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A Problem in Structural Chemistry.

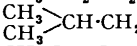
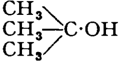
By W. WARDLAW, C.B.E., D.Sc., F.R.I.C.

THERE is in all well-regulated minds an instinctive love of order. Its appeal is both æsthetic and practical. The mere physical process of arranging, sorting, or classifying a miscellaneous heap of objects gives a certain pleasure. A cupboard of confused odds and ends, a littered desk, arouse in most of us at least an aspiration—not always I fear realised—to put things straight. The pleasure of producing order out of chaos among our possessions—if we really set ourselves to the task—is never-failing. Order is the basis of beauty and harmony as well as efficiency. It is particularly significant in science. A former President of the Chemical Society, Sir Cyril Hinshelwood, has stated in his book, " The Structure of Physical Chemistry " : " Science is not the mere collection of facts, which are infinitely numerous and mostly uninteresting, but the attempt by the human mind to order these facts into satisfying patterns. Now a pattern or design is not a purely objective function but something imposed by the mind on what is presented to it, as is seen in those pictures of piled cubes which can be made at will to appear in advancing or receding order. The imposition of design on Nature is in fact an act of artistic creation on the part of the man of science, though it is subject to a discipline more exacting than that of poetry or painting."

Today I propose to outline an investigation which has given considerable scope for the ordering of facts into satisfying patterns. In doing so I shall keep well in mind the advice of the old proverb which says that the shoemaker should not go beyond his last.

The silicon esters have been known for over a hundred years. The preparation of silicon tetrachloride by Berzelius in 1824 enabled A. Ebelmen in 1846 to produce ethyl and pentyl orthosilicates by the simple reaction, $SiCl_4 + 4ROH = Si(OR)_4 + 4HCl$. Since that time many simple and mixed alkoxides of silicon have been prepared and examined and their physical properties studied and recorded. In marked contrast the corresponding derivatives of titanium and zirconium were obtained for the first time in the twenties of this century. An examination of the boiling points of some of the tetraethoxides of these three elements discloses a remarkable change in physical properties (see Table 1). The important features which emerge from this preliminary survey are : (i) that the increases in boiling points of alkoxides containing a given *n*-alkyl group, when the central atom changes from silcon to titanium to zirconium, are much greater than is expected on the simple basis of increases in molecular weight; and (ii) that the increase in volatility resulting from branching of the alkyl groups, in isomeric alkoxides, is common to the alkoxides of these elements, but the magnitudes of this effect are in the order Zr > Ti > Si.

TABLE 1.

Alcohol	Boiling point of tetra-alkoxide of : silicon	titanium	zirconium
$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$	106·8°/0·5 mm.	155°/1 mm.	253°/0·3 mm.
 $(CH_3)_2{>}CH\cdot CH_2\cdot OH$	90—91°/0·5 mm.	141°/1 mm.	—
$CH_3\cdot CH_2\cdot CH(OH)\cdot CH_3$	86—88°/0·5 mm.	90—92°/0·8 mm.	178°/0·5 mm.
 $(CH_3)_3C\cdot OH$	—	62·3°/1 mm.	46°/0·2 mm.

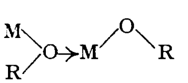
These points suggest that striking differences can be expected in either the degree of molecular complexity or the amount of ionic character in the alkoxides of silicon, titanium, and zirconium. It is also tempting to postulate that increased branching of the alkyl group sterically prevents close intermolecular bonding and thus leads to increased volatility. To test the validity of these ideas the isomeric pentyloxides of silicon, titanium, and zirconium were studied. This series was selected because the molecular weight of the alkyl group remained constant and particularly because little was known about the properties of these compounds. Table 2 summarises the results.

TABLE 2.

Alcohol	Titanium alkoxide B. p./mm.	*M*	Mol. comp.	Zirconium alkoxide B. p./mm.	*M*	Mol. comp.
$CH_2Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	175°/0·8	565	1·4	256°/0·01	1428	3·2
$CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	148°/0·1	490	1·2	247°/0·1	1462	3·3
$CHMeEt{\cdot}CH_2{\cdot}OH$	154°/0·5	422	1·1	238°/0·1	1615	3·7
$CMe_3{\cdot}CH_2{\cdot}OH$	105°/0·05	500	1·3	188°/0·2	1051	2·4
$CHEt_2{\cdot}OH$	112°/0·05	399	1·0	178°/0·05	868	2·0
$CHMePr^n{\cdot}OH$	135°/1·0	410	1·0	175°/0·05	860	2·0
$CHMePr^i{\cdot}OH$	131°/0·5	415	1·0	156°/0·01	870	2·0
$CMe_2Et{\cdot}OH$	98°/0·1	405	1·0	95°/0·1	455	1·0

In addition it was found that the *n*-pentyloxide of silicon (b. p. 134°/0·1 mm.), although monomeric, was much less volatile than the isomeric *neo*pentyl orthosilicate (b. p. 85°/0·1 mm.). The striking change in volatility of pentyloxides is seen more effectively in Table 2 where the boiling points are compared. The important points which emerge are that branching of the pentyl groups leads to increased volatility in the alkoxides of silicon, titanium, and zirconium but that the effect is most pronounced with the zirconium derivatives. Further it is established that volatility is directly related to molecular complexity (determined ebullioscopically in benzene) in the pentyloxides of zirconium. Although less pronounced, a similar trend in molecular complexity occurs with the titanium derivatives but there is little doubt that all the pentyloxides of silicon are monomeric.

It seems reasonable to suppose that intermolecular bonding accounts for the abnormally high boiling points of the less branched compounds and involves the mechanism (I). This type of molecular association will be strongly opposed when the central atom is shielded by branched alkoxide groups. In the monomeric alkoxides it is evident that the shielding is complete. It may well be that this behaviour is connected with the atomic radius of the central atom. Thus zirconium will require more effective shielding than the smaller silicon or titanium. It is noteworthy that in combination with oxygen the maximum covalency of silicon and titanium is 6 whereas zirconium can exhibit a covalency of 8.



(I)

*neo*Pentylalcohol, although a primary alcohol, has been shown to exhibit a pronounced steric effect in the ordinary reactions of organic chemistry. Both in the case of titanium and of zirconium the boiling points of the tetra*neo*pentyloxides are close to those of their secondary analogues, and their molecular complexity is only slightly higher than that of the secondary alkoxides.

It seems reasonable to suppose that all tetra-*tert.*-alkoxides of titanium and zirconium would be monomeric. This would allow a study to be made of the influence of molecular size on volatility whilst an examination of isomeric higher *tert.*-alkoxides should decide whether structural effects are still important. Further, the influence of the central atom on volatility could be assessed. Accordingly the series of alkoxides $M(O{\cdot}CMe_nEt_{3-n})_4$, $M(O{\cdot}CMe_2R)_4$, and $M(O{\cdot}CMeEtPr^i)_4$ have been prepared and examined where M = Ti or Zr, $n = 0, 1, 2,$ or 3, and R = Me, Et, Pr^n, Pr^i, or Bu^t. In ebullioscopic experiments all the compounds measured were found to be monomeric. Boiling points were measured at several pressures between 0·1 and 10 mm. for the more volatile compounds and in all cases the data fitted straight lines of the form $\log p_{mm.} = a - b/T$ in the pressure range 2—10 mm. The values for the constants a and b are listed in Table 3, together with boiling points (at 5·0 mm. pressure), latent heats of vaporisation (L_v), and entropies of vaporisation at 5·0 mm. ($\Delta S_{5\cdot 0}$). The boiling points from Table 3 are plotted against molecular weights in Fig. 1, and the boiling points of the higher alkoxides are given in Table 4. It will be seen that the boiling points do not increase linearly with molecular weight. Moreover the three tertiary heptyloxides gave boiling points in the order

$$M(O{\cdot}CMeEtPr^i)_4 > M(O{\cdot}CEt_3)_4 > M(O{\cdot}CMe_2Bu^t)_4$$

showing clearly that in the monomeric tertiary alkoxides the effect of chain branching is still significant. An interesting point that emerges from Table 3 is that although the latent heats increase with molecular size the entropies of vaporisation are sensibly constant ($42 \pm 2{\cdot}5$ cal. mole^{-1} deg.$^{-1}$) irrespective of whether the central atom is titanium or zirconium, thus emphasising the structural similarity of these compounds. For a given tertiary alkoxide it is seen that there is little difference in the boiling points of the titanium and the zirconium derivative. In fact it appears that the titanium analogue often has the higher boiling point.

Although the results so far considered support the theory that steric effects are most

TABLE 3.

Alkoxide	B. p.	L_v (kcal. mole^{-1})	a	b	$\Delta S_{5\cdot0}$ (cal. mole^{-1} deg.$^{-1}$)
$Ti(O\cdot CMe_3)_4$	93·8°	14·5	9·34	3170	39·5
$Zr(O\cdot CMe_3)_4$	89·1	15·2	9·90	3330	42·0
$Ti(O\cdot CMe_2Et)_4$	142·7	16·7	9·46	3640	40·0
$Zr(O\cdot CMe_2Et)_4$	138·4	16·3	9·34	3550	39·5
$Ti(O\cdot CMeEt_2)_4$	170·4	19·0	10·1	4170	43·0
$Zr(O\cdot CMeEt_2)_4$	171·4	19·0	10·1	4170	43·0
$Ti(O\cdot CMe_2Pr^n)_4$	167·0	19·5	10·4	4270	44·0
$Zr(O\cdot CMe_2Pr^n)_4$	161·6	19·0	10·2	2140	44·0

TABLE 4. *Boiling points.*

Alcohol	Ti alkoxide	Zr alkoxide
$CMe_2Pr^i\cdot OH$	147°/0·5 mm.	133°/0·1 mm.
$CEt_3\cdot OH$	180°/0·5 mm.	180°/0·4 mm.
$CMe_2Bu^t\cdot OH$	163°/0·5 mm.	168°/0·5 mm.
$CMeEtPr^i\cdot OH$	197°/1·0 mm.	194°/0·7 mm.

important in determining the physical properties of the alkoxides, the alternative explanation that the strong (+*I*) inductive effect of the tertiary alkyl group might be responsible for the striking properties of the tertiary alkoxides must be examined. In an endeavour to resolve these possibilities a detailed study of the following series of secondary alkoxides has been made: $M(O\cdot CHR_2)_4$ where R = Me, Et, Pr^n, Pr^i, or Bu^n; and $M(O\cdot CHMeR)_4$ where R = Et, Pr^n, Pr^i, Bu^n, Bu^t, or *n*-hexyl. In the first series, the derivatives of the symmetrical dialkylcarbinols, the steric effect will increase rapidly with size of the alkyl group but the +*I* effect will soon reach saturation. In the other series more gradual steric effects can be achieved. The results are collected in Table 5.

FIG. 1.

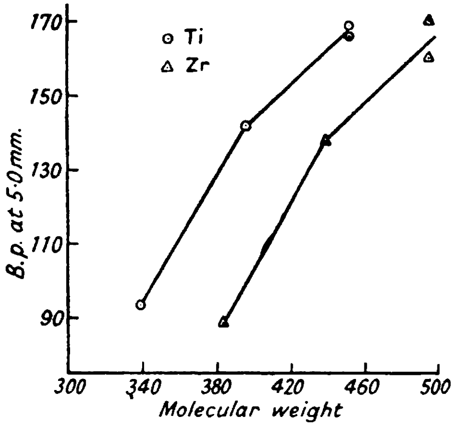


TABLE 5.

Alkyl	Ti alkoxide			Zr alkoxide		
	B. p./0·1 mm.	*M*	*x*	B. p./0·1 mm.	*M*	*x*
$CHMe_2$	49°	390	1·4	160°	967	3·0
$CHEt_2$	112	399	1·0	181	868	2·0
$CHPr^n_2$	156	500	1·0	163	545	1·0
$CHPr^i_2$	162	474	1·0	158	557	1·0
$CHBu^n_2$	195	—	—	198	—	—
CHMeEt	81	—	—	164	909	2·5
$CHMePr^n$	115	410	1·0	178	860	2·0
$CHMePr^i$	117	415	1·0	176	870	2·0
$CHMeBu^n$	126	—	—	190	—	—
$CHMeBu^t$	127	—	—	128	481	1·0
$CHMe\cdot C_6H_{13}$	182	—	—	212	1039	1·7

The contrast between titanium and zirconium is clearly shown. For example, in the dialkylcarbinol series the titanium derivatives, with the exception of the lowest member, are monomeric whereas in the zirconium series the molecular complexity, *x*, changes from 3 to 2 to 1 as the alkyl groups are changed from methyl to ethyl to propyl. It is noteworthy that the monomeric secondary alkoxides of zirconium are close in volatility to their titanium analogues as would be expected for monomeric alkoxides. In the alkylmethylcarbinol series the titanium derivatives are monomeric when R in $\mathrm{Ti(O{\cdot}CHMeR)_4}$ is propyl or higher, whilst the molecular complexity of the zirconium derivatives decrease from 3 to 2 to 1·7 as the alkyl chain is increased from methyl to ethyl to *n*-hexyl. This behaviour emphasises the steric nature of the effects being investigated since in the zirconium series none of the 1-methylalkoxides shows as complete shielding as the derivatives of the dipropylcarbinols. Moreover the introduction of more remote branching in the alkylmethylcarbinol series considerably enhances the shielding. Thus the zirconium derivative of *n*-butylmethylcarbinol (hexan-2-ol) is complex (*x* between 1·7 and 2·0) and has a much higher boiling point than the monomeric zirconium derivative of the isomeric *tert.*-butylmethylcarbinol (3 : 3-dimethylbutan-2-ol). The evidence so far presented strongly favours the suggestion that it is the steric effect of the alkoxide group and not the $+I$ effect of the alkyl group which is responsible for the remarkable properties of zirconium tetra-alkoxides. This view is supported by the data in Table 6 which show that the boiling points of isomeric monomeric alkoxides of titanium and zirconium are close together irrespective of whether the alkoxide is secondary or tertiary.

TABLE 6.

Alkyl	$\mathrm{Ti(OR)_4}$ B. p./0·1 mm.	$\mathrm{Zr(OR)_4}$ B. p./0·1 mm.	Alkyl	$\mathrm{Ti(OR)_4}$ B. p./0·1 mm.	$\mathrm{Zr(OR)_4}$ B. p./0·1 mm.
$\mathrm{CHMeBu^t}$ ...	127°	128°	$\mathrm{CHPr^i_2}$	162°	158°
$\mathrm{CMeEt_2}$	122	127	$\mathrm{CEt_3}$	166	168
$\mathrm{CHPr^n_2}$	156	163	$\mathrm{CMe_2Bu^t}$ ...	149	154

Until recently only a few secondary alkoxides were known. However, new silicon tetra-alkoxides have been made and their boiling points measured at various pressures. Boiling points have also been determined at various pressures for the first three members of the series of titanium secondary alkoxides and zirconium tetra*iso*propoxide. In the pressure range 2·0—10·0 mm. the data conformed to the characteristic equation : $\log p_{\mathrm{mm.}} = a - b/T$. The values of a and b, boiling points at 5·0 mm. ($T_{5{\cdot}0}$), and latent heats of vaporisation at 5·0 mm. ($\Delta S_{5{\cdot}0}$ cal. mole^{-1} deg.$^{-1}$) are presented in Table 7. This Table shows that although tetra*iso*propyl and tetra-(1-ethylpropyl) orthosilicate are undoubtedly monomeric they differ by 6·9 units in entropy of vaporisation and that the compound which has the more shielded central atom has unexpectedly the higher entropy of vaporisation. In addition, the monomeric titanium derivative of diethylcarbinol (pentan-3-ol) has an entropy of vaporisation 8·7 units greater than that of its silicon analogue. Hitherto attention has been focused on intermolecular attraction involving oxygen and the central atom in $\mathrm{M(OR)_4}$, but these new anomalies suggest that strong intermolecular attraction of another kind, involving the alkyl groups, is also present.

TABLE 7.

Alkoxide	$T_{5{\cdot}0}$	a	b	L_v	$\Delta S_{5{\cdot}0}$
$\mathrm{Si(OPr^i)_4}$	55·8°	8·1	2440	11·2	34·0
$\mathrm{Si(O{\cdot}CHEt_2)_4}$	139·0	9·7	3690	16·9	40·9
$\mathrm{Ti(OPr^i)_4}$	91·3	9·6	3225	14·7	40·5
$\mathrm{Ti(O{\cdot}CHMeEt)_4}$	127·8	11·9	4345	19·9	49·6
$\mathrm{Ti(O{\cdot}CHEt_2)_4}$	157·3	11·6	4640	21·4	49·6
$\mathrm{Zr(OPr^i)_4}$	203·8	15·16	6895	31·5	66·1

Two mechanisms seem reasonable to explain the abnormally greater degree of structure in the liquid than in the vapour as the size of the alkyl group is increased. The first mechanism involves " entanglement " of neighbouring alkyl groups in the liquid state, thus providing an additional entropy requirement in the vaporisation process, whilst an alternative explanation lies in the possibility that rotation of the alkoxy-groups is more restricted in the liquid than in the vapour. It is clear that alkyl-group interaction would be expected to feature decisively in the properties of the straight-chain normal alkoxides.

The following *n*-alkoxides of titanium and zirconium have been prepared and investigated : $\mathrm{Ti(OC_nH_{2n+1})_4}$ where n = 2—8 and $\mathrm{Zr(OC_nH_{2n+1})_4}$ where n = 2—6 or 8. Zirconium tetra-*n*-hexyloxide could not be distilled at 0·05 mm. without decomposition and no attempt was made to distil zirconium tetra-*n*-octyl oxide. Molecular weights (*M*) were determined on freshly distilled alkoxides in boiling benzene and the results, including molecular complexity (*x*) and boiling points, are presented in Table 8. This shows two outstanding features : (*a*) that

TABLE 8.

Alcohol	Titanium alkoxide B. p./0·1 mm.	*M*	*x*	Zirconium alkoxide B. p./0·1 mm.	*M*	*x*
Ethanol	103°	556	2·4	180° *	980	3·6
Propan-1-ol	124	—	—	208	—	—
Butan-1-ol	142	—	—	243	1290	3·4
Pentan-1-ol	158	565	1·4	276	1428	3·2
Hexan-1-ol	176	—	—	300	—	—
Heptan-1-ol	201	—	—	—	—	—
Octan-1-ol	214	781	1·4	—	2046	3·4

* Sublimed.

molecular complexity in the zirconium alkoxides is much greater than in the titanium alkoxides and (*b*) that molecular complexity in both series is little affected by chain length. That molecular complexity is greater in zirconium alkoxides than in the corresponding titanium alkoxides can be explained as due either to stereochemical effects or to a difference in strength of the intermolecular bonding. The stereochemical argument is very strong in view of the greater atomic radius and maximum covalency of zirconium, and evidence is available which suggests that the strength of intermolecular bonding involving titanium and oxygen is comparable with that involving zirconium and oxygen. Caughlan *et al.* (*J. Amer. Chem. Soc.*, 1951, **73**, 5652) have suggested that each titanium atom in the trimeric alkoxides is surrounded octahedrally by oxygen atoms from alkoxide groups and that the trimeric unit comprises three octahedra bound by common faces. A similar arrangement seems reasonable for trimeric zirconium alkoxides but the molecular complexity in zirconium normal alkoxides is significantly greater than three. The fractional value suggests that a species of higher molecular complexity is present, and a possible structure for a pentameric complex is shown in Fig. 2 in which octahedra share edges or faces. These structures involve zirconium with the co-ordination number 6, and the possibility that zirconium attains the co-ordination number 8 in these compounds cannot be ignored.

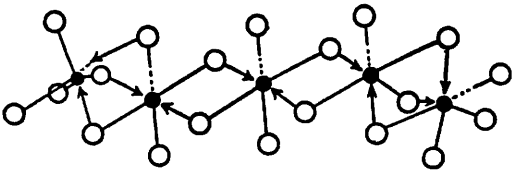
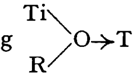
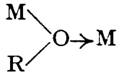


FIG. 2.
R *groups omitted.* $[Zr(OR)_4]_5$.
● = Zr; ○ = *Oxygen.*

It was suggested that the anomalous entropies of vaporisation of certain monomeric alkoxides of silicon and titanium were due to interaction of the alkyl groups, and this conception could be tested by studying the *n*-alkoxides of silicon and titanium. Cullinane *et al.* (*J. Appl. Chem.*, 1951, **1**, 400) gave boiling points at various pressures for the titanium tetra-*n*-alkoxides $Ti(OC_nH_{2n+1})_4$ where $n = 2—6$. Although their data do not conform very accurately to the relation $\log p = a - b/T$, provisional calculations of latent heats and entropies of vaporisation can be made from them. In addition the vapour pressures of tetra-*n*-butyl and tetra-*n*-hexyl orthosilicate have been measured, whilst the data for the tetraethyl orthosilicate have been taken from Post (" Organic Silicon Compounds," Reinhold Publ. Corp., New York, 1949). The latent heats and Trouton constants (Table 9) present strong evidence that alkyl-group interaction occurs in the *n*-alkoxides of silicon and titanium. For tetraethyl orthosilicate the intermolecular attraction involving silicon and oxygen must be relatively small, and it should decrease steadily with increase in size of alkyl group. However, it is found that the entropies of vaporisation increase with alkyl chain length. This effect is partly due to the increase in Trouton's constant with decrease in vapour concentration at 760 mm. at the higher boiling points (cf. Hildebrand, *J. Amer. Chem. Soc.*, 1915, **37**, 970). Accordingly, the entropies of vaporisation

TABLE 9.

Alkoxide	L_v	Trouton const.	Alkoxide	L_v	Trouton const.
$Si(OEt)_4$	11·25	25·7	$Ti(OEt)_4$	21·6	42·5
$Si(OBu^n)_4$	14·84	28·0	$Ti(OPr^n)_4$	15·7	29·1
$Si(O{\cdot}C_6H_{13}\text{-}n)_4$	21·78	33·5	$Ti(OBu^n)_4$	20·1	35·6
			$Ti(O{\cdot}C_5H_{11}\text{-}n)_4$	23·1	39·4
			$Ti(O{\cdot}C_6H_{13}\text{-}n)_4$	24·6	40·5

(cal. deg.$^{-1}$ mole^{-1}), corrected to the same vapour concentration, were calculated and found to be $Si(OEt)_4$ 25·7, $Si(OBu^n)_4$ 27·1, and $Si(O{\cdot}C_6H_{13}\text{-}n)_4$ 31·7. It is suggested that this increase in entropy of vaporisation with increase in chain length is due to molecular " entanglement " in the liquid state. A molecule $(MO{\cdot}C_nH_{2n+1})_4$ can be considered as equivalent to two chains of $(2n + 3)$ atoms fused at the central atom M, and the possibility of entanglement of such tenuous structures is evident. A molecule in the liquid will require special orientation in order to be disentangled before vaporisation, and this increases the entropy of vaporisation. This theory enables one to interpret the surprising order of Trouton constants for the titanium *n*-alkoxides (Table 9). First, the high value for the ethoxide is attributed to the presence of complex molecules involving  $\left.\begin{matrix}\text{Ti}\\ \text{R}\end{matrix}\right\rangle\text{O}\rightarrow\text{Ti}$ bonds and it is clear that the vaporisation process in $Ti(OEt)_4$ resembles that of the complex zirconium alkoxides. Thus $\Delta S_{5\cdot0}$ is 52·6 cal. deg.$^{-1}$ mole^{-1} for $Ti(OEt)_4$ [cf. 59·4 for $Zr(OEt)_4$] and E is 10 kcal. mole^{-1} [cf. 17·6 for $Zr(OEt)_4$]. If allowance is made for the greater shielding of titanium in $Ti(OEt)_4$ (complexity = 2·4) than of zirconium in $Zr(OEt)_4$ (complexity = 3·6) it seems possible that the energy of  $\left.\begin{matrix}\text{M}\\ \text{R}\end{matrix}\right\rangle\text{O}\rightarrow\text{M}$ bonds is approximately the same for M = Ti or Zr. The greater shielding power of propoxide groups explains the decrease in molecular complexity and Trouton constant in passing from the ethoxide to the *n*- or *iso*-propoxide of titanium. Further increase in length of alkyl group leads to an increase in Trouton's constant, which can be ascribed to the predominance of the " entanglement " process.

Although the alkyl-group interaction has provisionally been interpreted as due to molecular " entanglement " in the liquid an alternative explanation in terms of restricted rotation of alkoxide groups is possible. This would require free rotation in the vapour and restricted rotation in the liquid, whilst the amount of rotation in the liquid should decrease with increase in alkyl chain length. Unfortunately, the published data on the dipole moments of these compounds are inconsistent and more accurate measurements are required before a decision can be made.

It has been mentioned that for a given tertiary alkoxide there is little difference in the boiling points of the titanium and the zirconium derivative and it appears that the titanium analogue often has the higher boiling point. From general considerations it would be reasonable to expect that the order of volatilities for the tetra-*tert.*-alkoxides of silicon and the Group IVA elements would be

$$Si(OR)_4 > Ti(OR)_4 > Zr(OR)_4 > Hf(OR)_4 > Th(OR)_4$$

However, it has been established that the order of volatility is Hf > Zr. The boiling points of hafnium alkoxides and analogous zirconium compounds are given in Table 10. It is evident that the molecular complexity of hafnium alkoxides must be the same as that of the analogous zirconium derivatives. An important feature of this Table is the fact that in no case is a hafnium alkoxide less volatile than its zirconium analogue. As a result of boiling-point measurements in the pressure range 2·0—10·0 mm. on the *tert.*-pentyloxide the latent heat (L_v) and entropy of vaporisation at 5 mm. ($\Delta S_{5\cdot0}$) have been calculated. These results are shown below together with the density ρ (g./c.c.) and molar volume (V_1 c.c.) at 25° :

TABLE 10.

Alkyl	B. p. of $Hf(OR)_4$	B. p. of $Zr(OR)_4$
Ethyl	180—200°/0·1 mm.	180—200°/0·1 mm.
*iso*Propyl	170°/0·35 mm.	172°/0·35 mm.*
tert.-Butyl	90°/6·5 mm.	92·5°/6·0 mm.
tert.-Pentyl	92°/0·1 mm.†	95°/0·1 mm.

* Calc. from 160°/0·1 mm. † Calc. from 106°/0·5 mm.

Alkoxide	$T_{5\cdot0}$	L_v	a	b	$\Delta S_{5\cdot0}$	ρ	V_1
$Zr(O{\cdot}CMe_2Et)_4$	138·4°	16·2	9·34	3550	39·5	0·975	451·1
$Hf(O{\cdot}CMe_2Et)_4$	136·7°	16·3	9·41	3570	39·8	1·159	454·5

It is not surprising to find the close similarity in latent heat, entropy of vaporisation, or molar volume for these two compounds since the chemical similarity of zirconium and hafnium is well established. However the order of volatilities Hf > Zr > Ti demands examination. My colleague, Dr. D. C. Bradley (*Nature*, 1954, **174**, 323), has directed attention to the fundamental effect of molecular mass on volatility since it does not support the widely accepted view that volatility decreases with rising molecular weight. The latter view relies on the various empirical relations between molecular weight and boiling point but it has no theoretical basis. By contrast the fundamental effect of mass on volatility has a theoretical background and affords a rational explanation of certain boiling-point anomalies. Bradley points out that the fundamental effect is clearly revealed by the comparison of vapour pressures of compounds differing only in isotopic composition (isotopic molecules). These comparisons are least complicated by differences in intermolecular forces and it can be assumed that differences in vapour pressures are due to the effect of mass alone. The relative vapour pressures of isotopic molecules vary in a complex manner and it is intriguing to find that the lighter species is not always the more volatile. In fact the review by Clusius (*Z. Elektrochem.*, 1938, **44**, 21) of hydrogen and deuterium compounds shows that the relative vapour pressures vary with temperature in the sense that higher temperatures favour the volatility of the heavier species. Similar behaviour by other isotope molecules was reported by Urey (*J.*, 1947, 576) and by Stokland (*Kgl. Norske Videnskab. Selskab*, 1939, **12**, 122, 126). However, this peculiar behaviour is explicable in terms of statistical thermodynamics, although a rigorous treatment seems to be confined to simple cases such as that given by Ubbelohde ("Modern Thermodynamics," Oxford, 1952, p. 169). Bradley contends that if this mass effect is fundamental then it should be a general phenomenon recognisable whenever vapour pressures of two compounds are compared. However, it is a second-order effect usually obscured by the greater effect caused by differences in intermolecular forces and is only apparent under certain conditions such as obtain in the case of isotopic molecules. This theory predicts a super-isotope effect as a general phenomenon occurring in centro-symmetric systems such as $M'X_n$ and $M''X_n$ where M′ and M″ are *n*-valent elements with nearly identical atomic radii and X is a univalent shielding group. Besides zirconium and hafnium, it seems likely that the compounds of niobium and tantalum and also molybdenum and tungsten might fulfil these conditions. A survey of the literature revealed that this is indeed the case as is shown in Table 11, which gives data for pairs of compounds in which the heavier species is the more volatile. The relative boiling points of these "anomalous" pairs are quite inexplicable in terms of the conventional empirical rule connecting volatility and molecular weight, yet this behaviour is expected on the basis of what is here proposed as the fundamental effect of molecular weight on volatility.

TABLE 11.

	NbF_5	TaF_5	$NbCl_5$	$TaCl_5$	MoF_6	WF_6
Formula weight	187·9	275·9	270·2	358·2	210·0	297·9
Boiling point	234·9°	229·2°	254·0°	239·3°	35·0°	17·5°
Radius of orbital atom (Å)	1·34	1·34	1·34	1·34	1·36	1·37
Molar heat of vaporization (kcal. mole⁻¹)	12·9	13·0	13·2	13·6	8·34	8·69

In view of the conclusions arrived at to explain the remarkable physicochemical properties of the alkoxides of titanium, zirconium, and hafnium it is of interest to extend the investigation to tertiary alkoxides of thorium also. Eight new alkoxides $Th(OR)_4$ have been prepared by alcohol interchange involving thorium tetra*iso*propoxide and the appropriate alcohol :

$$Th(OPr^i)_4 + 4ROH \longrightarrow Th(OR)_4 + 4Pr^iOH$$

Molecular weights were determined ebullioscopically in benzene and, where possible, boiling points were measured under reduced pressure. The data, including the calculated molecular complexities ($x = M$/formula weight), are recorded in Table 12.

TABLE 12. *Thorium tetra-alkoxides.*

Alkyl	B. p./mm.	*M*	*x*	Alkyl	B. p./mm.	*M*	*x*
CMe_3	160°/0·1 (subl.)	1787	3·4	CMe_2Pr^i		1444	2·3
CMe_2Et	208°/0·3	1601	2·8	CEt_3	148°/0·05	714	1·0
$CMeEt_2$	148°/0·1	1156	1·8	$CMeEtPr^n$	153°/0·1	1171	1·7
CMe_2Pr^n	Decomp. 120°/0·1	1653	2·6	$CMeEtPr^i$	139°/0·05	709	1·0

The thorium derivative of ethylmethyl*iso*propylcarbinol (2 : 3-dimethylpentan-3-ol) appears to be the most volatile organic compound of thorium yet recorded and several of the other compounds listed in Table 12 are more volatile than the thorium–tetra(acetylacetone) complex, the only other volatilisable organic thorium compound hitherto reported.

It is evident from Table 12 that the volatility and molecular complexity of thorium alkoxides are determined by the size and shape of the alkyl group. There can be little doubt that this behaviour is predominantly the result of stereochemical effects. Thus there will be only minor variations in electronic effect from one alkyl group to another because they are all tertiary alkyl. Moreover, the molecular complexities decrease with increase in size of the alkyl group and this behaviour is consistent with the stereochemical theory previously advanced to account for the behaviour of the alkoxides of silicon, titanium, zirconium, and hafnium. This theory suggests that intermolecular bonding M···O involving the central atom M (= Ti, Zr, or Hf) and oxygen from a neighbouring alkoxide group gives rise to complex non-volatile alkoxides. In the monomeric alkoxides the central atom is shielded by the rotation of the branched alkoxide groups, intermolecular attraction is minimised, and the compounds are relatively volatile. The theory was supported by a comparison of the behaviour of the alkoxides of silicon, titanium, zirconium, and hafnium. This showed that the size of the central atom controlled the effectiveness of an alkoxide group in shielding. Thus the effect of chain branching on volatility was much greater for zirconium (or hafnium) than for titanium, and least for silicon. Thorium, whose atomic radius is the largest of those of the Group IVA elements, gives alkoxides with properties which accord with these stereochemical requirements. The contrast in the properties of thorium, zirconium, titanium, and silicon alkoxides is demonstrated in Table 13, which contains the boiling points (0·1 mm.) and molecular complexities (in parentheses) of selected compounds having an increasing degree of chain branching of the alkyl group.

TABLE 13.

	Si	Ti	Zr	Th
Atomic radius (Å)	1·17	1·36	1·48	1·65
Alkoxyl				
$O\cdot CH_2Me$	−15° * (1·0)	102° (2·4)	180° (3·4)	Non-volatile
$O\cdot CHMe_2$	15 (1·0)	49 (1·4)	160 (3·0)	210° (3·8)
$O\cdot CMe_3$	—	52 (1·0)	50 (1·0)	160 (3·4)
$O\cdot CMeEt_2$	—	128 (1·0)	128 (1·0)	148 (1·8)
$O\cdot CEt_3$	—	166 (1·0)	166 (1·0)	154 (1·0)

* Calculated.

An interesting feature of Table 13 is the behaviour of the monomeric tertiary C_7-alkoxides of titanium, zirconium, and thorium. Their boiling points are close together, suggesting that they have similar molar heats of vaporisation because the effect of the central atom has been obviated by the screen of organic groups. This emphasises the powerful effect of highly branched alkoxide groups in shielding a central atom. Thus, in addition to suppressing the intermolecular attraction involving the central atom and oxygen, it appears that the contribution due to the marked ionic character in the thorium alkoxide is also nullified.

I have confined my remarks to investigations involving quadrivalent elements. It will be recognised, however, that my subject today is capable of wide extension and already striking results have been obtained from a study of the alkoxides of the quinquevalent elements, niobium and tantalum, and sexavalent uranium.

It seems possible that these volatile derivatives of the metals may have important industrial applications where high purity is required. Preliminary experiments show that distilled zirconium alkoxides are spectroscopically pure with respect to many common metallic impurites. Moreover, it is possible to separate hafnium from zirconium by high-efficiency fractional distillation. A new method for the separation of niobium and tantalum by means of their alkoxides is also foreshadowed. The ability to prepare the alkoxides in a high state of purity and the ease with which they can be converted into the pure oxide is of great value, particularly when the metal can be derived by reduction of the oxide.

The investigator in any field of investigation must realise that however convincing his conclusions may seem they may require correction and modification when brought into relation with wider considerations. There is always the danger that the specialist, having formed opinions for himself, develops a parental affection for them which becomes emotional rather than scientific. On the other hand, accurate experimental data are incontestable and the attempt of the human mind to order facts into patterns is very satisfying.

From the earliest times the practitioners of a particular art have always shown a tendency to draw apart from the rest of the community and to constitute themselves a separate class or fraternity. The conception of a learned society such as the Chemical Society is different. It exercises, not a narrow and sectional influence, but an influence both broad and catholic which traverses national frontiers and which, by promoting free trade in all beneficent discoveries, advances the welfare of humanity at large.