^{-3}$ sq. cm., $D = 1$ cm., solid silver above the double line, liquid silver below the double line. Run 1, $L = 4.68$ cm., runs 2 and 3, $r = 4.45$ cm. [b] Ag^{110} used as a tracer.

Table II. $Ag_{(s)} \longrightarrow Ag_{(g)}$

T, ° K.	$\Delta\left(\frac{F - H_{298}}{T}\right)$, E.U.	$\frac{\Delta F}{T}$, E.U.	ΔH_{298}, Kcal./Mole
958	30.48	41.00	68.47
979	30.45	39.49	68.47
1010	30.42	36.93	68.02
1065	30.35	33.36	67.85
1085	30.33	32.44	68.10
1115	30.30	30.80	68.13
1123	30.29	30.34	68.10
1152	30.26	28.69	67.91
1190	30.22	27.14	68.23
1228	30.18	25.26	68.08
		Av.	68.14 ± 0.2

Table III. $Ag_{(l)} \longrightarrow Ag_{(g)}$

T, ° K.	$-\Delta\left(\frac{F - H_{298}}{T}\right)$, E.U.	$\frac{\Delta F}{T}$, E.U.	ΔH_{298}, Kcal./Mole
1237	30.22	24.85	68.12
1265	30.12	23.20	67.34
1265	30.11	22.97	67.15
1287	30.04	23.20	68.65
1313	29.95	21.96	68.16
1315	29.95	21.23	67.30
1335	29.86	21.00	67.90
1349	29.84	20.50	67.91
1356	29.53	19.45	66.82
1374	29.78	18.94	66.94
1392	29.74	19.17	68.08
1393	29.74	19.08	68.01
1402	29.71	18.58	67.70
1467	29.57	16.20	67.14
1503	29.49	15.92	68.25
		Av.	67.70 ± 0.50

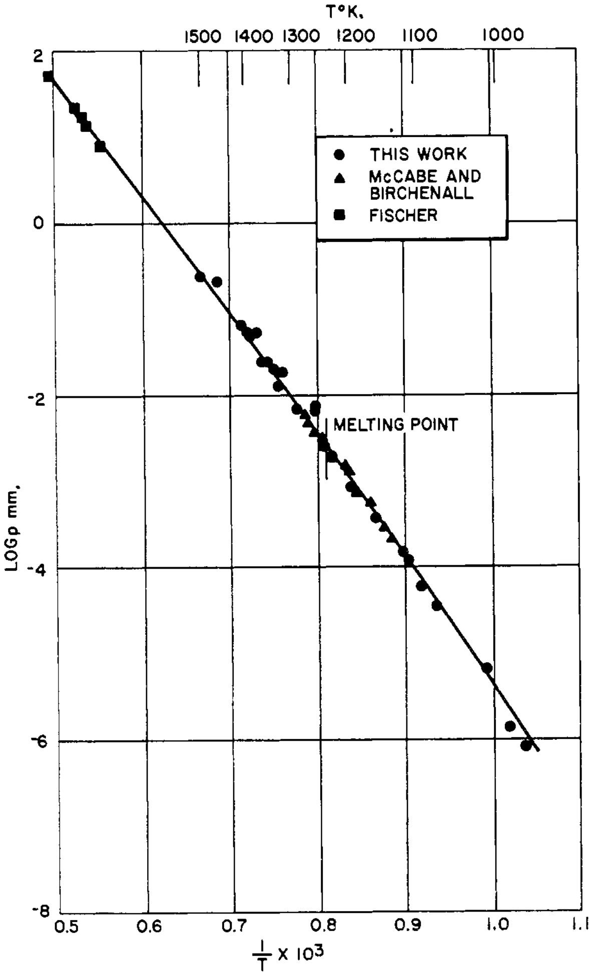

Figure 2. Log *p* vs. 1/*T* for silver

$$\left(\frac{F_T - H_{298}}{T}\right)_{Ag_{g}} - \left(\frac{F_T - H_{298}}{T}\right)_{Ag_{l\ or\ s}} = \frac{\Delta F_T}{T} - \frac{\Delta H_{298}}{T} \qquad (2)$$

and

$$\frac{\Delta F_T}{T} = - R \ln p \qquad (3)$$

where the left hand terms of Equation 2 are the free energy functions for gaseous and condensed silver, T is the temperature, ° K., and ΔF_T and ΔH_{298} are the free energy and enthalpy changes for the process at the indicated temperatures. In Equation 3, R is the gas constant and p the pressure in atmospheres.

The free energy functions used here were calculated by Stull and Sinke (*12*) from calorimetric and spectroscopic data. The calculated heats of vaporization for the solid appear to be more precise, and therefore the heat of vaporization of silver at 298° K. is taken to be 68.14 ± 0.2 kcal. per mole. This value and the $H_T - H_{298}$ values of Stull and Sinke were then used to determine Equations 4 and 5 which represent the vapor pressure of solid and liquid silver within a few hundred degrees of the melting point. Extrapolation of these curves for more than 300° C. leads to increasing errors because the assumed constant, ΔH_V, varies slightly with temperature.

Solid. $$\log p_{mm.} = \frac{-14580}{T} + 9.22 \qquad (4)$$

Liquid. $$\log p_{mm.} = \frac{-13840}{T} + 8.63 \qquad (5)$$

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Vapor Pressures of Titanium Tetrachloride–Carbon Tetrachloride Mixtures

G.A. RYDER[1], MUSA R. KAMAL[2], and L.N. CANJAR
Department of Chemical Engineering, Carnegie Institute of Technology, Pittsburgh, Pa.

VAPOR PRESSURE DATA for carbon tetrachloride–titanium tetrachloride systems are presented. Constants for the Van Laar equations which satisfy the total vapor pressure data are given for temperatures of 30°, 40°, and 50° C. Vapor liquid equilibrium data for this system were obtained by Nasu (*4*) who employed chemical analysis and conventional equilibrium techniques. However, Nasu's results are not consistent with standard thermodynamic tests.

EXPERIMENTAL COMPOUNDS

Chemicals used were Fisher Scientific reagent grade, carbon tetrachloride and Fisher Scientific Co. purified grade titanium tetrachloride.

PROCEDURE AND APPARATUS

Due to the extreme reactivity of titanium tetrachloride with the moisture in the atmosphere to form hydrogen chloride and titanium dioxide, it was necessary to handle the materials inside a Berkley-type dry box in which an atmosphere of dry nitrogen was maintained.

Vapor-liquid equilibrium data were obtained by measuring the total vapor pressure of different mixtures of the compounds at temperatures 30, 40, and 50° C. A glass spring manometer (modified Bourdon gage) was used in conjunction with static equilibrium equipment, as suggested by Kamal (2) and modified by Ryder (5). The sample and glass manometer were kept in an oil bath where the temperature was controlled to within ±0.1° C.

Compositions of samples were determined by weighing and negligible error was introduced in their preparation. Care was taken that no moisture or foreign gases were available to interfere in the measurements.

The major components of the experimental apparatus for measuring the vapor pressure of pure carbon tetrachloride and carbon tetrachloride–titanium tetrachloride mixtures are shown in Figure 1.

A 250-ml. sample preparation and introduction flask, *A*, is fitted with invertible vent and ground glass joint for connection to the vaporization chamber.

Pressure regulation system, *B*, consists of a 500-ml. gas sample bottle and two volume-calibrated glass tubing chambers between stopcocks 8 and 10.

A vaporization chamber is formed by the ground glass seal between vaporization chamber dome, *D*, and vaporization chamber jacket, C. A ground glass joint, *D*, forms the mouth of the jacket. The liquid bulb capacity is 250 ml. and the total vaporization chamber volume with *D* in place is approximately 525 ml. *D* houses a sample introduction tube at stopcock 3, a glass spring manometer (modified Bourdon gage), *E*, and a pressure release vent at stopcock 4 which interconnects both sides of the glass spring manometer diaphragm. A glass pointer needle extending into the vaporization chamber from the glass spring manometer diaphragm and a fixed glass reference pointer indicate the balancing of internal and external diaphragm pressures.

A variable level mercury manometer, *F*, is used for measuring the pressure on the regulated (internal) side of the glass spring manometer diaphragm.

A leveling bulb, *G*, controls the mercury level in manometer, *F*, for precision pressure regulation.

VAPOR-LIQUID EQUILIBRIUM DATA THEORY

The total vapor pressure of a binary system may be expressed by

$$P_T = \gamma_1 x_1 P_1^\circ + \gamma_2 x_2 P_2^\circ \tag{1}$$

If log γ does not vary much with pressure, the following relationship may be assumed valid:

$$x_1 \left(\frac{\partial \operatorname{Log} \gamma_1}{\partial x_1}\right)_T = x_2 \left(\frac{\partial \operatorname{Log} \gamma_2}{\partial x_2}\right)_T \tag{2}$$

In the present work, this condition is satisfied, and the van Laar equation can therefore be used to represent log γ.

$$\operatorname{Log} \gamma_1 = \frac{A x_2^2}{\left(\frac{A}{B} x_1 + x_2\right)^2} \tag{3}$$

$$\operatorname{Log} \gamma_2 = \frac{B x_1^2}{\left(x_1 + \frac{A}{A} x_2\right)^2} \tag{4}$$

By trial and error, constants *A* and *B* satisfying Equations 1, 3, and 4 can be determined.

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[1] Present address, U.S. Steel Corp., Pittsburgh, Pa.

[2] Present address, American Cyanamid Co., Stamford, Conn.