Vapor Pressure of $WOCl_4$

Adolfo E. Castro Luna,* Marta I. Ponzi, and Juan B. Rivarola

Facultad de Ingenieria y Administración, Universidad Nacional de San Luis, Villa Mercedes (San Luis), Argentina

$WOCl_4$ vapor pressure was measured by means of a Pyrex double-spoon manometer, in the range of 298–500 K. Results were adjusted to log p vs. $1/T$(K). Values of sublimation heat ΔH_s = 20.0 ± 0.4 kcal/mol and of vaporization heat ΔH_V = 15.8 ± 0.7 kcal/mol were obtained.

$WOCl_4$ and WO_2Cl_2 are products of reaction between tungsten compounds and chlorinated derivatives such as CCl_4, HCl, Cl_2, SO_2Cl_2, etc.

Some of the thermodynamic properties of both oxychlorides have been previously studied (*1*). In this paper, the vapor pressure of $WOCl_4$ has been measured as a function of temperature; from the obtained data, values of sublimation and vaporization were obtained.

These results help to complete the kinetic and thermodynamic information established in our laboratory by Papa et al. (*2*) and Calderõn et al (*3*). The substantial differences between values obtained by authors such as Reinders (*4*), Funaki (*5*), Shchukarev (*6*), and Suvorov (*7*) prompted us to undertake our own determinations.

Experimental Section

***Preparation of $WOCl_4$*.** $WOCl_4$ was obtained by the reaction of CCl_4 with WO_3 at 673 K. The equipment and methodology are described in a previous paper (*1*).

$WOCl_4$ was purified by successive sublimations under vacuum at 423–443 K. This compound is highly unstable in the presence of moisture. This fact forced us to manipulate the obtained crystals in a controlled dried nitrogen atmosphere; they were loaded under vacuum in closed capillaries and small bulbs to determine the fusion point and vapor pressure, respectively.

The purity of the crystals was determined by various methods. The fusion point was measured and the value obtained is compared in Table I with data from other authors.

The infrared spectrum obtained in the region between 400 and 600 cm^{-1} agrees with those given by Adams and Churchill (*8*).

***Measurement of $WOCl_4$ Vapor Pressure*.** The study of $WOCl_4$ vapor pressure requires a robust and sensitive enough manometer to withstand fairly large pressure changes without losing sensitivity. For $WOCl_4$, vapor pressure varies greatly with temperature, and, being highly reactive, all contact with mercury must be avoided.

A two-opposed-spoon gauge made of Pyrex glass was built after Swanwick's design (*9*). In such a system vapors are in contact only with Pyrex glass and Teflon. The lever principle was adapted to the relative movement of the opposed spoons. The equipment is shown in Figure 1.

The opposed spoons B communicate with each other and with the vaporization chamber D where the solid is stored. Two rigid supports are sealed to the gauges, extending along the line of movement of the gauges to within about 2 mm of the walls of jacket E. These rigid supports are connected to the lever by means of two fibers, F.

Pointer P had to be made of minimum weight consistent with rigidity; the optimum value was found to be 40 mg and 30 cm in length.

A fixed pointer N was sealed to the upper end of jacket E. The extremes of both pointers were tapered by chemical erosion with 30% HF solution. The desired thickness was similar to the thickness of the scale divisions on the lens of the telescope through which they were viewed. By using this gauge, we obtained a sensitivity of 1 mm of displacement per mmHg.

Table I. Melting Point of $WOCl_4$

ref	mp, K	ref	mp, K
4	482	*7*	484
5	482	this paper	483.1

Table II. Experimental Data Vapor Pressure vs. Temperature

P, mmHg	T, K	P, mmHg	T, K
3.501	395.7	21.37	423.2
4.627	399.5	25.40	426.6
4.880	401.0	33.18	431.4
7.050	401.1	33.58	431.8
6.190	403.2	34.02	432.1
7.286	404.1	34.50	432.3
7.448	405.3	34.95	433.1
6.960	405.8	43.64	435.3
7.221	407.0	47.09	439.0
8.690	407.7	59.14	442.7
9.170	408.2	73.41	446.8
9.440	409.5	457.1	486.1
11.51	411.3	499.0	489.1
12.02	412.4	507.0	490.7
11.34	413.4	530.9	491.4
14.86	414.8	575.4	493.9
13.80	416.5	579.4	493.9
18.54	420.3	606.7	495.1
19.12	420.3	619.4	496.1
17.12	421.2		

Tap L_1 had a Teflon stopcock and the tube connecting it to vapor chamber D had a coiled heating wire R_1 kept at a constant temperature of about 523 K so as to avoid condensation of the vapors from the compound.

The whole gauge was placed inside oven H; it was heated by forced air convention. Temperature control was carried out through a thermoregulator, the control being on the order of 0.05 K. The upper section of tube E outside the oven was kept at approximately the same temperature as in the inside by means of resistor R_2. The temperature was measured by quartz thermometer T_2. In the vaporization chamber, temperature was measured with another sensor of quartz thermometer T_1. The precision obtained was of 0.01 K. First, D, previously loaded with $WOCl_4$ and under vacuum, was adapted to the lower section of the spoon manometer. The vacuum was produced in the spoon chamber as well as inside tube E. The system was heated to about 423 K and the vacuum kept for a while until the equipment was "outgassed". Then the equipment was cooled to room temperature and the capillary separating tube D from the inside of the spoons was broken by means of a piece of iron covered by glass and operated from the outside by a magnet. L_1 was kept closed and heated until the reading of stem P was modified. After a constant temperature was obtained, a little air was let through L_2 until the pointer went back to its initial position.

Pressure corresponding to measurement pressure was read on manometer M by using a cathetometer. Readings were repeated until the pointer kept steady (after about 15 min). The same procedure was repeated at successively higher temperatures.

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Table III. Comparison of Results

ref	*A*	*B*	ΔH_s, kcal/mol	*A*	*B*	ΔH_v, kcal/mol
5	4400	11.76	20.14 ± 0.02	3330	9.53	15.16 ± 0.05
7			21.70 ± 1			11.0 ± 1
4	4000	10.83	18.3	3684	10.18	16.84
6			18.3 ± 0.5			16.5 ± 0.5
this work	4380	11.67	20.0 ± 0.4	3449	9.74	15.8 ± 0.7

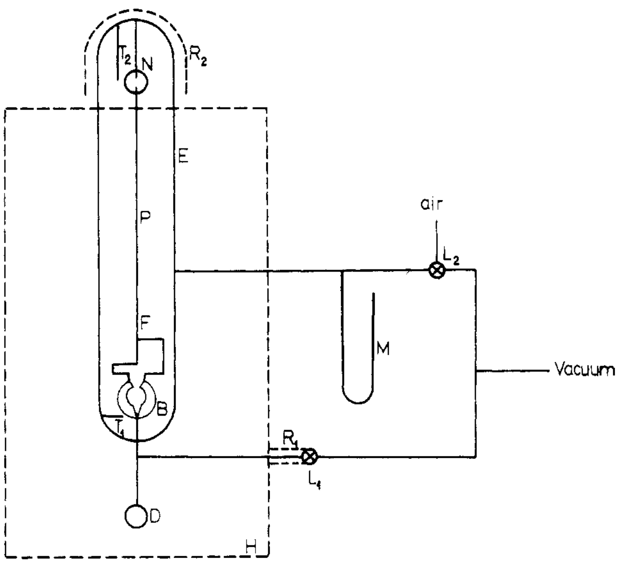

Figure 1. Schematic diagram of equipment: (D) vaporization chamber, (B) double-spoon gauge, (E) jacket, (F) fulcrum, (H) oven, (L_1, L_2) valves, (M) Hg manometer, (N) fixed pointer, (P) pointer, (R_1, R_2) heating wire, (T_1, T_2) thermometers.

Measurements proceeded during cooling cycles at each run; thus, delay in reaching equilibrium could be detected, showing at the same time formation of decomposition products. The zero reading remained unaltered up to 523 K during blank test. Within the pressure range used in this work the gauge was found to give a linear response with pressure and to be free of hysteresis.

For a purity test of the sample the following criterion was applied along with the ones previously mentioned: a sample was submitted to successive vapor pressure measurements and subsequent vacuum, all at the same temperature, until the solid sample was almost exhausted. The value obtained was used as a reference for all samples under test.

For testing the accurate performance of the whole device vapor pressure of benzoic acid was measured.

Results and Discussion

Data on vapor pressure vs. temperature are shown on Table II for processes of sublimation and vaporization of $WOCl_4$.

The results mentioned above were adjusted through a computer program using the expression $\log p(\text{mmHg}) = -A/T(\text{K}) + B$.

1. Sublimation pressure was given by

$$\log p(\text{mmHg}) = (-4380/T + 11.67) \pm 0.03$$

from which

$$\Delta H_s = 20.0 \pm 0.4 \text{ kcal/mol}$$

could be calculated.

2. Vaporization pressure may be expressed by

$$\log p(\text{mmHg}) = (-3449/T + 9.74) \pm 0.006$$

from which

$$\Delta H_v = 15.8 \pm 0.7 \text{ kcal/mol}$$

could be calculated.

In Table III these results are compared with those given by other authors. This shows that the sublimation heat obtained here, ΔH_s, differs from Funaki's (*5*) by 0.24%. The difference with the results of Reinders (*4*) and Shchukarev (*6*) is 9.4%.

With regard to vaporization heat our values are reasonably close to Funaki's (*5*), the greatest difference being with the results obtained by Suvorov (*7*).

Registry No. $WOCl_4$, 13520-78-0.

Literature Cited

(1) Castro Luna, A. E.; Rivarola, J. B. *Lat. Am. J. Chem. Eng. Appl. Chem.* **1971**, *1*, 77–82.
(2) Papa, J.; Calderón, J. B.; Marchese, J.; Rivarola, J. B. *AIChE J.* **1977**, *23*, 938–40.
(3) Calderón, J. B.; Papa, J.; Rivarola, J. B. *Ind. Quím.* **1969**, *27*, 27–31.
(4) Reinders, W.; Van Liempf, J. A. M. *Recl. Trav. Chim. Pays-Bas* **1931**, *50*, 997–1003.
(5) Funaki, K.; Uchimura, K. *Denki Kagaku* **1962**, *30*, 35.
(6) Shchukarev, S. A.; Novikov, G. I.; Vasil'kova, I. V.; Suvorov, A. V.; Andreeva, N. V.; Scharupin, B. N.; Baev, A. K. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1960**, *5*, 802–4.
(7) Suvorov, A. V.; Novikov, G. I.; Dobrotin, R. B.; Tarasov, A. V. *Khim. Redk. Elem.* **1964**, 26–32.
(8) Adams, D. M.; Churchill, R. G. *J. Chem. Soc. A* **1968**, 2310.
(9) Swanwick, J. D. *J. Chem. Soc.* **1956**, 3214–5.

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Sound Velocity in Simple Carboxylic Acids

M. A. Goodman and Scott L. Whittenburg*

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

The speed of sound and isentropic compressibility of formic, acetic, and propionic acid were measured by Brillouin spectroscopy in the temperature range from 293 to 353 K.

Introduction

The sound velocity and isentropic compressibility of the simple carboxylic acids were measured from 293 to 353 K by using Brillouin light scattering. The measurements were made as part

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