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Thermodynamic Properties of $WOCl_4$

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The vapour pressure of solid and liquid $WOCl_4$ has been measured by a transpiration method. Comparison with earlier results from static methods indicates that the species in the gas phase mainly consist of $WOCl_4$. From the vapour pressure data heats and entropies of fusion, vaporization, and sublimation have been calculated. The melting point 205°C obtained from the vapour pressure data has been confirmed by DTA.

The refractory metals, the transition metals of groups IV and V, are of great industrial importance and so are many of their compounds, *e.g.* carbides and borides.[1] The interest in the refractory metal chlorides often used in separation and reduction methods is therefore increasing and consequently a thorough knowledge of their thermodynamic properties is necessary. Several compilations have been made [2–6] but accurate data on many refractory metal chlorides, *e.g.* tungsten oxychloride, are lacking.

This investigation comprises measurement of the vapour pressure of solid and liquid $WOCl_4$.

EXPERIMENTAL

Materials. The $WOCl_4$ used was produced by the Axel Johnson Institute for Industrial Research in Nynäshamn, Sweden. Before delivery it was redestilled at 228°C and only a medium fraction was selected for our purpose.

Analysis indicated that the only important impurity was iron. The Fe-content was 0.06 % by weight. By a further distillation process it was reduced so that the Fe-content in the selected material was less than 0.02 %. The salt was stored in a closed glass bottle in an argon-filled drybox. The argon in the drybox was kept dry with the aid of phosphorus pentoxide.

The argon used as carrier gas was delivered by AGA, Stockholm, and had a purity better than 99.99 %. The gas was further purified by passing it through silica gel and dehydrite to remove H_2O and ascarite to remove CO_2. Remaining oxygen and nitrogen were removed by letting the argon pass through two furnaces containing, respectively, copper gauze and magnesium chips at 500°C. The purified gas was checked by letting it pass over a heated iron ribbon with a temperature ranging from 25°C to 500°C. Already with a slight oxygen contamination in the argon interference colours appeared on the iron ribbon. During the investigation the gas was checked at intervals and the absence of oxygen proved.

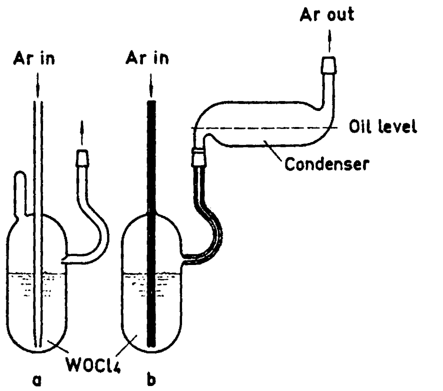

Fig. 1. Apparatus for saturation of Ar with $WOCl_4$.

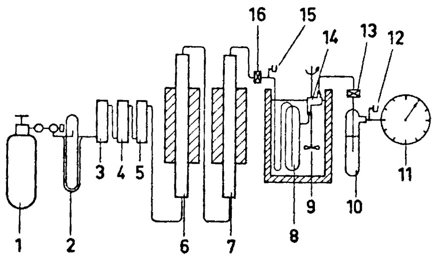

Fig. 2. Transpiration apparatus. 1. Argon cylinder. 2. Capillary flowmeter. 3. Silica gel. 4. Ascarite. 5. Dehydrite. 6. Furnace with Cu-gauze at 500°C. 7. Furnace with Mg-chips at 500°C. 8. Pyrex tube for saturation of Ar with $WOCl_4$. 9. Oilbath with stirrer. 10. Dibutylphthalate. 11. Gas meter. 12 and 15. Manometer. 13 and 16. Stopcocks. 14. Condenser.

Apparatus and procedure. The salt to be investigated was contained in a pyrex glass apparatus made with a narrow entrance for the carrier gas and a narrow exit for the gas saturated with chloride vapour (Fig. 1, a and b). By giving this shape to the apparatus the thermal diffusion could be kept on a negligible level by selection of a suitable carrier gas velocity. Apparatus 1 a was used for the experiments with solid $WOCl_4$. In order to decrease the blank correction at higher temperatures the 1 b variant with entrance and exit made from capillary tubes was used for experiments with liquid $WOCl_4$.

The general experimental arrangement is shown in Fig. 2. The argon gas velocity was measured by a capillary flow meter and the gas volume measured either with a Ströhlein meter ($V > 100$ ml; accuracy ± 1 ml) or with a gas buret ($V < 100$ ml; accuracy ± 0.1 ml). The external pressure over the salt was given by the sum of the barometric pressure and the reading on manometer 12.

The $WOCl_4$-containing apparatus was submerged in an oilbath (Shell Nassa Oil 89) with a firing-point of 335°C. The oil was heated with an electrical immersion heater and was vigorously stirred by a motordriven stainless steel propeller. The temperature of the oilbath was controlled to ± 0.5°C by an Osmund regulator which is a proportional thyristor type instrument, the sensing part being a Chromel-Alumel thermocouple. The temperature of the bath was measured to ± 0.1°C with Hg-thermometers with individual control certificates. Separate runs showed that the temperature of the oilbath and of the sample were equal within the limit of accuracy of the thermocouples.

In the experiments with solid $WOCl_4$ the salt was put into the apparatus (Fig. 1a) as powder in a dry argon atmosphere. Before the vaporization experiments with liquid $WOCl_4$ the salt was distilled into apparatus 1b. The experiments started by closing the stop-cock 16 (Fig. 2) and raising the container with the hot oil to the predetermined level. After a preheating period (5 or 15 min) the stop-cock was opened and an argon stream with constant velocity passed through the salt in order to be saturated with $WOCl_4$. When passing the condenser (14 in Fig. 2) the total amount of the $WOCl_4$ was condensed as crystals which were subsequently weighed. The volume of the argon gas was then measured. Before calculating the vapor pressure the weight was corrected for the amount of $WOCl_4$ vaporized during the preheating period and for the small $FeCl_3$-content.

After each experiment the $WOCl_4$ was dissolved in an NaOH-solution. Phosphoric acid and nitric acid were added to a final content of 8 ml H_3PO_4, 8 ml HNO_3 and 1 g NaOH per 100 ml solution, which gave a composition suitable for atomic absorption determination of W and Fe. From the W-content in solution the amount of condensed $WOCl_4$ was calculated.

The mol fraction $n_{WOCl_4}/(n_{WOCl_4}+n_{Ar})$ was calculated both from the weighing results and from the analytical results. The partial pressure of $WOCl_4$ was obtained from the relation

$$P_{WOCl_4} = \frac{n_{WOCl_4}}{n_{WOCl_4}+n_{Ar}} \cdot P_{tot}$$

where $P_{tot} = P_{barom} + P_{manom}$

At different temperatures the carrier gas velocity was changed in order to find the region where the calculated vapor pressures were independent of the gas velocity, this value being selected as P_{WOCl_4} at that temperature.

In the differential thermal analysis (DTA) of the $WOCl_4$ the sample was kept in a platinum crucible. The crucible was made from 40 by 45 by 0.05 mm platinum sheet that was folded together and spotwelded. The crucible was loaded and mechanically closed in an argon filled drybox and then quickly sealed by spotwelding. Thermocouple leads of Pt/Pt 13 % Rh were spotwelded on to the crucible which in this way acted as the hot junction. The DTA was carried out in a Kanthal wound resistance furnace. The crucible was placed in a ceramic holder in the furnace and the reference junction was located in the even temperature zone about 10 mm from the crucible wall. The differential emf from the thermocouples was recorded on a Honeywell Brown two point electronic recorder which also recorded the temperature of the sample.

RESULTS AND DISCUSSION

In Table 1 the results from all experiments are given; the P_{WOCl_4}-values being calculated only from the weighings. After calculation of the $WOCl_4$ pressure, values from adjacent temperatures were collected into groups and the P_{WOCl_4}-values corrected to these selected temperatures. In Fig. 3. the calculated and corrected P_{WOCl_4}-values are plotted as a function of carrier gas velocity at different temperatures. The full length of the plateau was only investigated at two temperatures, namely at 182.8 and 205.5°C. The values corresponding to the plateaus in Fig. 3 were accepted as the vapour pressure of $WOCl_4$ at the temperature in question. These values are given in Table 1 and their logarithms are plotted as a function of $10^3/T$ in Fig. 4.

As can be seen from Fig. 4 and Table 1 log P of $WOCl_4$(l) is a linear function of $1/T$. For $WOCl_4$(s), however, the slope of the curve changes remarkably. The following formulas, calculated from Table 1, give a close fit to the experimental values.

Solid:

$$\log P_{WOCl_4}(\text{torr}) = -\frac{5433}{T} - 5.033 \ \log T + 0.08334 \ T - 9\times10^{-5} + 8.143 \qquad (1)$$

temperature range (165°C – 205°C)

Liquid:

$$\log P_{WOCl_4}(\text{torr}) = -\frac{3245}{T} + 9.354 \qquad (2)$$

temperature range (205°C – 224°C)

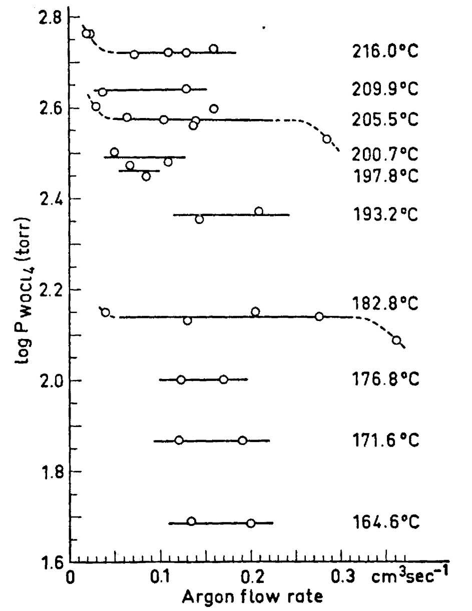

Fig. 3. Calculated and corrected P_{WOCl_4} values at different temperatures and argon flow rates.

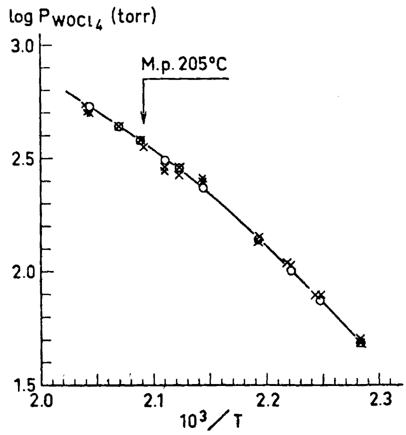

Fig. 4. Vapour pressures of $WOCl_4$. O, calculated from weighing results (mean values from Table 1). ×, calculated from analytical results.

The corresponding curves from these equations are drawn in Fig. 4. In this figure values calculated from the chemical analysis are also plotted for comparison. The point of intersection of the curves from eqns. (1) and (2) correspond to a melting point of $WOCl_4$ of 205.3°C. The DTA investigation of the $WOCl_4$ gave a melting point of 204.5°C. From eqn. (2) a boiling point of 228°C is calculated.

From the slopes of the curves the following enthalpy values are obtained:

Heat of sublimation	at 478 K = 17.26 kcal/mol
Heat of vaporization	at 501 K = 14.84 kcal/mol
Heat of fusion	at 478 K = 2.42 kcal/mol

As can be seen from the curve, however, the heat of sublimation obtained from the slope varies to a large extent with the temperature. At 175°C, *e.g.*, the ΔHs is about 22.9 kcal/mol.

Because of the large change in curvature of the vapour pressure/temp. relation for the solid $WOCl_4$ around 190°C it was first thought that this was due to a transformation in the solid at this temperature. The DTA-investigation showed, however, no sign of a transformation of a lower order as no change on the DTA-curve could be detected. It is, however, possible that a transformation of a higher order is causing this change in curvature.

Table 1. log P_{WOCl_4} (torr), calculated from weighing results.

$\frac{10^3}{T}$	log P_{WOCl_4}	Gas velocity cm³/sec	$\frac{10^3}{T}$ corr.	log P_{WOCl_4}	Mean value [b]
2.194	2.143	0.204	2.193	2.148	
2.193	2.137	0.275	2.193	2.137	
2.193	2.086	0.361	2.193	2.086 [a]	2.141
2.193	2.130	0.129	2.193	2.130	
2.193	2.149	0.039	2.193	2.149	
2.284	1.681	0.198	2.284	1.681	1.686
2.284	1.690	0.134	2.284	1.690	
2.222	2.000	0.171	2.222	2.000	1.999
2.219	2.013	0.123	2.222	1.998	
2.248	1.863	0.191	2.248	1.863	1.865
2.244	1.887	0.117	2.248	1.867	
2.144	2.354	0.143	2.144	2.354	2.363
2.144	2.371	0.210	2.144	2.371	
2.092	2.549	0.187	2.089	2.560	
2.091	2.566	0.104	2.089	2.573	
2.089	2.578	0.065	2.089	2.578	
2.089	2.601	0.030	2.089	2.601 [a]	2.575
2.089	2.597	0.159	2.089	2.597	
2.089	2.532	0.284	2.089	2.532 [a]	
2.089	2.569	0.140	2.089	2.569	
2.123	2.473	0.067	2.123	2.473	2.460
2.123	2.446	0.084	2.123	2.446	
2.110	2.479	0.111	2.110	2.479	2.492
2.110	2.504	0.049	2.110	2.504	
2.043	2.723	~0.11	2.044	2.720	
2.042	2.725	~0.13	2.044	2.719	
2.044	2.764	0.021	2.044	2.764 [a]	2.721
2.042	2.735	~0.16	2.044	2.729	
2.043	2.768	0.023	2.044	2.765 [a]	
2.039	2.731	0.072	2.044	2.716	
2.070	2.641	0.130	2.070	2.641	2.638
2.070	2.635	0.038	2.070	2.635	

[a] Values not on the plateau.
[b] The values outside the plateau not included.

Ward and Stafford [7] investigated the gas phase of tungsten oxychloride and other gaseous halides of molybdenum and tungsten by infrared spectroscopy. For all the oxytetrahalides they found a high frequency of the metal oxygen vibration band (*ca.* 1030 cm^{-1}) indicating the absence of polymer species with bonding through a metal-oxygen bridge system. This is in agreement with the results from group VI-oxychlorides other than $WOCl_4$ obtained by Barraclough and Stals [8] and by Iorns and Stafford [9] who found that the vapour phase contains predominantly monomeric species.

In the calculation of the vapour pressures in this work it has been assumed that the gas phase only consists of monomeric $WOCl_4$. This assumption is of course not necessary when a static method is used. In Fig. 5 the results

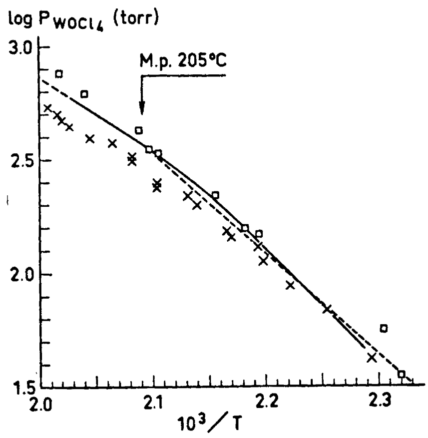

Fig. 5. Vapour pressures of $WOCl_4$ (comparison with earlier work). ×, Reinders and van Liempt.[10] □, Shchukarev and Novikov.[11] – – –, Funaki and Uchimura.[12]

from our investigation are compared with values reported by Reinders and van Liempt,[10] Shchukarev and Novikov[11] and Funaki and Uchimura[12] who all used static methods. As can be seen from this figure the results from our work lie between these earlier reported values; Shchukarev and Novikov's results being somewhat higher while Reinders and van Liempt's values are lower. The apparent agreement is a further indication that the main molecular species in the gas phase is monomeric $WOCl_4$.

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