150. *Vapour Pressures of Metal Alkoxides. Part II.*[1] *Zirconium Tetra*-tert.*-butoxide and -amyloxide.*

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The vapour pressures of zirconium tetra-*tert.*-butoxide and -amyloxide have been measured by the static method in the pressure ranges 0·06—162 mm. Hg and 0·02—42 mm. Hg respectively. The results were confirmed by hypsometric measurements in the pressure ranges 9·5—464 mm. Hg and 2·5—42 mm. Hg respectively. The data show that the zirconium compounds are more volatile than the corresponding titanium compounds over the regions studied.

RECENTLY [1] we reported measurements of the vapour pressures of titanium *tert.*-butoxide and -amyloxide made in a specially designed apparatus. Now we report measurements on zirconium tetra-*tert.*-butoxide and -amyloxide in the same type of apparatus. In addition the current results have been checked and confirmed with an all-glass hypsometer.

EXPERIMENTAL

Preparation of Zirconium Tetra-tert.*-alkoxides.*—Both compounds were prepared by alcohol interchange involving purified zirconium *iso*propoxide solvate and the appropriate tertiary alcohol. For the *tert.*-amyloxide the method used was essentially that already described [2] whilst for the *tert.*-butoxide a large excess of *tert.*-butyl alcohol–benzene azeotrope (*ca.* 3·5 l.) was added to the *iso*propoxide (*ca.* 40 g.) and the *iso*propyl alcohol–benzene azeotrope was fractionated out during 2 weeks' continuous distillation through an efficient column (130 cm., packed with Fenske glass helices). In each case the *tert.*-alkoxide was vacuum-distilled and analysed before being finally purified for vapour-pressure measurements. The zirconium contained 0·5% of hafnium but, in view of the small difference in volatilities of zirconium and hafnium *tert.*-alkoxides, no correction was applied to the vapour pressures.

Vapour-pressure Measurements.—(i) *The static method.* Most of the work was carried out by this method which was described in full previously.[1] The same criteria of purity were also employed.

(ii) *Hypsometer method.* Whilst the static method has proved invaluable for measurements on these extremely reactive compounds its major virtue, the detection of decomposition, has

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[1] Part I, Bradley and Swanwick, *J.*, 1958, 3207.

[2] Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 4204.

also been a limitation in that it has set an upper limit to the temperature at which reliable measurements could be made. Moreover, the volatilities of zirconium and hafnium *tert.*-alkoxides are so close that it was desirable to check the static results by an independent method. A hypsometric method was chosen because it was considered to be least affected by the products of decomposition and could thus be used at higher temperatures. The all-glass hypsometer and adaptor shown in Fig. 1 fitted on to the vacuum-purification line of the static apparatus at the BS14 joint 3. The sample (10—15 c.c.) of alkoxide, purified as in the static measurements, was caused by the dropper 1 to fall cleanly through the key of the high-vacuum tap 2 into the hypsometer. After closure of tap 2 the hypsometer unit was transferred to the manometer side of the static apparatus, and pure dry nitrogen was admitted. The hypsometer was immersed to a depth which just covered the boiler 4 in a thermostat-controlled bath. Smooth ebullition was promoted by carefully purified glass wool in vessel 4. The thermometer pocket 8 was placed well above the boiler to avoid superheating by radiation and the wide-diameter tubes 6 and 7 facilitated conduction of the vapour stream past point 8—this is very important at the lower pressures. The condenser pocket 9 was well away from pocket 8 and the condensate was returned to the boiler through the narrow tube 5 which ensured rapid reheating of the condensate. A partial-immersion standard thermometer was used at its correct depth of immersion and a small quantity of mercury was required to make thermal contact between the thermometer and pocket 8. The alkoxide was made to boil under an atmosphere of nitrogen at a pressure which was read on the accurate manometer [1] and controlled by a manostat (Fig. 2) which operated on the Cartesian Diver principle. The diver 1 was just free to move in the jacket 3 and carried a Neoprene cushion 2 which closed the pump jet 4 at its ground orifice. Slight leakage through this valve was compensated by a controlled leak of nitrogen. Enough mercury was used to give a clearance of 1—2 mm. between the cushion and the jet during evacuation: this ensured rapid evacuation when the valve opened and only a small change in pressure was needed to shut the valve. By means of the tap 5 the manostat could be set to operate at the required pressure. Extensive tests proved that this manostat was far superior in sensitivity and stability over long periods to two other types which used valves employing mercury and sintered-glass discs. For example, the manostat showed fluctuations of 0·04 mm. at 2·3 mm. and 0·15 mm. at 42 mm. Hg each during an hour.

FIG. 1. *Boiling-point apparatus and adaptors. (Outside diameters shown.)*

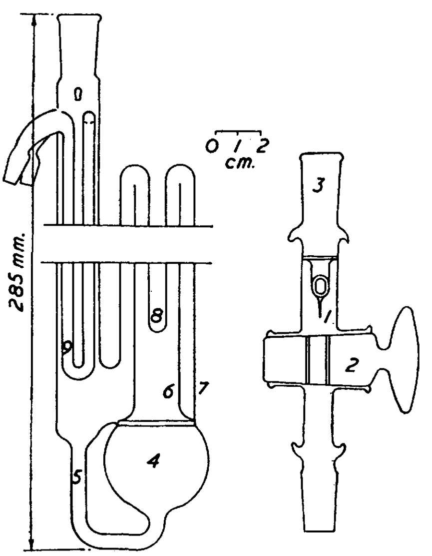
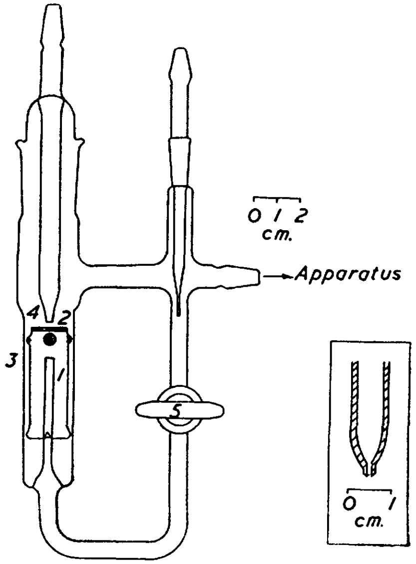


FIG. 2. *Cartesian manostat. Inset = pumping jet.*



At a given pressure the steady readings of the thermometer (at 8) were recorded at several temperatures of the heating-bath in the vicinity of the true b. p. The thermometer readings were plotted as ordinates against the bath-temperatures as abscissæ and the curve showed a plateau in which the thermometer temperature changed by less than 0·1° whilst the bath-temperature rose by 15°. The position of the plateau was independent of increasing or decreasing bath-temperature, but equilibrium was approached much more rapidly from the high-temperature end. The temperature of the plateau was recorded as the b. p.

RESULTS AND DISCUSSION

Zirconium Tetra-tert.*-butoxide.*—The results are presented in Table 1 in which $P_{\text{calc.}}$ is the vapour pressure calculated from the equation:

$$\log P_{\text{calc.}}(\text{mm.}) = 51{\cdot}0296 - 5281{\cdot}72/T - 13{\cdot}9703 \log T \quad . \quad . \quad . \quad (1)$$

The values of P in parentheses and in italics were not used in computing this equation which was obtained by the laborious procedure already described.[1] Values in italics were determined by the hypsometer method and involved two different samples. The results by the static method were obtained from four different experiments, and the values in parentheses were excluded from the computation either because they were too low to be reasonably accurate or because they were subject to slight errors due to thermal decomposition.

For the 39 points used in computing the equation the coefficient of variation was ±1·8%, corresponding to a most probable error of a single point of ±1·2%. When these points are taken in order of ascending temperature irrespective of the number of the experiment (as shown in Table 1), the errors ($\Delta P = P - P_{\text{calc.}}$) show 26 changes in sign compared with the 20 required for random distribution of errors. Clearly, equation (1) represents these points well. In the low-pressure region 0·06—0·26 mm. (not computed) the observed pressures are more frequently lower than calculated, whilst the coefficient of variation is ±0·01 mm. which is reasonable in view of the probable error of ±0·005 mm. in the pressure measurements. The 11 pressures determined by the static method in the high-temperature region (403·8—448·3°) are predominantly higher than the calculated but in no case does the error exceed 2% and the coefficient of variation is ±1·3%. Considering now the results obtained by the hypsometric method, we find that the 4 points obtained in the " computed " region are in close agreement with the calculations based on equation

TABLE 1. *Zirconium tetra*-tert.*-butoxide.*

Temp. (K)	P (mm.)	$P_{\text{calc.}}$	Temp. (K)	P (mm.)	$P_{\text{calc.}}$	Temp. (K)	P (mm.)	$P_{\text{calc.}}$	Temp. (K)	P (mm.)	$P_{\text{calc.}}$
299·4°	(0·06)	0·06	308·6°	(0·12)	0·14	349·5°	2·40	2·424	403·8°	(35·37)	34·72
300·4	(0·07)	0·07	308·8	(0·13)	0·14	350·0	2·50	2·498	410·7	(46·00)	45·56
300·6	(0·07)	0·07	312·0	(0·16)	0·18	353·6	3·07	3·085	411·0	(46·29)	45·98
301·6	(0·08)	0·08	313·4	(0·20)	0·20	353·9	3·12	3·138	416·7	(56·94)	56·86
301·7	(0·07)	0·08	315·3	(0·20)	0·23	354·4	3·17	3·230	417·0	(57·67)	57·47
302·2	(0·08)	0·08	316·7	(0·24)	0·26	357·6	3·85	3·872	*417·3*	*58·10*	58·20
302·3	(0·08)	0·08	319·1	0·31	0·314	360·9	4·78	4·647	*418·7*	*61·10*	61·10
303·2	(0·08)	0·09	322·3	0·40	0·399	363·0	5·18	5·208	*420·2*	*62·80*	64·50
303·6	(0·10)	0·09	324·6	0·46	0·472	366·1	6·17	6·14	420·9	(67·14)	66·13
303·8	(0·09)	0·09	327·1	0·58	0·565	368·7	6·93	7·03	*423·4*	*71·00*	72·20
303·9	(0·09)	0·09	328·1	0·60	0·606	370·2	7·65	7·59	424·1	(73·83)	73·98
304·0	(0·09)	0·09	329·3	0·63	0·659	*374·8*	*9·46*	9·55	427·9	(85·95)	84·26
304·3	(0·09)	0·10	330·6	0·74	0·721	375·4	9·79	9·85	*431·8*	*94·90*	95·70
304·8	(0·09)	0·10	331·4	0·79	0·762	379·6	12·10	12·07	432·9	(101·1)	99·46
305·1	(0·09)	0·10	331·9	0·81	0·783	381·1	12·95	12·96	*439·9*	*124·1*	124·3
305·3	(0·10)	0·10	334·2	0·90	0·921	*383·7*	*14·42*	14·63	440·6	(129·0)	127·1
305·4	(0·10)	0·10	335·5	1·03	1·005	384·4	15·14	15·11	*448·1*	*159·7*	159·3
305·6	(0·10)	0·11	336·8	1·11	1·095	387·9	17·60	17·71	448·3	(162·6)	160·2
305·7	(0·10)	0·11	338·1	1·16	1·192	389·1	18·72	18·69	*454·0*	*192·2*	188·8
306·6	(0·10)	0·12	339·4	1·32	1·297	*392·6*	*21·67*	21·78	*457·0*	*216·3*	205·2
306·6	(0·11)	0·12	341·1	1·42	1·446	394·9	24·05	24·05	*457·9*	*215·3*	210·5
307·1	(0·12)	0·12	343·5	1·71	1·682	395·2	24·28	24·35	*477·6*	*372·4*	349·5
307·4	(0·12)	0·12	343·6	1·66	1·692	*402·3*	*32·49*	32·70	*480·9*	*412·3*	378·0
308·3	(0·13)	0·13	347·8	2·24	2·190	402·4	32·93	32·82	*486·3*	*464·6*	428·4
308·4	(0·12)	0·13	348·2	2·20	2·243						

(1) which was computed from the static measurements. In fact, the agreement extends to higher pressures and the 11 points from 9·46 to 159·3 mm. gave a standard deviation of only ±1·1% although the observed pressures tended generally to be lower than the calculated. It seems reasonable to suggest that equation (1) is valid for calculations of the vapour pressures of zirconium tetra-*tert.*-butoxide in the pressure range 0·05—200 mm. Hg (300—450° K). Above ~450° K the observed pressures are considerably and increasingly higher than calculated and the spoon-gauge method showed that thermal decomposition becomes significant. Nevertheless, it is surprising that the hypsometer method gives such high results because non-volatile products of decomposition stay in the boiler (4) whilst the volatile products (olefin and alcohol) should diffuse out of the vapour and merely displace an appropriate volume of nitrogen through the manostat. Thus the thermometer is bathed in condensing vapour of alkoxide and, provided the manostat can cope with the volatile products of decomposition, the true boiling point should be measured. During the testing of the manostat we found that a deliberate leakage of nitrogen which could raise the pressure in the apparatus by 35 mm. Hg per min. (in the absence of the manostat) was dealt with efficiently by the manostat and caused a rise of only 0·3 mm. Hg in the apparatus. Hence it is possible that equation (1) should not be extrapolated above 450° K and that the vapour pressures determined hypsometrically are more accurate than the $P_{\text{calc.}}$ data imply.

In comparing these results on zirconium tetra-*tert.*-butoxide with those on the titanium derivative [1] it is clear that the zirconium compound is significantly the more volatile over the whole range of pressures studied.

TABLE 2. *Zirconium tetra*-tert.*-amyloxide.*

Temp. (K)	P (mm.)	$P_{\text{calc.}}$	Temp. (K)	P (mm.)	$P_{\text{calc.}}$	Temp. (K)	P (mm.)	$P_{\text{calc.}}$	Temp. (K)	P (mm.)	$P_{\text{calc.}}$
331·0°	(0·02)	0·02$_{6}$	343·6°	(0·06)	0·07$_{6}$	374·6°	0·73	0·71	406·4°	4·26	4·18
332·1	(0·03)	0·03	343·8	(0·06)	0·07$_{7}$	375·5	0·77	0·75	409·1	4·71	4·77
333·2	(0·03)	0·03	344·5	(0·07)	0·08	376·6	0·81	0·80	*409·4*	*4·85*	4·84
333·4	(0·03)	0·03	344·9	(0·07)	0·08$_{5}$	378·0	0·85	0·87	*409·5*	*4·86*	4·86
335·1	(0·03)	0·03$_{7}$	345·6	(0·08)	0·09	378·9	0·94	0·92	*410·3*	*5·02*	5·05
335·9	(0·03)	0·04	345·7	(0·08)	0·09	379·5	0·98	0·95$_{6}$	412·8	5·70	5·69
336·3	(0·03)	0·04	345·9	(0·08)	0·09	382·4	1·19	1·14	412·9	5·76	5·72
337·8	(0·04)	0·04$_{7}$	345·9	(0·08)	0·09	382·9	1·13	1·17	*413·4*	*5·79*	5·85
337·9	(0·04)	0·04$_{7}$	346·6	(0·08)	0·09$_{7}$	383·4	1·21	1·21$_{4}$	415·8	6·38	6·54
338·1	(0·04)	0·04$_{8}$	347·4	(0·08)	0·10$_{3}$	384·6	1·30	1·29$_{6}$	417·1	6·96	6·94
338·5	(0·03)	0·05	349·4	(0·11)	0·12	387·1	1·44	1·50	*419·4*	*7·67*	7·70
338·9	(0·04)	0·05	351·8	(0·14)	0·14$_{5}$	388·7	1·66	1·64	422·5	8·79	8·82
339·4	(0·04)	0·05$_{4}$	352·1	(0·15)	0·14$_{8}$	390·1	1·76	1·77	426·1	10·41	10·30
339·6	(0·04)	0·05$_{5}$	352·8	(0·14)	0·16	390·1	1·82	1·77	426·5	10·46	10·48
340·1	(0·05)	0·05$_{7}$	352·9	(0·15)	0·16	391·9	1·99	1·96	*428·6*	*11·47*	11·44
340·4	(0·04)	0·05$_{9}$	354·2	(0·17)	0·17$_{4}$	392·8	2·00	2·06	*431·5*	*12·96*	12·89
340·5	(0·04)	0·05$_{9}$	355·6	(0·18)	0·19	393·1	2·10	2·09$_{6}$	*432·0*	*13·35*	13·16
340·9	(0·05)	0·06	356·0	(0·20)	0·19$_{6}$	*394·7*	*2·28*	2·28	432·3	(13·28)	13·31
341·2	(0·04)	0·06$_{3}$	357·5	(0·21)	0·22	394·8	2·29	2·30	434·1	(14·58)	14·33
341·5	(0·06)	0·06$_{4}$	360·7	(0·27)	0·28	395·5	2·42	2·39	*434·3*	*14·68*	14·43
341·8	(0·05)	0·06$_{6}$	361·3	0·29	0·29	*396·4*	*2·45*	2·50	438·7	(17·24)	17·14
341·9	(0·05)	0·06$_{6}$	363·7	0·34	0·34$_{3}$	397·9	2·70	2·71	*439·5*	*18·14*	17·68
341·9	(0·05)	0·06$_{6}$	364·0	0·34	0·35	398·6	2·85	2·81	443·8	(22·11)	20·78
342·1	(0·06)	0·06$_{7}$	367·3	0·43	0·44	398·7	2·84	2·83	*447·4*	*25·02*	23·70
342·2	(0·06)	0·06$_{8}$	367·9	0·46	0·45$_{7}$	*400·0*	*3·02*	3·02$_{6}$	448·4	(25·60)	24·57
342·4	(0·05)	0·06$_{9}$	369·3	0·49	0·50	*401·1*	*3·16*	3·20	450·9	(28·82)	26·85
342·4	(6·06)	0·06$_{9}$	370·1	0·52	0·52$_{8}$	404·0	3·71	3·71	455·9	(33·93)	31·79
342·4	(0·06)	0·06$_{9}$	372·3	0·61	0·60$_{9}$	404·3	3·68	3·77	460·4	(40·65)	37·01
342·5	(0·06)	0·07				405·2	3·95	3·94	*461·3*	*41·70*	38·13
342·6	(0·05)	0·07							462·0	(42·42)	39·00

Zirconium Tetra-tert.*-amyloxide.*—The results for four runs by the static method and two by the hypsometric method are given in Table 2 in the same manner as for the *tert.*-butoxide in Table 1. Computation of the results of the static method in the pressure range 0·29—10·46 mm. gave the equation:

$$\log P\ (\text{mm.}) = 78{\cdot}7844 - 7566{\cdot}42_{3}/T - 22{\cdot}8232_{8} \log T \quad . \quad . \quad . \quad (2)$$

The 42 computed results gave a coefficient of variation of ±1·7% corresponding to a probable error for a single point of ±1·2%. Arranged in ascending order of temperature irrespective of the number of the run, the data give 27 changes of sign in error (ΔP) compared with 22 required for a random distribution of errors. The coefficient of variation for the uncomputed results (in parentheses) in the lower pressure region is ±0·014 mm. and, as was found for the *tert.*-butoxide, the observed results tend to be lower than those calculated from equation (2). In the high-temperature region the static method gave good agreement with equation (2) up to about 440° K, but above this the observed pressures were considerably higher than calculated and thermal decomposition was detected. The hypsometric method gave results in the computed zone in good agreement with equation (2) and the 12 points had a percentage standard deviation of ±0·9% with 6 negative errors (ΔP) and 4 positive. The agreement with equation (2) also extended beyond the upper limit of the computed zone to about 440° K, but at higher temperatures the pressures measured were considerably higher than calculated. It appears that equation (2) is valid for the calculation of vapour pressures for zirconium tetra-*tert.*-amyloxide over the pressure range 0·02—20·0 mm. Hg (330—440° K). Comparing these results with those on the corresponding titanium compound[1] shows that the zirconium compound is the more volatile in the region studied as was found in the case of the *tert.*-butoxides.

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