

650. *Vapour Pressures of Metal Alkoxides. Part I. Titanium Tetra-tert.-butoxide and -amyloxide.*

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Vapour-pressure measurements in the range 0.05—50 mm. have been made on titanium tetra-*tert.*-butoxide and -amyloxide, by a static method, in an all-glass apparatus incorporating a novel type of spoon-gauge. The apparatus and technique were developed for compounds which are sensitive to hydrolysis and to thermal decomposition. The computed results conformed to equations of the type, $\log P = C - \alpha/T - \gamma \log T$ for certain ranges, but it is believed that their extrapolation is valid.

RECENT work in these laboratories on the preparation of volatile metal alkoxides suggested the possibility of separating and purifying metals by fractional distillation of the alkoxides. It was necessary therefore to determine vapour pressures accurately over a wide range of pressures. In addition these data were required for calculations of thermodynamic properties and thermochemical data. Preliminary measurements of the boiling points of monomeric alkoxides of titanium,¹ zirconium,¹ and hafnium² at various pressures had revealed that their volatilities were in the unexpected order, $\text{Hf}(\text{OR})_4 > \text{Zr}(\text{OR})_4 > \text{Ti}(\text{OR})_4$, whose theoretical implications³ provided yet another need for vapour-pressure measurements of the highest possible accuracy. Considerable difficulties were experienced in attempting these accurate measurements and the present communication is mainly devoted to describing the experimental method. The titanium alkoxides were studied first because experience has shown that they are less difficult to deal with than the zirconium and the hafnium compounds. The results obtained were of sufficient accuracy to require a "three-constant" vapour-pressure equation.

¹ Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 4204.

² *Idem.*, *J.*, 1953, 1634.

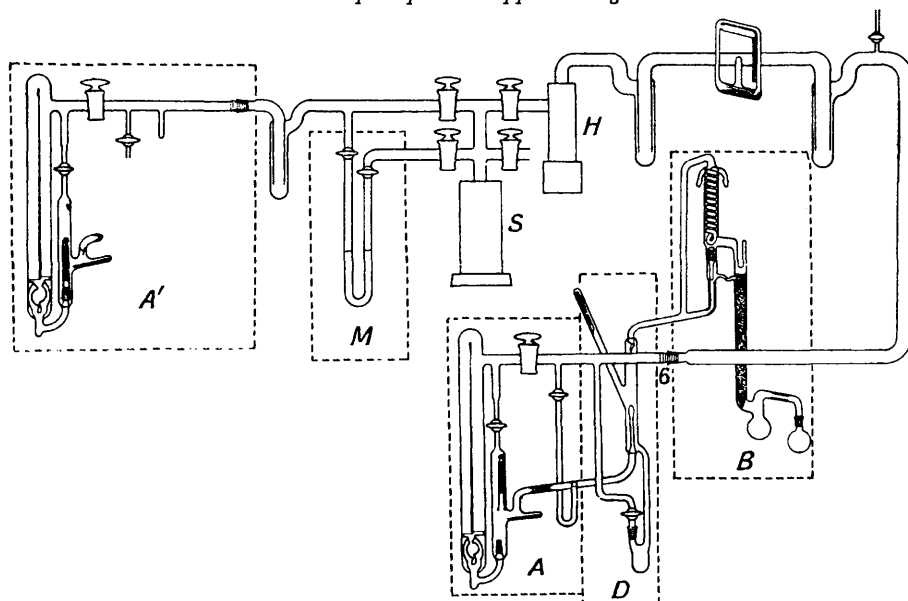
³ Bradley, *Nature*, 1954, **174**, 323.

EXPERIMENTAL

Preparation of Titanium tert.-Alkoxides.—The *tert.*-butoxide and *tert.*-amyloxide were prepared by the methods described previously¹ from titanium tetrachloride which had been first refluxed over copper turnings (to remove vanadium) and then fractionally distilled. Although a conventional analysis for titanium established the purity of the compounds within 0.2% this was not a satisfactory criterion since a trace of volatile impurity could cause a large error in the vapour pressure. The reactivity of metal alkoxides precluded any chemical method of purification and it was necessary to devise physical methods (described below). Finally, it was decided that the best criterion was the establishment of a reproducible vapour pressure which did not alter whilst the sample was gradually evaporated. A special apparatus was developed during three years' studies and the final apparatus is described.

Apparatus.—General layout (Fig. 1). The sample was introduced at section *B* and distilled through the separator *D* into section *A* where it was isolated under a double-spoon gauge of

FIG. 1. Vapour-pressure apparatus: general.



S, "Speedivac" pump. *H*, mercury diffusion pump. For further explanation see text.

novel design. Section *A* was then transferred and attached (as *A'*) to the manometer section *M*. Here the sample was immersed in a thermostat, and its vapour pressure was determined by a null method. The apparatus was constructed entirely of "Pyrex" glass which was first cleaned with chromic acid, then washed, immersed in distilled water for 24 hr., and steamed for several hours. The assembled apparatus was then "outgassed" at about 10^{-5} mm. for several hours during which section *A* was heated at 300° and the rest of the apparatus was "flamed."

Section B (Fig. 2). A redistilled sample of alkoxide under an atmosphere of dry nitrogen in flask 1 was attached as shown in Fig. 2 and then distilled under a high vacuum into flask 2. The seal 3 was then "outgassed" and sealed-off. From this stage onward the alkoxide did not come into contact with any greased joints or taps and a high vacuum was maintained throughout. The sample was fractionally distilled at a high reflux ratio (40:1) which was controlled by the magnetically operated valve 4 which was ground into the seating 5. The column was packed with single-turn Fenske glass helices and was made adiabatic by an electrically heated jacket. This method of purification was adopted after extensive research on bulb-to-bulb vacuum-distillation had shown that the sealing-off procedure after each distillation actually introduced volatile impurities from the glass and the sample became

progressively less pure as determined by its vapour pressure. In fact the avoidance of contamination of the sample by traces of water and carbon dioxide liberated by molten glass proved to be a major problem (see section *A*). This experience is not new because Fairbrother *et al.*^{4,5} had observed a similar difficulty in their work on the niobium and tantalum halides. The distillate from section *B* passed along a short inclined tube into the separator *D*.

Section D (Fig. 3). The distillate from *B* was caused to fall directly on to the thin finger-septum 2 by the drip-guide 1. The first runnings were thus made to run into the reservoir 3 which was cooled to *ca.* -78° . The magnetically controlled hammer 4 was used to break the septum and then withdrawn. The drip-guide was arranged so that the distillate then fell clear through the hole in the septum and thence ran into section *A* until the required sample had been collected. The final fraction was diverted into the reservoir 3 by placing the specially shaped end of the magnetic hammer over the hole in the septum.

Section A. This is shown in detail (except for the spoon gauge) in Fig. 4. The sample ran along from section *D* and dropped from the fixed drip-guide 2 on to another guide 3 which could be moved magnetically into a position which caused the alkoxide to fall clear through the standard (A.10) cone 4 into the spoon gauge compartment. The guide 3 was then withdrawn and the magnetically controlled standard (A.10) socket 5 was lowered on to the cone, thus isolating the pure sample. The residual film of alkoxide in the rest of section *A* was evaporated off and condensed in the trap 8 and the thickened glass at point 1 was outgassed at dull red-heat and then sealed off. With taps 7, 9, and 10 closed the apparatus was also sealed off below tap 9 and above tap 5 (Fig. 3), and section *A* was then placed at *A'* (Fig. 1). The new double spoon gauge, described in the following Note, has a sensitivity of *ca.* 5 mm. deflection per mm. pressure difference, and a change of pressure of <0.01 mm. Hg could thus be detected. The zero position was unaltered when the empty apparatus was heated to 300° .

Section M. The U-tube type of manometer with di-*n*-butyl phthalate as the manometric liquid is shown in Fig. 5. The limbs 1 and 2 were of "Veridia" precision bore (10 mm. diam.) to obviate surface tension effects and they were backed by a silvered glass scale (100 cm.) graduated in mm. The tubes and scale were mounted in a glass jacket (38 mm. diam.) containing a thermometer. Glass valves (3 and 4) were inserted above the tubes to prevent ejection of the manometric fluid by a sudden leak. Taps 5 and 6 could isolate the manometer tubes from the rest of the apparatus and it was necessary to include the reservoirs 7 and 8 to collect Silicone grease which drained out of the taps over a long period and thus avoid contamination of the manometric fluid. The bottom of the U-tube was joined to the oil reservoir 9 and the auxiliary taps 10, 11, 12, and 13. During use, the limb 1 was continuously evacuated through tap 5 to 5 microns pressure to eliminate traces of air which slowly diffused through the oil from the high-pressure side. During a measurement taps 6 and 10 were open, and 11, 12, and 13 closed, until the spoon gauge registered a deflection. This was balanced by introducing small quantities of dry air through 12 and 13. For small changes in level in the U-tube about 5 min. were allowed for drainage of the oil. The difference in levels was then read off (for pressures less than 10 mm. of Hg a travelling microscope was used). Tap 10 was then closed and by admission of more air through 12 and 13 or exhaustion through 11 the oil levels in 1 and 2 were simultaneously raised or lowered so that the pressure difference could be checked by using different parts of the U-tube. The di-*n*-butyl phthalate was purified by conventional methods and finally distilled *in vacuo*. Samples were taken at various times for density measurement.

The thermostat. The heating bath consisted of a 3-litre beaker filled with Silicone fluid (D.C.550). The thermoregulator was in the form of a helical coil which slid just inside the beaker and was made from tubing of external diam. 4 mm. (2.5 mm. bore) and was 4.5 m. long. The bottom was sealed off and the open end was joined to a vertical capillary (0.8 mm.). A Nichrome heating wire (250 w) was coiled evenly along the glass helix and the helix was supported on a glass framework made from 4 mm. rod which fitted into the clearance between the helix and the beaker. The helix was filled with mercury, and temperature control was effected by a "Sunvic" vacuum switch operated by the mercury regulator. An efficient paddle stirrer prevented temperature gradients, and the beaker was thermally insulated. Below 100° the temperature was constant within $\pm 0.015^{\circ}$ and above 100° no variation was detected by a thermometer reading to 0.1° . Temperatures were read to $\pm 0.05^{\circ}$ on a set of British Standard

⁴ Alexander and Fairbrother, *J.*, 1949, 2472.

⁵ *Idem*, *J.*, 1951, 3051.

thermometers of the partial-immersion type. A duplicate set which had been calibrated by N.P.L., Teddington, was kept for routine checking of the set in use.

FIG. 2. Section B. Still for fractional distillation. Inset is the magnetic valve.

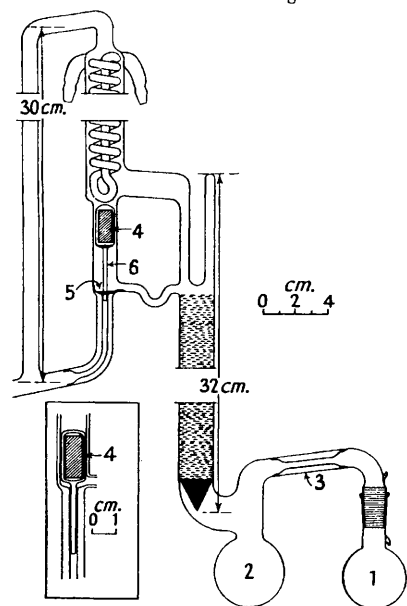


FIG. 4. Section A.

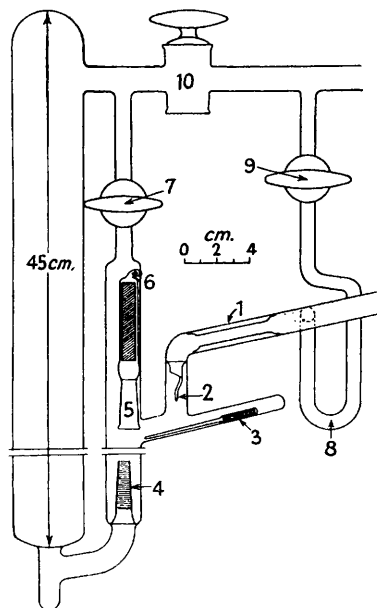


FIG. 3. Section D. The separator.

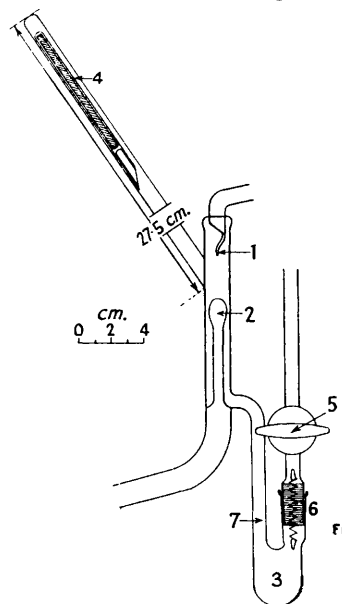
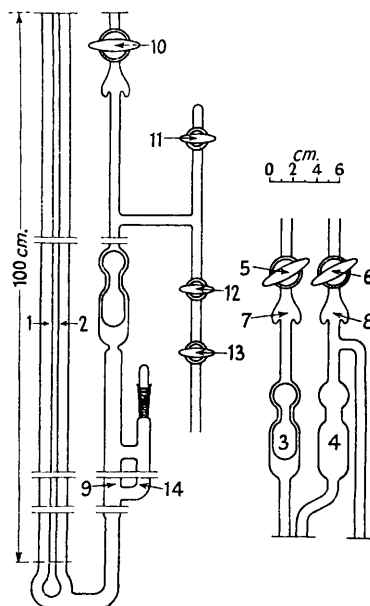


FIG. 5. Section M. The oil manometer.



Lubrication of joints. Tap no. 7 (Fig. 4) became hot during the outgassing process and during vapour pressure measurements at the higher temperatures. It was lubricated with Silicone high-vacuum grease, and a positive inward pressure was exerted on its key by a spring clip to prevent leakage. On all other taps and joints Apiezon M grease gave the best performance.

Tests for Purity.—The relative effect of a trace of volatile impurity in a sample of alkoxide is greatest at the lower vapour pressures and for this reason exhaustive tests for purity were carried out on samples at vapour pressures of *ca.* 0.050 mm. (*i.e.*, at about 30° for the *tert.*-butoxide and 70° for the *tert.*-amyloxide). With tap 7 and the A.10 joint (Fig. 4) closed the sample was allowed 20 min. at the appropriate temperature to reach equilibrium and the vapour pressure was then measured. The tap and joint were next opened and a portion of the sample was allowed to evaporate under a high vacuum. The sample was then isolated and its vapour pressure redetermined. This procedure was continued until all of the sample had evaporated. The sample was considered to be pure if it gave a constant vapour pressure throughout this procedure (except in the final stages when there was insufficient sample to give the saturated vapour pressure). The value of the vapour pressure thus determined was taken as the standard of purity by which to judge subsequent samples which were used for measurements over a wide temperature range. This criterion could be misleading if the impurity formed an azeotrope with the metal alkoxide, but in view of the analytical evidence and other considerations it seemed reasonable to rule out this possibility.

Measurement of Vapour Pressures.—Having established the purity of a sample at the low temperature, T_1° , a series of measurements were made at approximately 5° intervals in ascending order of temperatures over a range of about 30° up to, say T_2° . This was immediately followed by a descending series of measurements back to T_1° . The procedure was then repeated, but rising to a higher temperature T_3° ($>T_2^\circ$) followed by a return to T_1° . This somewhat laborious procedure was important for two reasons. First, the ascending-descending sequence would reveal by hysteresis any lag in attainment of equilibrium. Secondly, by raising the temperature in stages it was possible to approach the onset of decomposition without spoiling the sample too soon. Thus, if detectable decomposition had occurred at the high temperature T_x° this would be revealed in the subsequent descent to T_1° . This is a major advantage of a static method of measurement over a dynamic method and proved invaluable in this work. One other feature of the technique remains to be described, namely, the prevention of leakage of sample through the A.10 cone and socket (Fig. 4). This could become serious at the higher vapour pressures and it was prevented by winding an auxiliary heating tape around the dead space between the socket and tap 7 in order to stop condensation of the very small quantity of alkoxide which slowly leaked through the cone and socket joint.

RESULTS AND DISCUSSION

The results are presented as vapour pressures in mm. of mercury at 0° c (corrected for latitude and height above sea-level) and the temperatures are in degrees Kelvin. The temperature measurements are regarded as accurate within $\pm 0.05^\circ$ and the pressures within ± 0.005 mm.

When the results were plotted in the familiar form of $\log P$ against $1/T$, curvature was noted over the entire range investigated for both the *tert.*-butoxide and the *tert.*-amyloxide. The literature reveals at least fifty different vapour-pressure equations most of which are empirical, but the appearance of the curves for $\log P$ against $1/T$ suggested that the Kirchoff-Rankine equation might be applicable to our results and this equation has a theoretical basis. By following Frost and Kalkwarf's treatment⁶ it can readily be shown that the Kirchoff-Rankine equation ($\ln P = a + b/T + c \ln T$, where a , b , and c are constants) can be rearranged into the following form containing two constants:

$$\ln (P/P_t) = b(1/T - 1/T_t) + c \ln (T/T_t) \quad (1)$$

The parameters P_t and T_t correspond to any chosen experimental point. Equation (1) was further rearranged to the linear relation

$$Y = bX + c \quad (2)$$

where $Y = \log (P/P_t) / \log (T/T_t)$, and $X = [(T_t - T)/TT_t] / 2.3026 \log (T/T_t)$. The best straight line for equation (2) was determined by the least-squares method and the

⁶ Frost and Kalkwarf, *J. Chem. Phys.*, 1953, **21**, 264.

constants b and c thus evaluated. The third constant a was deduced as follows. An arbitrary value of temperature T_n being used and T_f known, the function X was evaluated. The function Y for this value of temperature was then evaluated from the known values of X , b , and c . The value of the pressure P_n corresponding to the temperature T_n was deduced by solving the function Y . Finally, a was calculated by substituting the values of P_n , T_n , b and c in the original Kirchoff-Rankine equation. The main problem in this computation lies in making the correct choice of the arbitrary parameters P_f and T_f for there is no *a priori* method of selecting an experimental point which will be exactly on the line of best fit. In practice we adopted a graphical method of successive approximations to find the correct value of P_f and T_f starting from an experimental point in the high-pressure end of the results. This procedure was feasible because the linear equation (2) was found to be sensitive to the values of P_f and T_f and exhibited pronounced curvature when P_f was in error by more than *ca.* 1%. Satisfactory values of P_f and T_f were established by this graphical trial-and-error method. In principle the three-constant Kirchoff-Rankine equation can be solved by the least-squares method but with our data this was not possible because the constant c proved to be indeterminate.

The results for titanium *tert.*-butoxide and *tert.*-amyloxide are presented in Tables 1 and 2. The experimentally determined vapour pressures P are given in order of ascending temperature although two completely independent series of measurements were carried out on each compound. The values in parentheses were excluded from the above computation for the following reasons. Values below 0.3 mm. are liable to an error of *ca.* 3% in view of the estimated limit of ± 0.005 mm. in the accuracy of measurements. On the other hand an error arises at the high-pressure end due to slight thermal decomposition and accordingly these values were excluded although the amount of decomposition was very small. The values of $P_{\text{calc.}}$ were obtained from the computed equation on the assumption that there was no error in the temperature reading.

Titanium Tetra-tert.-butoxide.—The computed results in Table 1 gave the equation:

$$\log P = 51.0192 - 5278.11/T - 14.0219 \log T$$

For the 25 values used in the computation the percentage standard deviation $\sigma = (\Delta P)^2/(n - 1)$ [where $\Delta P = 100(P_{\text{calc.}} - P/P_{\text{calc.}}$, and $n = \text{no. of observations}$] is 1.1%

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

Temp. (K)	P (mm.)	$P_{\text{calc.}}$	Temp. (K)	P (mm.)	$P_{\text{calc.}}$	Temp. (K)	P (mm.)	$P_{\text{calc.}}$
299.1°	(0.039)	0.045	312.0°	(0.139)	0.135	352.2°	2.110	2.100
300.1	(0.036)	0.050	312.8	(0.147)	0.144	354.9	2.456	2.453
301.1	(0.049)	0.054	316.0	(0.188)	0.184	355.6	2.546	2.553
301.1	(0.051)	0.054	317.3	(0.198)	0.204	357.9	2.918	2.905
301.5	(0.046)	0.056	320.5	(0.269)	0.260	358.9	3.071	3.071
301.7	(0.055)	0.057	322.3	0.299	0.297	361.0	3.495	3.446
302.1	(0.056)	0.059	322.8	0.300	0.308	361.6	3.596	3.560
303.2	(0.067)	0.065	324.9	0.362	0.358	365.1	4.271	4.293
303.4	(0.062)	0.066	327.7	0.449	0.437	368.7	5.161	5.177
303.8	(0.064)	0.068	331.4	0.576	0.566	368.9	5.226	5.230
305.0	(0.078)	0.076	332.1	0.592	0.593	371.7	6.035	6.031
305.2	(0.078)	0.077	334.9	0.707	0.716	382.3	10.11	10.06
305.3	(0.078)	0.078	335.1	0.737	0.726	387.7	12.82	12.87
306.5	(0.083)	0.086	338.5	0.907	0.907	393.6	(16.62)	16.66
307.9	(0.099)	0.097	345.6	1.405	1.417	398.1	(20.15)	20.14
308.5	(0.095)	0.101	347.3	1.583	1.571	402.1	(24.09)	23.72
309.1	(0.109)	0.107	349.5	1.788	1.792	409.1	(31.88)	31.23
309.5	(0.109)	0.110						

and corresponds to a probable error for any point of 0.74%. Moreover there are 15 changes of sign in the error ΔP in ascending this series of 25 points and this is in accordance with the requirements of a good statistical fit⁷ to the proposed equation: *e.g.*, the number of

⁷ Bond, "Probability and Random Errors," Arnold, London, 1935, p. 117.

changes of sign should be $\{(n-1+m)/2\} \pm 0.34\sqrt{(n-1-m)}$, where n is the number of observation and m the number of constants in the equation. It is noteworthy that for the pressures at 402.1° and 409.1° the deviation $P - P_{\text{calc.}}$ agreed closely with the decomposition pressure calculated by applying the gas laws to the residual pressure found on returning to the low pressure region when the technique described in the Experimental section was used. Also, it is interesting to compare values of $P_{\text{calc.}}$ with the experimental results (in parentheses) in the low-pressure region. The agreement between P and $P_{\text{calc.}}$ is remarkably good and the standard deviation for the 23 points is 0.007 mm. with 11 changes of sign.

Titanium Tetra-tert.-amyloxyde.—The computed results in Table 2 gave the equation:

$$\log P = 43.1238 - 5472.28/T - 11.1706 \log T$$

TABLE 2. *Titanium tetra-tert.-amyloxyde.*

Temp. (K)	P (mm.)	$P_{\text{calc.}}$	Temp. (K)	P (mm.)	$P_{\text{calc.}}$	Temp. (K)	P (mm.)	$P_{\text{calc.}}$
343.0°	(0.062)	0.071	385.3°	1.081	1.085	415.4°	5.014	5.017
343.7	(0.049)	0.074	388.5	1.291	1.297	416.8	5.344	5.349
345.6	(0.086)	0.086	388.9	1.321	1.326	421.1	6.485	6.495
346.2	(0.061)	0.089	391.4	1.541	1.519	423.0	7.065	7.066
349.0	(0.111)	0.109	391.6	1.531	1.535	423.2	7.105	7.128
349.1	(0.078)	0.110	392.5	1.611	1.611	424.0	(7.494)	7.382
350.3	(0.108)	0.120	392.5	1.621	1.611	424.9	(7.906)	7.680
352.4	(0.147)	0.139	394.8	1.801	1.819	430.0	(9.917)	9.553
353.7	(0.141)	0.152	398.0	2.161	2.149	433.3	(11.33)	10.96
354.3	(0.149)	0.159	399.1	2.262	2.273	435.2	(12.28)	11.86
355.3	(0.179)	0.170	399.7	2.348	2.344	440.3	(15.19)	14.56
356.1	(0.161)	0.179	401.3	2.542	2.542	444.0	(17.51)	16.83
357.5	(0.193)	0.197	401.4	2.552	2.554	446.3	(19.19)	18.38
360.1	(0.207)	0.235	404.7	3.053	3.012	451.6	(23.64)	22.44
361.2	0.251	0.252	404.9	3.053	3.041	453.1	(25.01)	23.72
366.2	0.350	0.348	408.9	3.683	3.694	453.7	(25.58)	24.25
371.1	0.479	0.473	410.2	3.943	3.932	460.2	(32.58)	30.62
377.7	0.690	0.703	411.2	4.103	4.123	469.6	(45.20)	42.26
378.8	0.749	0.750						

The computation was carried out in the same manner as for the butoxide and the standard deviation for the 28 points involved was $\pm 0.66\%$, corresponding to a probable error for any point of $\pm 0.44\%$. The number of changes of sign of ΔP in ascending the series was 12 which is close to the statistical requirement of 15 ± 2 for a random distribution of errors. Comparing the observed vapour pressures (in parentheses) at the low-pressure end of the series with those calculated from the vapour-pressure equation shows that the observed values are mainly lower than the calculated. However, in view of the probable error in the measurements in this region the agreement is good. For the 14 points involved the standard deviation is ± 0.017 mm. with 8 changes of sign (cf. 8 ± 1 sign changes required for random distribution). It seems reasonable to suggest that vapour pressures in the temperature range $340\text{--}360^\circ \text{K}$ may be calculated by extrapolation of the vapour-pressure equation with greater precision than we have been able to measure them. The data in parentheses in the higher-pressure region show some interesting features. The experimental vapour pressures are all higher than calculated, and the deviation increases with rise in temperature. In fact, as shown in Fig. 6, there is a striking correlation between the % deviation from the calculated and the % of $P_{\text{obs.}}$ due to volatile products of decomposition. This suggests the simple relation: $P_{\text{calc.}} = P_{\text{obs.}} - \delta$, where δ is the partial pressure of volatile products of decomposition measured in the manner already mentioned. Accordingly we suggest that vapour pressures in the temperature range $425\text{--}470^\circ \text{K}$ may be reliably calculated by extrapolation of the vapour-pressure equation. Concerning the thermal decompositions at the higher temperatures we should point out that even at the highest temperatures studied no increase in pressure was detected during the time taken in making a pressure measurement and hence the decomposition was slow.

Nevertheless, during the longer time interval involved in changing from one temperature to the next a significant quantity of decomposition products could accumulate and was detected by the procedure already outlined. Finally we emphasize that in the computation of the vapour-pressure equation all the experimental results are taken in the temperature

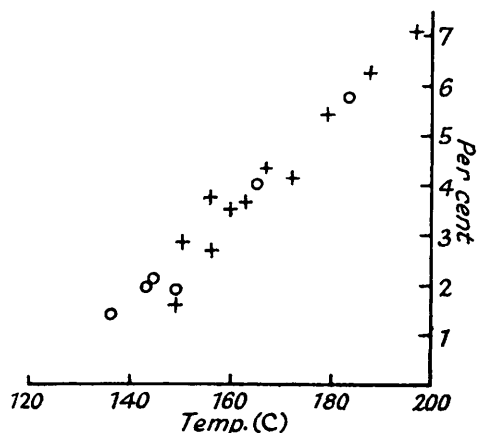


FIG. 6. Correlation of thermal decomposition and deviation of vapour pressure from calculated values, for titanium tetra-tert.-amyloxyde.

O, Percentage of $P_{obs.}$ due to residual gas.
+, Deviation of $P_{obs.}$ from calculated curve.

region in which no decomposition was detected even by the very sensitive method of measuring the residual pressure at low temperature.

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