Vaporization behaviour of uranium tetrafluoride

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The vapour pressure of solid and liquid UF_4 has been measured in the temperature range 1169 to 1307 K and 1312 to 1427 K respectively, by both transpiration and evaporation-temperature methods. The vapour pressures obtained by the two methods agree well and were, therefore, combined to give the equations:

 $log_{10}{p(UF_4, s)/kPa} = (12.03 \pm 0.14) - (15994 \pm 176)(K/T),$ $log_{10}{p(UF_4, l)/kPa} = (8.99 \pm 0.24) - (12014 \pm 335)(K/T).$

The melting temperature, normal boiling temperature, and the standard enthalpy of fusion at the melting temperature were calculated to be 1309 K, 1720 K, and (70.3 ± 7.3) kJ mol⁻¹ respectively. The standard enthalpy of vaporization $\Delta H^{\circ}(vap, 298.15 \text{ K})$, as calculated from the vapour pressures of UF₄(s) by the second law, is (326.1 ± 3.3) kJ mol⁻¹ and the standard entropy of vaporization $\Delta S^{\circ}(vap, 298.15 \text{ K})$ is (217.6 ± 15.7) J K⁻¹ mol⁻¹. The vapour pressures and other thermodynamic quantities are compared with data from the literature.

1. Introduction

A number of publications exist in the literature on the vaporization behaviour of UF₄ but in no case do the vapour pressures obtained by two independent methods agree with one another. Vapour-pressure measurements on UF₄(s) have been carried out by Ryon and Twichell,⁽¹⁾ Akishin and Khodeev,⁽²⁾ and Chudinov and Choporov⁽³⁾ using effusion techniques, and by Popov *et al.*⁽⁴⁾ by a transpiration technique. Vapour pressures of UF₄(l) were measured by Langer and Blankenship⁽⁵⁾ and Ryon and Twichell⁽¹⁾ by the evaporation-temperature method. Compilations by Brown⁽⁶⁾ and Rand and Kubaschewski⁽⁷⁾ suggest the need for further work for establishing the vaporization behaviour of UF₄ unambiguously. In the present study two independent methods, namely transpiration and evaporation-temperature, have been used for vapour-pressure measurements of UF₄(s and l) in the temperature range 1169 to 1427 K.

2. Experimental

TRANSPIRATION APPARATUS

The apparatus was similar to the one described earlier⁽⁸⁾ and consisted of a 9 mm i.d. nickel reaction tube which had provision for introducing purified argon carrier gas

and a 6 mm o.d. nickel thermowell at one end. The gas outlet was through a 6 mm o.d. nickel condenser with a 0.5 mm orifice. The sample was kept in a 8 cm long molybdenum boat and heated by a Kanthal Al wire-wound furnace having a 13 cm long constant-temperature (± 0.5 K) zone. The temperature of the sample was measured using a calibrated chromel-to-alumel thermocouple with the reference junction at 273.15 K. Carrier-gas argon was purified by passing through beds of molecular sieve and hot (1000 K) uranium and had $x(H_2O) < 10^{-6}$ and $x(O_2) < 10^{-6}$. The mass of UF₄ transported, per unit volume of the carrier gas passed, was found to be independent of the flow rate in the range of 5.5×10^{-7} m³ s⁻¹ to 7.5×10^{-7} m³ s⁻¹. Mass-spectroscopic measurements by Kukavadze (private communication to Chudinov and Choporov⁽³⁾) revealed that the vapour phase contains monomeric UF₄ molecules. Hence the masses of UF₄ transported in the transpiration experiments were determined by the mass change of the condenser.

EVAPORATION TEMPERATURE TECHNIQUE

The apparatus used for measurements by this method is similar to that described earlier.⁽⁹⁾ It consisted of a 25 mm i.d. nickel reaction-tube closed at one end. At the other end of the tube, provisions were made for introducing a nickel thermowell and connecting to a high-vacuum line. About 100 g of UF₄ was loaded in the nickel tube and system was evacuated, flushed, and filled with high-purity argon. The sample was heated in the constant-temperature zone of a Kanthal Al furnace to the required temperature. The temperature of the sample was measured using a calibrated chromel-to-alumel thermocouple. The e.m.f. of the thermocouple was back-biased by a known potential so that the balance could be recorded on the 100 μ V scale of a Honeywell Electronik-196 recorder. When the temperature became constant (steady base-line) the argon pressure over the sample was slowly decreased by evacuation. When the pressure of argon became equal to the vapour pressure of UF_4 , a sharp decrease (1 to 2 K) in temperature was observed due to fast evaporation. The pressure of the system at this stage was measured within an accuracy of 1 mm on a differential manometer using Apiezon oil or Fluorolube oil, depending on the pressure range, as the manometric liquid. This was taken as the vapour pressure of UF₄ at the base-line temperature. All the thermocouples used in these studies were calibrated at the melting temperatures of bismuth, antimony, and silver.⁽¹⁰⁾

MATERIALS

The uranium tetrafluoride used in these experiments was prepared by treating nuclear-grade uranium dioxide (99.99 mass per cent) with anhydrous hydrogen fluoride at 775 K. The product was analysed for fluorine content by pyrohydrolysis and for uranium content by gravimetry and was found to be better than 99.5 moles per cent pure. X-ray diffraction analysis of UF_4 did not indicate the presence of uranium oxide or oxyfluoride.

	UF4	.(s)		UF ₄ (l)				
T/\mathbf{K}	10(p/kPa) ^a	T/K	$10(p/\mathbf{kPa})^b$	T/\mathbf{K}	10(p/kPa) ^a	T/\mathbf{K}	10(p/kPa) ^b	
1169.0	0.22	1246.0	1.58	1318.5	6.97	1312.5	7.51	
1195.0	0.45	1261.0	2.30	1333.0	9.63	1333.0	9.90	
1213.5	0.71	1278.0	3.24	1347.0	11.15	1344.0	12.12	
1238.5	1.33	1281.0	3.67	1359.0	13.19	1364.0	14.59	
1260.5	2.31	1284.0	3.92	1380.0	20.23	1369.0	17.06	
1276.0	2.95	1300.5	5.46	1396.0	22.27	1387.0	21.67	
1307.5	5.79	1305.0	6.14	1414.0	31.27	1399.5	26.33	
100/10				1427.0	36.94	1424.0	37.99	

TABLE 1. Vapour pressures of solid and liquid UF₄

^a Transpiration method. ^b Evaporation-temperature method.

3. Results

The vapour pressures for solid and liquid UF_4 obtained by the transpiration and evaporation-temperature methods are given in table 1. As these two sets of results agree with each other within 7 per cent, they were combined to give the equations:

$$log_{10}\{p(UF_4, s)/kPa\} = (12.03 \pm 0.14) - (15994 \pm 176)(K/T),$$
(1169 to 1307 K), (1)
$$log_{10}\{p(UF_4, l)/kPa\} = (8.99 \pm 0.24) - (12014 \pm 335)(K/T),$$
(1312 to 1427 K), (2)

where the indicated errors are standard durations. From these equations the melting temperature and the normal-boiling temperature were calculated to be 1309 K, and 1720 K respectively.

Investigators and temperature range	$\frac{\Delta H^{\circ}(\text{vap, 298.15 K})}{\text{kJ mol}^{-1}}$	$\frac{\Delta S^{\circ}(\text{vap, 298.15 K})}{\text{J K}^{-1} \text{ mol}^{-1}}$	p(UF ₄ , 1200 K	s)/kPa 1300 K	<i>p</i> (UF ₄ 1350 K	, l)/kPa . 1450 K
Ryon and Twichell ^{(1), a} (1013 to 1133 K)	331.08	221.8	0.051 °	0.556 °		
Popov <i>et al.</i> ^{(4), b} (1148 to 1273 K)	329.24	218.4	0.042	0. 45 1 °		
Akishin and Khodeev ^{(2), a} (917 to 1041 K)	315.60	218.0	0.152 °	1.476 <i>°</i>		
Langer and Blankenship ^{(5), c} (1314 to 1573 K)	332.21	222.2			1.298	5.375
Chudinov and Choporov ^{(3), a} (823 to 1280 K)	293.17	193.7	0.079	0.573 <i>*</i>		
Present study ^{b.c} (1169 to 1427 K)	326.14	217.6	0.051	0.545	1.232	5.064 °

TABLE 2. Thermodynamic quantities and vapour pressures of UF4 and comparison with literature

^c Evaporation temperature.

^e Extrapolated value.

The combined results were also used to calculate the enthalpy of vaporization by the second-law analysis using the 'sigma' method reported by Darken *et al.*⁽¹¹⁾ The relation between Σ and temperature for UF₄(s) and UF₄(l) can be represented by

$$\begin{split} \Sigma_{\rm s} &= -(52.12\pm0.63) + (78194\pm792)({\rm K}/T), \\ \Sigma_{\rm 1} &= -(143.0\pm1.13) + (73454\pm1545)({\rm K}/T), \end{split}$$

where

$$\Sigma = \{-R \ln(p/kPa) + \Delta a \ln(T/K) + \Delta b/2(T/K) + \Delta c/2(K/T)^2\}/J K^{-1} \text{ mol}^{-1},$$

and Δa , Δb , and Δc are constants derived from the heat-capacity equations of the type: $C_p = a + bT + c/T^2$, for UF₄ solid, liquid, and gas. These were evaluated using the heat capacities for UF₄(s) and UF₄(l) reported by Barin and Knacke⁽¹²⁾ and the ideal value of 13R for UF₄(g). This procedure gave $\Delta H^{\circ}(vap, 298.15 \text{ K}) = (326.1 \pm 3.3) \text{ kJ mol}^{-1}$ and $\Delta S^{\circ}(vap, 298.15 \text{ K}) = (217.6 \pm 15.7 \text{ J K}^{-1} \text{ mol}^{-1}$ for the standard enthalpy and entropy of vaporization and $\Delta H^{\circ}(fus, 1309 \text{ K}) = (70.3 \pm 7.3) \text{ kJ mol}^{-1}$ for the standard enthalpy of fusion. Third-law analysis of the results could not be carried out as the thermodynamic functions for UF₄ are not available. The vapour pressures and the thermodynamic quantities obtained in the present study are compared with those of the other investigations in table 2.

4. Discussion

The vapour pressures of solid UF₄ from this study agree very well with the extrapolated data of Ryon and Twichell⁽¹⁾ and are 16 per cent higher than those of Popov *et al.*⁽⁴⁾ The five points reported by Popov *et al.*⁽⁴⁾ all correspond to temperatures below the experimentally determined melting temperature,⁽¹³⁾ (1309 ± 2) K, but these authors report vapour-pressure equations for solid and liquid UF₄ which gave a melting temperature of 1242 K. Hence their results are unreliable. The present vapour pressures are lower than those of Chudinov and Choporov,⁽³⁾ but the difference in the vapour pressure decreases as the temperature increases and, near the melting temperature, the agreement is within 10 per cent. The vapour pressures of Akishin and Khodeev⁽²⁾ for solid UF₄ are higher than ours by a factor of three. Langer and Blankenship⁽⁵⁾ have reported three points for solid UF₄ covering only 20 K. Hence their work was not considered further.

The vapour pressures of liquid UF₄ obtained from the present study agree very well with the data of Langer and Blankenship.⁽⁵⁾ The data of Ryon and Twichell⁽¹⁾ for liquid UF₄, obtained by the evaporation-temperature method, have been compared by Langer and Blankenship with their data. It is reported that the two sets of results agree with one another above a pressure of 2 kPa and that at lower pressures the results of Ryon and Twichell⁽¹⁾ are lower.

The melting temperature obtained from the solution of equations (1) and (2) is 1309 K, which is the same as the experimentally determined value:⁽¹³⁾ (1309±2) K. The standard enthalpy and entropy of vaporization from this study agree with those of Ryon and Twichell, Langer and Blankenship, and Popov *et al.* within

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3.1 kJ mol⁻¹ and 2.1 J K⁻¹ mol⁻¹ respectively. The values for the standard enthalpy of vaporization of Akishin and Khodeev and of Chudinov and Choporov, and the standard entropy of vaporization of Chudinov and Choporov do not agree with the present values. However, it is only in the present study that two independent techniques have been used for the study of the vaporization behaviour of both solid and liquid UF₄. The agreement between the two techniques is quite good. Hence, the present results can be considered to be a better representation of the vaporization behaviour of UF₄.

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