

Vapour Pressure Studies on the Thermal Decomposition of NbO_2F

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Using the transpiration method, the vapour pressure of NbOF_3 , formed by the reaction $4 \text{NbO}_2\text{F} = \text{Nb}_3\text{O}_7\text{F} + \text{NbOF}_3$, has been determined at temperatures between 700° and 760°C , giving a value of ΔH of 30.8 ± 3.0 kcal/mole.

In a previous report¹ the thermal decomposition of NbO_2F in an argon atmosphere was found to proceed by the formation of gaseous NbOF_3 according to the reaction: $4 \text{NbO}_2\text{F} = \text{Nb}_3\text{O}_7\text{F} + \text{NbOF}_3\uparrow$. Using the transpiration method vapour pressure determinations have been carried out and will here be reported.

A diagram of the apparatus used in the experiments is shown in Fig. 1. The transporting argon stream was controlled with a capillary flowmeter and the volume was measured by a wet gasmeter. After passing through the meters the gas was dried by CaCl_2 , KOH , and silica gel and then conducted into a silica glass tube, about 13 mm wide, ending with a closely fitting but removable platinum reaction chamber. This chamber as well as the gas inlet tube was surrounded with another silica glass tube, about 35 mm wide, divided in two separable parts, one of which was fixed in a resistance furnace. Through the outer tube a second argon stream was continuously flowing during the experiments to prevent back diffusion in the reaction chamber. The flow rate of this second argon stream was observed with a separate capillary flowmeter. The temperature of the furnace was kept constant by means of a commercial controller actuated by a Pt-Pt/Rh thermocouple. With this arrangement a constant temperature zone of 5 cm length was obtained. The reaction temperature was measured by means of a chromel-alumel thermocouple connected with a potentiometer bridge. All joints in the carrier gas inlet system were sealed with araldite. The details of the reaction chamber are shown in Fig. 1b.

NbO_2F was synthesized as previously reported¹ and weighed in the platinum boat before and after the experiment.

The procedure during an experiment was as follows: With the furnace at the correct temperature and the inner and outer gas stream at the desired

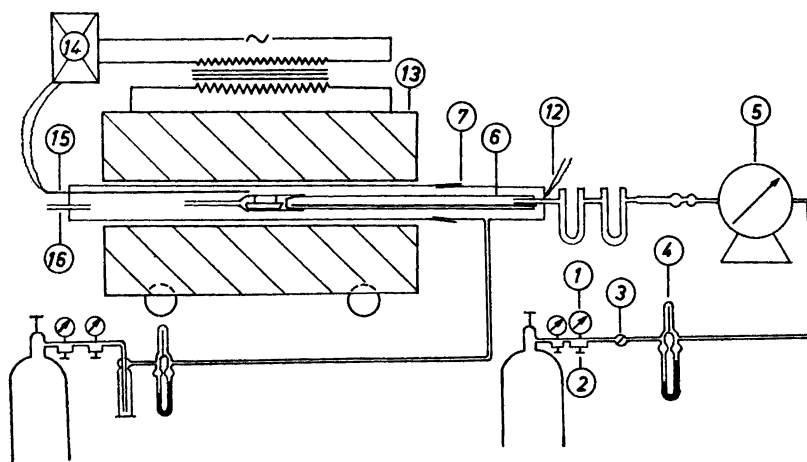


Fig. 1a. Apparatus for determining the vapour pressure of NbOF_5 . 1, precision manometer; 2, precision regulating cock; 3, cock with 4 (2) outlets; 4, capillary flow-meter; 5, rotary displacement gasmeter; 6, silica glass tube, about 13 mm wide; 7, joint lubricated with silicone grease; 8, platinum tube; (8–12 see Fig. 1b); 13, furnace; 14, controller; 15, thermocouple; 16, gas outlet tube.

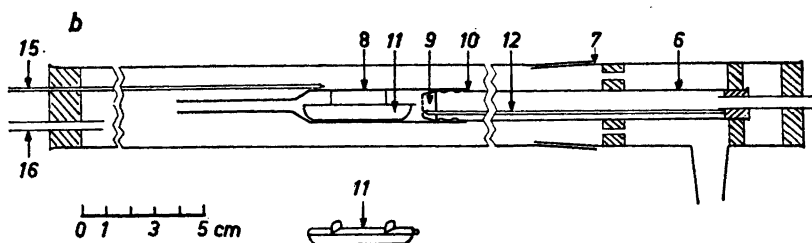


Fig. 1b. Details of reaction tube. 6–7, see Fig. 1a above; 8, platinum tube; 9, perforated platinum capsule tightly fitted on the silica glass inlet tube 6; 10, joint between the platinum tube and the silica glass tube, sealed with thin platinum foil; 11, platinum boat; 12, thermocouple; 15–16 see Fig. 1a above.

rate of flow, the joint (7), *cf.* Fig. 1a and b, was loosened and the furnace was moved to the left so that the reaction chamber was brought entirely out of the furnace and allowed to cool in air with the inner argon stream continuously flowing. After a sufficient time of cooling the platinum tube (8) was loosened by hand at the joint (10), the boat withdrawn and weighed with its content. Then it was replaced in the tube and the whole reaction chamber fixed in the proper position. Before moving the furnace to the right the air in the platinum chamber was swept away by the argon stream. During this period, about 5 min, any desirable change of the flow rate could be made

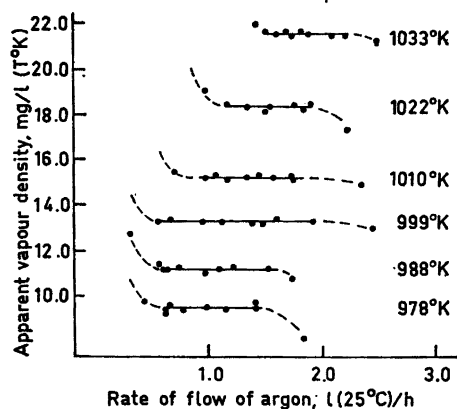


Fig. 2. Regions of constant vapour density at various flow rates of the carrying argon stream and different temperatures.

through setting the controlling cock (2) and the precision manometer (1). The furnace was now moved rather slowly to the right so that the joint (7) was properly sealed, and simultaneously the inner argon flow was stopped through turning the cock (3), and the gasmeter-(5)-reading was observed. After thermal equilibrium had been attained, the time being exactly measured in order to make a necessary dummy test at each temperature, the run was

Table 1. Experimental data and calculated vapour pressures in the regions of constant density as shown in Fig. 2.

Barometric pressure mm	$T^{\circ}\text{K}$	Rate of flow of argon l (25°C)/hour	Carrier gas volume l (25°C)	Weight loss mg	Vapour density mg/l ($T^{\circ}\text{K}$)	Average value of constant density	$^{10}\log p_{\text{mm}}$
754.8	978 ± 1	0.43	0.427	13.7	9.8	9.5	0.5411
		0.62	0.720	22.0	9.3		
		0.62	0.312	9.6	9.4		
		0.66	0.655	20.6	9.6		
		0.78	0.382	11.8	9.4		
		0.98	0.506	15.8	9.5		
		1.16	0.390	12.0	9.4		
		1.42	0.953	30.0	9.6		
		1.81	1.192	32.1	8.2		
		758.9	988 ± 1	0.30	0.858		
0.56	0.344			13.0	11.4		
0.61	0.487			18.1	11.2		
0.63	0.420			15.6	11.2		
0.74	0.400			15.0	11.3		
0.98	0.492			17.9	11.0		
1.09	0.576			21.4	11.2		
1.22	0.713			26.7	11.3		
1.53	0.695			25.8	11.2		
1.73	0.536			19.2	10.8		

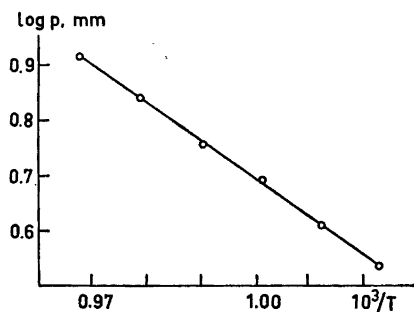
Table 1. Continued.

Barometric pressure mm	$T^{\circ}\text{K}$	Rate of flow of argon l (25°C)/hour	Carrier gas volume l (25°C)	Weight loss mg	Vapour density mg/l ($T^{\circ}\text{K}$)	Average value of constant density	$^{10}\log p_{\text{mm}}$
760.1	999 ± 1	0.55	0.302	13.5	13.3	13.3	0.6958
		0.66	0.481	21.6	13.4		
		0.94	0.475	21.2	13.3		
		1.12	1.123	50.1	13.3		
		1.38	0.607	26.9	13.2		
		1.47	0.893	39.5	13.2		
		1.60	0.800	35.9	13.4		
		1.92	0.858	59.3	13.3		
		2.45	1.222	53.2	13.0		
764.7	1010 ± 1	0.70	0.695	36.5	15.5	15.2	0.7579
		0.99	0.247	12.7	15.2		
		1.06	0.530	27.5	15.3		
		1.17	0.610	31.2	15.1		
		1.34	0.673	34.7	15.2		
		1.45	1.093	56.7	15.3		
		1.58	0.780	40.2	15.2		
		1.73	0.433	22.3	15.2		
		1.75	0.875	44.8	15.1		
2.33	0.866	43.7	14.9				
751.2	1022 ± 1	0.97	0.485	31.6	19.0	18.3	0.8431
		1.16	0.578	36.5	18.4		
		1.34	0.721	45.3	18.3		
		1.50	0.625	38.8	18.1		
		1.54	0.639	40.1	18.3		
		1.77	0.885	55.9	18.4		
		1.84	0.920	57.4	18.2		
		1.90	0.948	59.8	18.4		
		2.21	1.110	65.9	17.3		
749.0	1033 ± 1	1.42	0.715	54.3	21.9	21.5	0.9167
		1.50	0.533	39.9	21.6		
		1.60	0.839	62.5	21.5		
		1.64	0.817	61.2	21.6		
		1.73	0.587	43.5	21.4		
		1.82	0.900	67.4	21.6		
		1.88	0.470	35.0	21.5		
		2.09	0.938	69.6	21.4		
		2.21	0.692	51.3	21.4		
2.48	0.853	62.7	21.2				

started by admitting the carrier gas again. At the end of the experiment the joint (7) was loosened and the furnace was moved to the left, the gasmeter-reading at this moment being observed and the procedure continued as mentioned above.

At each temperature a set of runs with different flow-rates of the carrier gas were performed in order to determine a region in which this gas was

Fig. 3. Temperature dependence of the vapour pressures of NbOF₃ in the reaction
 $4 \text{NbO}_2\text{F} = \text{Nb}_3\text{O}_7\text{F} + \text{NbOF}_3\uparrow$.



essentially saturated with NbOF₃. A diagram showing these regions of constant density is given in Fig. 2. The connected experimental data and the calculated vapour pressures are given in Table 1. $\log p_{\text{NbOF}_3}$ was plotted against the reciprocal absolute temperature as shown in Fig. 3. From the slope of the straight line, ΔH_T for the heterogeneous reaction was calculated to 30.8 ± 3.0 kcal/mole.

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