Studies on $(2UF_4 + H_2 = 2UF_3 + 2HF)$ and vapour pressure of UF_3

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Equilibrium constants for $2UF_4(s) + H_2(g) = 2UF_3(s) + 2HF(g)$ have been measured in the temperature range 967 to 1120 K. The results can be expressed in the form: $\log_{10}K^{\circ} = (6.35 \pm 0.17) - (12270 \pm 78)(K/T)$. The results have been treated by second- and third-law methods to obtain $\Delta H^{\circ}(298.15 \text{ K})$ and the values are (253.5 ± 0.8) and $(256.0 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$ respectively. The value of $\Delta S^{\circ}(298.15 \text{ K})$ has been calculated by the second-law method to be 146.4 J · K⁻¹·mol⁻¹. The vapour pressure of UF₃(s), measured by the transpiration technique in the range 1229 to 1367 K, can be expressed in the form: $\log_{10}(p/kPa) = (10.26 \pm 0.23) - (15666 \pm 302)(K/T)$. The standard enthalpy of vaporization $\Delta H^{\circ}_{\circ}(298.15 \text{ K})$ have been calculated to be $(328.7 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$ and $(193.9 \pm 0.9) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ respectively. The vaporization calculated to be $(328.7 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$ and $(193.9 \pm 0.9) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ respectively. The vaporization results have also been used for the calculation of $\Delta H^{\circ}_{f}(UF_{3}, g, 298.15 \text{ K})$ and $\Delta S^{\circ}_{f}(UF_{3}, g, 298.15 \text{ K})$: $-1165.4 \text{ kJ} \cdot \text{mol}^{-1}$ and $311.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ respectively.

1. Introduction

The equilibrium between UF₄ and UF₃ was investigated by Long and Blankenship both in molten salt media⁽¹⁾ and in the solid state.⁽²⁾ These workers have evaluated the equilibrium constants K^{\ominus} for the reaction: UF₄(s) + $\frac{1}{2}$ H₂(g) = UF₃(s) + HF(g) in the temperature range 838 to 1245 K. Above 1173 K they observed an abrupt lowering of values for K^{\ominus} which was attributed to the formation of a solid solution between UF₃ and UF₄. However, the only available phase diagram of UF₄ and UF₃ by Khripin *et al.*⁽³⁾ rules out that possibility. Hence an equilibrium study was considered desirable. In the present work, equilibrium studies have been carried out in the temperature range 967 to 1168 K.

No results are available on the vaporization behaviour of UF₃. This is not surprising, since the preparation of pure UF₃ is difficult and the problem is further complicated by the disproportionation of UF₃ into UF₄ and U(s). In the present study, vapour-pressure measurements on UF₃(s) were carried out in the temperature range 1229 to 1367 K by the transpiration technique using hydrogen as the carrier gas.

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2. Experimental

MATERIALS

Uranium tetrafluoride used in the present work was prepared by hydrofluorination of nuclear-grade UO₂ (99.95 mass per cent) at 800 K. The purity of UF₄ was checked by X-ray diffraction analysis and by pyrohydrolysis. Uranium trifluoride was prepared by the action of H₂ on UF₄ at 1120 K.⁽⁴⁾ X-ray diffraction analysis showed no peaks for UF₄ or UO₂. Hydrogen and argon gases used in this investigation were purified by passing them separately through towers of molecular sieves and hot titanium sponge (1170 K), to remove moisture and oxygen respectively. The mole ratios of O and H₂O in the purified gas stream were $< 10^{-6}$.

APPARATUS

The apparatus used for the equilibrium and vapour pressure measurements is shown schematically in figure 1. The reaction vessel is made of 10 mm i.d., 600 mm long nickel tube with 'O'-ring-sealed water-cooled end couplings. The couplings had



FIGURE 1. Apparatus for equilibrium studies on UF₃.

provisions for gas entry, for a 6 mm o.d. nickel thermowell, and a 6 mm o.d. nickel condenser with 0.5 mm orifice. A Kanthal wire-wound furnace with a flat zone $(\pm 0.5 \text{ K})$ of 130 mm at the centre was used for heating. The sample was contained in a nickel boat, and the temperature was measured by a calibrated chromel-to-alumel thermocouple, with the reference junction at 273.15 K. The thermocouple was calibrated at the melting temperatures⁽⁵⁾ of bismuth (544.4 K), antimony (904.0 K), and silver (1234.0 K).

PROCEDURE

An intimate mixture of $(0.9UF_4 + 0.1UF_3)$ was placed in a nickel boat and loaded inside the reaction tube. The system was thoroughly flushed with high-purity hydrogen up to 550 K and then the temperature was rapidly raised to the desired

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$$2UF_4 + H_2 = 2UF_3 + 2HF$$
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value; H_2 reacted with UF₄ to produce HF which was carried through the nickel condenser, a fluorolube oil bubbler, and a nickel capillary dipping into standard alkali. The condenser tube, oil bubbler, and capillary tube were kept above 475 K to avoid condensation of HF in the line. Thermodynamic equilibrium was obtained by determining the flow-rate plateau, where the mole ratio of $n(HF)/n(H_2)$ was independent of hydrogen flow-rate. For the present system it was found to be in the range of 1.6×10^{-6} to 2.5×10^{-6} m³ s⁻¹. A typical flow rate plateau is shown in figure 2. All equilibrium measurements were carried out in this flow-rate region. Equilibrium was attained when the time taken for neutralization of a given volume of standard alkali became constant. For each temperature, a fresh sample was taken and the reduction was carried out to 50 per cent completion. The equilibrium constant for



FIGURE 2. Flow-rate plateau at 1110 K for equilibrium studies: plot of $n(HF)/V(H_2)$ against $\dot{V}(H_2)$.

the reduction reaction: $2UF_4(s) + H_2(g) = 2UF_3(s) + 2HF(g)$, can be evaluated from the equation

$$K^{\ominus} = [\{p(\mathrm{HF})\}^2/p(\mathrm{H}_2)p^{\ominus}]\{a(\mathrm{UF}_3, s)/a(\mathrm{UF}_4, s)\}^2$$

Assuming UF₄ and UF₃ have no solid solubility, $a{UF_3, s} = 1$ and $a(UF_4, s) = 1$; also $p(H_2) = 101.325$ kPa.

For vapour-pressure measurements, the sample of UF₃ was heated in a molybdenum boat to the desired temperature in a current of high-purity H₂ flowing at a constant rate. Since UF₃ disproportionates to give UF₄, it must be reconverted to UF₃ as soon as it is formed to avoid any contribution of UF₄ vapours to the measured vapour pressure of UF₃. This was achieved by using H₂ as carrier gas and confirmed by X-ray diffraction analysis of the condensate, which did not reveal any peaks for UF₄. The HF produced as a result of disproportionation was removed from the carrier gas by scrubbing in alkali and the total volume of hydrogen passed was monitored using a wet test meter. The flow-rate plateau obtained was in the range of 1.2×10^{-6} to 2.0×10^{-6} m³ · s⁻¹. All the experiments were carried out in this flow-rate region. The vapour pressure was evaluated using the relation $p_i = x_i p$ where p_i is the partial pressure of UF₃, x_i is the mole fraction of UF₃ in the vapour phase, obtained from the mass gain of the condenser, and p is the total pressure.

3. Results

Equilibrium measurements were carried out in the temperature range 967 to 1120 K and the values of K^{\ominus} were calculated. The variation of K^{\ominus} with temperature is given by

$$\log_{10} K^{\ominus} = (6.35 \pm 0.17) - (12270 \pm 78)(K/T).$$

The present values are compared with those of Long and Blankenship in table 1. The equilibrium results were treated by the "sigma" method⁽⁶⁾ to obtain enthalpies and entropies for the reaction. Heat capacities for this calculation were taken from the compilation of Barin and Knacke.⁽⁷⁾ The values of $\Delta H^{\circ}(298.15 \text{ K})$ and $\Delta S^{\circ}(298.15 \text{ K})$ are $(253.5 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$ and $146.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ respectively. The values of $\Delta H^{\circ}(298.15 \text{ K})$ were calculated for each point by the third-law method using thermodynamic functions for all the species listed by Barin and Knacke.⁽⁷⁾ The mean value is $(256.0 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$. The Gibbs free energy of formation of UF₃, $\Delta G_{f}^{\circ}(\text{UF}_{3}, \text{ s})$ has been evaluated at various temperatures using $\Delta G_{f}^{\circ}(\text{UF}_{4}, \text{ s})$ and $\Delta G_{f}^{\circ}(\text{HF}, \text{ g})$ values from Barin and Knacke. $\Delta G_{f}^{\circ}(\text{UF}_{3}, \text{ s})$ values at a few temperatures are compared with values from the literature in table 2.

The vapour pressure of $UF_3(s)$ was measured using the transpiration technique in the temperature range 1229 to 1367 K. The experimental results are given in table 3 and can be represented by the relation:

$$\log_{10}(p/kPa) = (10.26 \pm 0.23) - (15666 \pm 302)(K/T).$$

TABLE 1. Equilibrium constant $K^{\ominus} = \{p(HF)\}^2/p(H_2)p^{\ominus}$ with $p^{\ominus} = 101.325$ kPa for $2UF_4(s) + H_2(s) = 2UF_3(s) + 2HF(g)$

$10^7 K^{\ominus}$								
T/K	Present study	Ref. 2"	T/K	Present study	Ref . 2"	T/K	Present study	Ref. 2"
967	4.62	2.64	1019	21.1	14.5	1084	108	96.6
985	6.75	4.86	1032	27.8	21.6	1096	135	134
997	10.2	7.21	1042	40.6	29.1	1110	201	194
1000	13.2	7.94	1059	58.8	47.9	1120	239	251
1006	14.9	9.63	1068	67.1	61.9			

^a Obtained from least-square equation.

TABLE 2. Comparison of values of $\Delta G_{f}(UF_{3}, s)/(kJ \cdot mol^{-1})$

T/K	Present study	Refs. 1, 2	Ref . 7	
298	- 1521 °	- 1509 °	- 1529	
900	-1581 °	-1578	- 1639	
1000	- 1596	- 1594	- 1663	
1100	- 1612	-1611		

^a Extrapolated.

$2UF_{4} + H_{2} =$	$2UF_3 + 2HF$
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TABLE 3. Vapour pressure of $UF_3(s)$

T/K	1229	1240	1263	1291	1308	1333	1347	1367	
p/Pa	3.29	4.29	7.56	12.48	19.99	31.42	42.58	68.51	

The standard enthalpy of vaporization $\Delta H^{\circ}_{v}(298.15 \text{ K})$ and standard entropy of vaporization $\Delta S^{\circ}_{v}(298.15 \text{ K})$ were evaluated by the second-law method, using heat capacities from Barin and Knacke⁽⁷⁾ for UF₃(s) and the ideal value of $83.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for UF₃(g). The respective values are $328.7 \text{ kJ} \cdot \text{mol}^{-1}$ and $193.9 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. The enthalpies and entropies of vaporization of solid UF₃ were combined with the corresponding results for the formation of solid UF₃,⁽⁷⁾ to obtain the values for the enthalpy and entropy of formation of gaseous UF₃. The values of $\Delta H^{\circ}_{f}(\text{UF}_{3}, \text{ g}, 298.15 \text{ K})$ and $\Delta S^{\circ}_{f}(\text{UF}_{3}, \text{ g}, 298.15 \text{ K})$ are $-1165 \text{ kJ} \cdot \text{mol}^{-1}$ and $311.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ respectively.

4. Discussion

Long and Blankenship have assumed solid solubility of UF₃ and UF₄ to explain the abrupt lowering of K^{\ominus} above 1173 K. However, the phase diagram of $(UF_3 + UF_4)^{(3)}$ does not indicate any region of solid solubility. Also our X-ray diffraction analysis of UF₃ and UF₄ mixtures after equilibrium indicated no solid solubility. Hence our assumptions that $a(UF_4, s) = 1$ and $a(UF_3, s) = 1$ are justified for the calculation of K^{\ominus} . But an abrupt lowering in K^{\ominus} observed above 1144 K was attributed to the appearance of a liquid phase. The formation of a liquid phase considerably decreases the surface area for gas-solid interaction with consequent reduction in p(HF). A small contribution to lowering of p(HF) is also possible due to disproportionation of UF₃. resulting in the reaction of U with HF. The values of K^{\ominus} from the present work are compared with those of Long and Blankenship (calculated assuming no solid solubility) in table 1. The sizes of the two sets of results is roughly the same although the agreement between the values is good only in a narrow temperature range. The values of $\Delta H^{\circ}(298.15 \text{ K})$ calculated by the second-law, $(253.5 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$, and the third-law, (256.0+1.3) kJ·mol⁻¹, methods are in good agreement and no systematic error was detected in the third-law analysis of the equilibrium results. From table 2 it is seen that $\Delta G_{f}^{\circ}(UF_{3}, s)$ values from the present study are in good agreement with those of Long and Blankenship whereas the values reported by Barin and Knacke are higher.

The vapour pressure of UF₃(s) could be measured only in the temperature range of 1229 to 1367 K; below 1229 K the rate of condensate collection was too low for practical investigation, and above 1367 K UF₄ produced as a result of disproportionation could not be reduced by H₂ before it entered the condenser. Apparently, the disproportionation rate is higher than the reduction rate above 1367 K and hence vapour pressures calculated from mass gain of the condenser will be higher than the true vapour pressures. No other experimental vapour pressures of UF₃ are available and estimated values⁽⁶⁾ based on trivalent rate-earth fluorides are

approximately 100 times lower. Non-availability of thermodynamic functions for $UF_3(g)$ also precluded any third-law analysis of the vapour pressures.

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REFERENCES

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- 1. Long, G.; Blankenship, F. C. USAEC Report ORNL-TM-2065, Part II. 1969.
- 2. Long, G.; Glankenship, F. C. USAEC Report ORNL-TM-2065, Part I. 1969.
- 3. Khripin, L. A.; Poduzova, S. A.; Zadneprovskii, G. M. Russ. J. Inorg. Chem. 1968, 13, 1439.
- 4. Roy, K. N.; Prasad, R.; Bhupathy, M.; Venugopal, V.; Singh, Z.; Sood, D. D. Thermochim. Acta 1981, 43, 333.
- 5. International Practical Temperature Scale 1968. Metrologia 1976, 12, 7.
- 6. Darken, L. S.; Gurry, R.; Bever, M. B. Physical Chemistry of Metals. McGraw-Hill: New York. 1953.
- 7. Barin, I.; Knacke, O. Thermochemical Properties of Inorganic Substances. Springer-Verlag: Berlin. 1973.
- 8. Brewer, L.; Bromely, L. A.; Gilles, P. W.; Lofgren, N. L. USAEC Report TID-5290 Book I. 1958.