762. *Vapour Pressures of Metal Alkoxides. Part III.*[1] *Hafnium Tetra-t-butoxide and -t-pentyloxide.*

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The vapour pressures of hafnium tetra-t-butoxide and -t-pentyloxide have been measured over the range 0·05—50 mm. Hg by the static method. These results were confirmed by hypsometric measurements at pressures $>8·0$ mm. It is shown that for t-butoxides and t-pentyloxides the order of volatilities is Hf $>$ Zr $>$ Ti over the pressure range studied. From the vapour-pressure equations it is deduced that the molar heats of vaporisation are markedly temperature-dependent. The significance of these results is discussed.

In previous papers we reported vapour-pressure measurements on the t-butoxides and t-pentyloxides of titanium [2] and zirconium,[1] in which we used an elaborate technique for studying compounds which are extremely readily hydrolysed and susceptible to thermal decomposition. These results proved that the zirconium compound was more volatile than its titanium analogue over a wide range of pressures. In view of the possibility of separating hafnium and zirconium by distillation of their alkoxides, it was necessary to obtain accurate data on the hafnium compounds. In addition, these results should be of special interest from the theoretical viewpoint in connexion with the relation between volatility and molecular weight.[3] We now present results for hafnium tetra-t-butoxide and -t-pentyloxide obtained by the same method as for titanium and zirconium derivatives.

Experimental

Hafnium Alkoxides.—These were prepared by essentially the methods reported previously.[4] Hafnium contents were determined by precipitation of hafnium hydroxide (cf. zirconium) followed by ignition to HfO_2. Careful analyses of (i) dipyridinium hafnium hexachloride $(C_5H_6N)_2HfCl_6$, (ii) hafnium isopropoxide solvate $Hf(OPr^i)_4,Pr^iOH$, (iii) hafnium tetra-t-butoxide, and (iv) hafnium tetra-t-pentyloxide established that the zirconium content of the hafnium was $<0·5\%$. In view of the similar volatilities of the hafnium and the zirconium compounds and the accuracy of the measurements, it was considered unnecessary to correct the results for this small zirconium impurity.

Vapour-pressure Measurements.—The static [2] and the hypsometric [1] method were applied as previously described.

Results.—*Hafnium tetra-t-butoxide.* The results are presented in Table 1. The vapour pressures in italics or in parentheses were not used in computing the vapour-pressure equation (1). Results in italics were obtained by the hypsometric method. The plot of log *P versus*

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[1] Part II, Bradley and Swanwick, *J.*, 1959, 748.
[2] Part I, Bradley and Swanwick, *J.*, 1958, 3207.
[3] Bradley, *Nature*, 1954, **174**, 323.
[4] Bradley, Mehrotra, and Wardlaw, *J.*, 1953, 1634.

$1/T$ showed significant curvature, and accordingly the results were fitted to the " three-constant " equation by the least-squares method described before.[2] Values of P (calc.) were obtained from equation (1).

$$\log P \text{ (calc.) (mm.)} = 67{\cdot}1326 - 6082{\cdot}25_5/T - 19{\cdot}3857 \log T \quad . \quad . \quad . \quad (1)$$

For the 22 measurements from 322·6° to 391·7° K used in computing equation (1), the coefficient of variation is ±0·62%, corresponding to a probable error for any individual point of ±0·43%. These results were obtained from three separate experiments. The number of changes of sign in the deviations ΔP [$P - P$ (calc.)] with the results arranged in order of ascending temperature is 10, and this confirms the validity of the " three-constant " equation (statistically 12 ± 2 changes of sign are required). In establishing the purity of the alkoxide, many measurements were made in the range 0·05—0·3 mm. and the 11 points shown in Table 1 are some representative examples. In fact the standard deviation of ΔP in this low-pressure region is ±0·016 mm., with the observed vapour pressures predominantly lower than calculated. The four hypsometric readings within the computed range are in reasonable agreement with the calculated values. Vapour pressures at temperatures above 391·7° K are all higher than calculated. This could be due to increasing thermal decomposition with rise in temperature, although this should not appreciably affect the hypsometric measurements. In the case of zirconium t-butoxide the hypsometric determinations agreed with the calculated values up to 448·1° K (159·3 mm.) before similar deviations were encountered. We are thus faced with the alternatives of suggesting either that the hafnium compound begins to decompose significantly at a temperature of 60° lower than the zirconium analogue does or that equation (1) is not suitable for extrapolation to temperatures above 391·7° K. This is important because of the need to predict the relative volatilities of hafnium and zirconium compounds at the higher pressures in connection with the efficiency of the separation by fractional distillation. We did not observe a very marked difference in thermal stability and this fact, coupled with the similar behaviour of zirconium and hafnium t-pentyloxides, suggests that equation (1) is not suitable for extrapolation to higher temperatures. Accordingly, it is suggested that the experimental values of P between 391·7° and 444·3° K are probably more reliable than P (calc.).

TABLE 1. *Hafnium tetra-t-butoxide.*

Temp. (°K)	*P* (mm.)	*P*, calc.	Temp. (°K)	*P* (mm.)	*P*, calc.	Temp. (°K)	*P* (mm.)	*P*, calc.	Temp. (°K)	*P* (mm.)	*P*, calc.
300·1	(0·06)	0·07	323·8	0·48	0·48$_5$	354·0	3·41	3·44	391·1	21·22	21·26
301·1	(0·06)	0·07$_5$	329·6	0·73	0·73$_5$	354·5	3·53	3·54	391·7	21·89	21·81
302·0	(0·06)	0·08	329·9	0·75	0·75	355·5	3·75	3·75	396·8	(27·79)	26·87
302·3	(0·07)	0·08$_5$	332·2	0·89	0·88	357·7	4·25	4·24	404·7	(37·50)	36·52
303·6	(0·08)	0·09$_5$	333·2	0·93	0·94	360·3	4·90	4·88$_5$	*412·4*	*51·19*	48·35
305·6	(0·11)	0·11	337·5	1·27	1·25$_5$	369·8	7·94	8·00	415·3	(55·74)	53·51
306·2	(0·11)	0·12	337·9	1·29$_5$	1·29	*371·5*	*8·49*	8·71	*416·0*	*60·55*	56·71
307·2	(0·12)	0·13	338·0	1·29	1·30	*376·4*	*10·81*	11·03	*418·1*	*62·69*	58·86
309·0	(0·14)	0·15	341·6	1·64	1·63$_5$	*377·8*	*11·36*	11·79	*442·6*	*144·7*	124·6
312·2	(0·18)	0·20	343·3	1·83	1·82	378·2	12·01	12·01	*444·3*	*153·7*	130·6
315·5	(0·24)	0·26	349·2	2·61	2·60$_5$	384·3	15·83	15·85	*457·7*	*229·5*	183·9
322·6	0·44	0·44	349·3	2·64	2·62	*388·2*	*18·71*	18·79			

TABLE 2. *Hafnium tetra-t-pentyloxide.*

Temp. (°K)	*P* (mm.)	*P*, calc.	Temp. (°K)	*P* (mm.)	*P*, calc.	Temp. (°K)	*P* (mm.)	*P*, calc.	Temp. (°K)	*P* (mm.)	*P*, calc.
337·6	(0·04)	0·05	364·4	0·37	0·37$_5$	408·3	4·77	4·82	435·4	16·19	16·23
338·6	(0·05)	0·05	370·3	0·56$_5$	0·56	408·7	4·88	4·92	*437·0*	*16·94*	17·32
340·4	(0·06)	0·06	370·5	0·56	0·56$_5$	413·5	6·19	6·20	446·3	(24·98)	24·86
341·6	(0·06)	0·07	370·9	0·58	0·58	414·3	6·30	6·44	448·6	(27·30)	27·09
343·3	(0·07)	0·08	373·8	0·71$_5$	0·70	*419·7*	*8·08*	8·27	453·5	(32·45)	32·39
346·2	(0·10)	0·10	378·5	0·94$_5$	0·94	*823·0*	*9·33*	9·59	*455·9*	*35·28*	35·26
350·2	(0·14)	0·13$_5$	383·3	1·29$_5$	1·25	*424·9*	*10·18*	10·43	465·2	(49·34)	48·41
351·0	(0·13$_5$)	0·14$_5$	390·0	1·86$_5$	1·84	426·2	11·00	11·04	*467·6*	*53·43*	53·37
354·4	(0·19)	0·18$_5$	390·7	1·93	1·91$_5$	427·7	11·85	11·77	471·4	(60·74)	59·14
357·4	0·22$_5$	0·23	395·7	2·58	2·52	*429·5*	*12·41*	12·71	*475·2*	*68·8*	66·6
361·4	0·31	0·30$_5$	398·9	2·97	2·99	432·4	14·33	14·35	477·3	(73·9)	71·0
361·6	0·31	0·31	403·6	3·83	3·81$_5$	435·0	16·04	15·97			

TABLE 3. *Titanium, zirconium, and hafnium t-butoxides.*

Temp. (°K)	300		320		340		360		380		400	
	P, calc.	ΔH_v	*P*, calc.	ΔH_v	*P*, calc.	ΔH_v	*P*, calc.	ΔH_v	*P*, calc.	ΔH_v	*P*, calc.	ΔH_v
$Ti(OBu^t)_4$	0·049	15·8	0·25	15·2	1·00	14·7	3·26	14·1	9·04	13·5	21·41	13·0
$Zr(OBu^t)_4$	0·066	15·9	0·34	15·3	1·35	14·8	4·42	14·2	12·30	13·7	29·77	13·1
$Hf(OBu^t)_4$	0·069	16·3	0·36	15·5	1·48	14·7	4·80	13·9	13·05	13·2	30·49	12·4
P_{Zr}/P_{Ti}	1·34		1·34		1·35		1·36		1·36		1·39	
P_{Hf}/P_{Zr}	1·05		1·08		1·09		1·09		1·06		1·02	

TABLE 4. *Titanium, zirconium, and hafnium t-pentyloxides.*

Temp. (°K)	350		370		390		410		430		450	
	P, calc.	ΔH_v	*P*, calc.	ΔH_v	*P*, calc.	ΔH_v	*P*, calc.	ΔH_v	*P*, calc.	ΔH_v	*P*, calc.	ΔH_v
$Ti(OC_5H_{11}{}^t)_4$	0·117	17·3	0·44	16·8	1·41	16·4	3·89	15·9	9·55	15·5	21·14	15·0
$Zr(OC_5H_{11}{}^t)_4$	0·126	18·7	0·52	17·8	1·77	16·9	4·98	16·0	12·13	15·1	26·01	14·2
$Hf(OC_5H_{11}{}^t)_4$	0·134	18·5	0·55	17·7	1·84	17·0	5·24	16·2	12·98	15·5	28·53	14·7
P_{Zr}/P_{Ti}	1·08		1·19		1·24		1·28		1·27		1·23	
P_{Hf}/P_{Zr}	1·06		1·04		1·04		1·05		1·07		1·10	

Hafnium tetra-t-pentyloxide. The results for 4 experiments on this alkoxide are presented in ascending order of temperatures in Table 2 in the same manner as for the t-butoxide. The plot of log *P* *versus* $1/T$ gave a curve, and the " three-constant " equation (2) was computed from the results in the temperature range 357·4—435·4° K.

$$\log P \text{ (calc.) (mm.)} = 66·6423 - 6897·19/T - 18·7923 \log T \quad . \quad . \quad . \quad (2)$$

The coefficient of variation for the 24 points used in computing equation (2) was ±1·7%, corresponding to a probable error for a single point of ±1·2%. There were 11 changes of sign in ΔP compared with 13 ± 2 required statistically, confirming the validity of equation (2). The nine results in the low-pressure range (0·04—0·2 mm.) are representative of a large number of measurements which gave a standard deviation of ±0·01 mm. in ΔP. The hypsometric results are in reasonable agreement with equation (2). In fact, good agreement between observed and calculated vapour pressures extends up to 467·6° K (53·37 mm.), and it appears that equation (2) may be extrapolated to this point with confidence.

DISCUSSION

The vapour pressures of the t-butoxides and -pentyloxides of titanium, zirconium, and hafnium have now been shown to conform to the " three-constant " Kirchoff–Rankine equation (3), where *a*, *b*, and *c* are constants;

$$\log P = a - b/T - c \log T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This equation is a logical development of the simpler Clausius–Clapeyron equation with allowance for the temperature-variation of the molar heat of vaporisation. Therefore our vapour-pressure results suggest that the molar heats of vaporisation (ΔH_v) for these compounds vary considerably with temperature. This has an important bearing on the fact that for these two series of monomeric derivatives the order of volatilities (Hf > Zr > Ti) is the reverse of that expected according to the common belief that increased molecular weight leads to decreased volatility. For example, if the order of molar heats of vaporisation were Ti > Zr > Hf, then the " anomaly " could simply be explained in terms of differences in intermolecular forces. However, this simple view is not supported by the data presented in Tables 3 and 4. Values of ΔH_v (kcal./mole) have been calculated at selected temperatures and are shown with *P* (calc.) and the relative volatilities P_{Hf}/P_{Zr} and P_{Zr}/P_{Ti}.

It is difficult to assess the errors in the ΔH_v data, but bearing in mind the coefficients of variation of *ca.* ±1% for the vapour pressures, we feel that the error in ΔH_v should not exceed 5%. Thus the data in Table 3 show that the molar heats of vaporisation for the t-butoxides are the same within 5% error for titanium, zirconium, and hafnium at each temperature. Therefore, the order of volatilities cannot be linked in a simple manner with intermolecular forces, especially since at 300° and 320° K the order of ΔH_v, *viz.*, Hf > Zr > Ti, would favour an order of volatility Ti > Zr > Hf. The relative volatility of zirconium and titanium compounds is practically independent of temperature, whereas for hafnium and zirconium the relative volatility appears to have a maximum at about 350° K. In view of our previously expressed doubts concerning the reliability of extrapolating equation (1) to higher temperatures, we are sceptical about this maximum and suggest that the relative volatility remains at *ca.* 1·02—1·05 up to about 500° K instead of falling below unity.

The molar heats of vaporisation for titanium, zirconium and hafnium t-pentyloxides are the same within 5% for each temperature except 350° and 370° K where the order is Hf ~ Zr > Ti. Therefore, the order of volatilities cannot be explained in terms of intermolecular forces and it is clear that an entropy effect[3] is involved. With regard to the relative volatility of zirconium and titanium pentyloxides, a significant temperature-dependence is apparent. Nevertheless, these values are considerably lower than those found for the t-butoxides. For hafnium and zirconium t-pentyloxides the relative volatility is practically constant at *ca.* 1·06 over the whole temperature range.

These results show that in principle it is possible to separate hafnium from zirconium by fractional distillation of either the t-butoxides or the t-pentyloxides under reduced pressure with a column of high efficiency.

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