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Alkoxides Old and New.

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FELLOWS of the Chemical Society when meeting in Nottingham cannot fail to recall with pride the fruitful and distinguished work which was done in this University on organic compounds of silicon by a former Fellow of the Society—Professor F. S. Kipping. Perhaps it is fitting that at this Anniversary Meeting, the President of the Chemical Society should address you on a related topic.

Although we are warned against the deceitfulness which lurks in generalities, like other warnings it has more often proved an incentive rather than a deterrent. So, undismayed by the attendant risks, I propose to re-examine today a generalisation I outlined last year in my Presidential Address.

The results presented in Table 1 seem to establish the claim that the structure and volatility of the alkoxides of some Group IV elements are governed by the configuration of the alkyl groups and the atomic radius of the central metal atom. The boiling points (at 0·1 mm.) and molecular complexity (in parentheses) are given of selected compounds having an increasing degree of chain branching of the alkyl group.

TABLE 1.

	Si	Ti	Zr	Th
Atomic radius (Å)	1·17	1·36	1·48	1·65
Alkoxyl				
O·CH₂Me	−15° * (1·0)	102° (2·4)	180° (3·4)	Non-volatile
O·CHMe₂	15 (1·0)	49 (1·4)	160 (3·0)	210° (3·8)
O·CMe₃	—	52 (1·0)	50 (1·0)	160 (3·4)
O·CMeEt₂	—	128 (1·0)	128 (1·0)	148 (1·8)
O·CEt₃	—	166 (1·0)	166 (1·0)	154 (1·0)

* Calculated.

An interesting feature of Table 1 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. The widely accepted view that volatility decreases with rising molecular weight is not supported by the data in Table 1. In fact the volatility of the monomeric thorium alkoxide Th(O·CEt₃)₄ is greater than that of the corresponding monomeric alkoxides of zirconium and titanium. An important feature of the alkoxides of zirconium and hafnium is that for analogous compounds the order of volatility is Hf > Zr although the atomic weights of the elements are 178·6 and 91 respectively. Actually the fundamental effect of mass on volatility has a theoretical background and explains certain boiling-point anomalies. In the case last mentioned it follows from the Clausius–Clapeyron equation that the relative volatility P_{Zr}/P_{Hf} over a small temperature range will take the form :

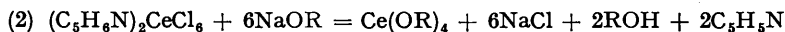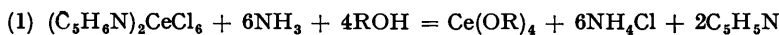$$\log_{10} P_{Zr}/P_{Hf} = (a_{Zr} - a_{Hf}) - (b_{Zr} - b_{Hf})/T$$

In the case where $b_{Zr} \rightleftharpoons b_{Hf}$ the temperature-independent terms a_{Zr} and a_{Hf} will assume major importance. It is noteworthy that for the relative volatilities P_1/P_2 of solid monatomic compounds the difference between the temperature-independent terms a_1 and a_2 can be calculated by the method of statistical thermodynamics and reduces to the simple form $a_1 - a_2 = \frac{3}{2} \log_{10} M_1/M_2$, where M_1 and M_2 are the molecular weights. Hence for $b_1 = b_2$ it follows that $\log_{10} P_1/P_2 = \frac{3}{2} \log_{10} M_1/M_2$ and the substance with the greater molecular weight is the more volatile. For polyatomic molecules $a_1 - a_2$ will exceed $\frac{3}{2} \log_{10} M_1/M_2$ by an amount

which is determined by a function of the ratios of the various moments of inertia, *e.g.*, $\frac{1}{2}\log_{10}(I_A \times I_B \ldots I_H/I_P \times I_Q \ldots I_Z)$, and whose complexity depends on the number and arrangements of atoms in the molecule. Since molecular weight is included in the moment of inertia, it is evident that in polyatomic molecules (with $b_1 = b_2$) there is a possibility that this "molecular-weight effect" will enhance the greater volatility of the compound with higher molecular weight.

With regard to the *tert.*-amyloxides of zirconium and hafnium, the data show $b_{Hf} > b_{Zr}$ and $a_{Hf} > a_{Zr}$, which suggests that in spite of greater intermolecular attraction in the hafnium compound its higher molecular weight leads to a greater volatility. However, it is realised that a variation of 1% would reverse the orders to $a_{Zr} > a_{Hf}$ and $b_{Zr} > b_{Hf}$, and more accurate vapour-pressure determinations (now in progress) are required before a confident explanation for the observed volatility order can be advanced. It is noteworthy that in the borohydrides $M(BH_4)_4$,[1] which are the most volatile known compounds of zirconium or hafnium, the hafnium compound is the more volatile and again $a_{Hf} > a_{Zr}$ and $b_{Hf} > b_{Zr}$. Moreover, the relative volatility P_{Hf}/P_{Zr} is greater in the borohydrides where $M_{Hf}/M_{Zr} = 1\cdot58$ than in the *tert.*-amyloxides where $M_{Hf}/M_{Zr} = 1\cdot18$, in qualitative agreement with the above theory.

A notable omission from the list of elements so far considered is cerium. The position of cerium in Group IVa of the Periodic Table is peculiar. It cannot be treated as a member of the linear series Ti–Zr–Ce–Hf–Th. More appropriately it may be regarded as one of the alternative links between zirconium and thorium, Ti–Zr$\underset{Hf}{\overset{Ce}{<}}$Th. The atomic radii of hafnium and zirconium are identical and in the literature those of cerium and thorium are generally quoted as identical, $1\cdot65$ Å. To test how far the alkoxides of cerium fitted into the general pattern for alkoxides of Group IVa elements, my colleague, Dr. A. K. Chatterjee, began a study of these substances. At the time he started his investigation cerium alkoxides were unknown and it seemed possible that they would be difficult to isolate.

Of the available methods for the preparation of alkoxides those involving the use of the chloride had to be eliminated owing to the non-existence of a tetrachloride of cerium. Any attempts to prepare the alkoxides of quadrivalent cerium were thus limited to the methods involving the pyridinium cerium hexachloride and thus suggested the following possibilities :

$$(1) \quad (C_5H_6N)_2CeCl_6 + 6NH_3 + 4ROH = Ce(OR)_4 + 6NH_4Cl + 2C_5H_5N$$

$$(2) \quad (C_5H_6N)_2CeCl_6 + 6NaOR = Ce(OR)_4 + 6NaCl + 2ROH + 2C_5H_5N$$

Preliminary experiments showed that the most suitable starting material was the *iso*propoxide prepared by method (1). It was isolated first as $Ce(OPr^i)_4, C_5H_5N$. On recrystallisation from *iso*propyl alcohol a beautiful yellow crystalline alcoholate $Ce(OPr^i)_4, Pr^iOH$ was obtained. In this respect cerium behaves more like zirconium than thorium. Accordingly, for all subsequent work cerium *iso*propoxide was exclusively prepared by this method and converted into any other cerium alkoxide by alcohol interchange. The primary alkoxides prepared are listed in Table 2, together with the molecular weights determined ebullioscopically in benzene and in toluene. These substances are in general very readily hydrolysed and unstable even in dry air. The slight decrease in molecular complexity of the compounds in boiling toluene is due purely to the thermal effect of difference in boiling points of the solvents.

TABLE 2. *Primary alkoxides of cerium.*

		Benzene		Toluene	
Alkoxide	Volatility	Mol. weight	Mol. complexity	Mol. weight	Mol. complexity
Methoxide Ce(OMe)$_4$	Non-vol.	Insol.	—	—	—
Ethoxide Ce(OEt)$_4$	Non-vol.	Insol.	—	—	—
n-Propoxide Ce(OPr^n)$_4$	Non-vol.	1618	4·3	1295	3·44
n-Butoxide Ce(OBu^n)$_4$	Non-vol.	1819	4·21	1504	3·48
*iso*Butoxide Ce(OBu^i)$_4$	Non-vol.	1814	4·20	1469	3·40
Pentyloxide Ce(O·CH$_2$Bu^n)$_4$	Non-vol.	2050	4·2	1665	3·41
*neo*Pentyloxide Ce(O·CH$_2$Bu^t)$_4$	B. p. 260°/0·01 mm.	1236	2·53	1202	2·46

Table 2 shows the following outstanding features : (*a*) the high molecular complexity of these compounds, except the *neo*pentyloxide ; (*b*) the lack of appreciable effect of chain length on molecular complexity ; (*c*) the anomalous behaviour of the *neo*pentyl oxide.

[1] Hoekstra and Katz, *J. Amer. Chem. Soc.*, 1949, **71**, 2488.

The only volatile cerium compound in this series is the *neo*pentyloxide, which sublimes unchanged at 260°/0·01 mm. and shows a surprisingly low molecular complexity of 2·5 in boiling benzene. As the *neo*pentyl group has a much greater steric hindrance than other primary alkyl groups, such anomalous behaviour of the *neo*pentyl grouping was not very surprising. The molecular complexities of the normal alkoxides of titanium, zirconium, and cerium in benzene are given in Table 3, and it is clear that molecular complexity is greater in cerium alkoxides than in the corresponding titanium and zirconium alkoxides. This can be explained as due to stereochemical effects or to a difference in strength of the intermolecular bonding or to a combination of both the factors. Thus cerium with an atomic radius of 1·65 Å will require more effective shielding than the smaller silicon, titanium or zirconium atom (Si = 1·17 Å; Ti = 1·36 Å; Zr = 1·48 Å).

TABLE 3. *Molecular complexities of normal alkoxides of* Ti, Zr, *and* Ce *in benzene.*

Alkoxides	Ti	Zr	Ce
Ethoxide	2·4	3·6	—
Propoxide	—	—	4·3
Butoxide	—	3·4	4·2
Pentyloxide	1·4	3·2	4·2

It is not surprising that the primary alkoxides of cerium are non-volatile and complex in nature, since the atomic radius of cerium equals that of thorium where the methoxide and ethoxide are insoluble non-volatile compounds.

In the secondary series the following compounds were prepared : $Ce(O\cdot CHR_2)_4$ where R = Me or Et, and $Ce(O\cdot CHMeR)_4$ where R = Et, Pr^n, or Pr^i. The *iso*propoxide was the only member of the series which responded to any attempt at sublimation. Table 4 summarises the

TABLE 4. *Secondary alkoxides of cerium.*

Alkoxides	Volatility	Benzene		Toluene	
		Mol. wt.	Mol. complexity	Mol. wt.	Mol. complexity
*iso*Propoxide * $(O\cdot CHMe_2)_4Ce$	B. p. 160—170°/ 0·05 mm.	1179	3·13	1045	2·78
sec.-Butoxide $(O\cdot CHMeEt)_4Ce$	Non-volatile	1293	2·99	1210	2·80
1-Methyl-*n*-butoxide $(O\cdot CHMePr^n)_4Ce$	Non-volatile	1520	3·11	1363	2·79
2 : 3-Dimethyl-*n*-propoxide $(O\cdot CHMePr^i)_4Ce$	Non-volatile	1464	3·00	1377	2·82
1-Ethyl-*n*-propoxide $(O\cdot CHEt_2)_4Ce$	Non-volatile	1420	2·90	1370	2·80

* Mol. wt. of *iso*propoxide in propan-2-ol = 850 and hence mol. complexity = 1·99.

results. The most striking point brought out by this Table is the non-volatile and complex nature of the secondary alkoxides. All the corresponding titanium *sec.*-alkoxides (with the exception of the lowest member) are monomeric, whereas in zirconium the complexity of the secondary alkoxides changes from 3 to 2 to 1 as the alkyl groups in $Zr(O\cdot CHR_2)_4$ are changed from methyl to ethyl to propyl In the case of cerium all the compounds exhibit a complexity of 3 in boiling benzene whilst in toluene the complexity has declined to 2·8. This behaviour accords with the prediction that a rise in temperature of the solvent should cause dissociation of the trimers. A glance at Table 5 shows how the size of the central atom plays a decisive

TABLE 5. *Volatilities and molecular complexities of* iso*propoxides of* Si, Ti, Zr, Ce, *and* Th.

Elements	Atomic radii (Å)	*iso*Propoxide	Volatility (B. p.)	Molecular complexity	
				Benzene	Propan-2-ol
Si	1·17	$Si(OPr^i)_4$	15°/0·1 mm.	1·0	—
Ti	1·36	$Ti(OPr^i)_4$	49°/0·1 mm.	1·4	—
Zr	1·48	$Zr(OPr^i)_4$, Pr^iOH	160°/0·1 mm.	3·0	2
Ce	1·65	$Ce(OPr^i)_4$, Pr^iOH	170°/0·05 mm.	3·1	1·99
Th	1·65	$Th(OPr^i)_4$	210°/0·05 mm.	3·8	1·84

part in the structure of the *iso*propoxides. The larger the atom the greater would be its shielding requirements. Four *iso*propoxy-groups are sufficient to shield the small silicon atom, whereas already in titanium the shielding is incomplete till finally, on coming to the bigger atoms of zirconium, cerium, and thorium, incomplete shielding gives rise to higher complexity.

The tertiary alkoxides of quadrivalent cerium proved to be especially interesting from the stereochemical viewpoint. The following new alkoxides were prepared :

$$Ce(OR)_4 \text{ where } R = CMe_3, CMe_2Et, CMeEt_2, CEt_3, CMe_2Pr^n, CMe_2Pr^i, \text{ and } CMeEtPr^n.$$

All were prepared by alcohol interchange involving the crystalline cerium *iso*propoxide and the appropriate alcohol. These represent the only volatile compounds of quadrivalent cerium yet recorded. The tertiary butoxide and the tertiary amyloxides were yellow crystalline solids whilst the other tertiary alkoxides were yellow liquids which could be distilled unchanged. The data, including volatility and molecular complexity, are summarised in Table 6.

TABLE 6. *Tertiary alkoxides of cerium.*

		Benzene		Toluene	
Alkoxides	Volatility (B. p.)	Mol. wt.	Mol. compl.	Mol. wt.	Mol. compl.
tert.-Butoxide (O·CMe₃)₄Ce	140—150°/ 0·01 mm.	1062	2·46	968	2·24
tert.-Amyloxide (O·CEtMe₂)₄Ce	240°/0·01 mm.	1150	2·36	1050	2·15
1 : 1-Dimethyl-*n*-butoxide (O·CPrⁿMe₂)₄Ce	140°/0·06 mm.	746·2	1·37	580·4	1·06
1 : 1 : 2-Trimethyl-*n*-propoxide (O·CPrⁱMe₂)₄Ce	146°/0·05 mm.	761·7	1·40	600	1·1
1-Ethyl-1-methyl-*n*-propoxide (O·CEt₂Me)₄Ce ...	132°/0·05 mm.	584	1·07	541·6	0·99
1 : 1-Diethyl-*n*-propoxide (O·CEt₃)₄Ce	154°/0·05 mm.	650·3	1·08	604·7	1·00
1-Ethyl-1-methyl-*n*-butoxide (O·CMeEtPrⁿ)₄Ce...	150°/0·05 mm.	604·5	1·00	—	—

The data reveal that all *tert.*-alkoxides of cerium are volatile, that volatility and molecular complexity vary with shape and size of the alkyl groups, and that for a given alkoxide molecular complexity is always lower in toluene than in benzene (except when the alkoxide is monomeric in benzene). All these findings are consistent with the stereochemical theory already advanced to account for the behaviour of the alkoxides of silicon, titanium, zirconium, hafnium, and thorium. This theory explains the associated and non-volatile nature of primary and secondary alkoxides as due to the intermolecular bonding M· · ·O involving a central metal atom and oxygen from a neighbouring alkoxide group. The steric hindrance of tertiary alkyl groups prevents such co-ordination and tertiary alkoxides are therefore less complex. In the monomeric alkoxides the central atom is sufficiently shielded by the rotation of the branched alkoxide groups to prevent any co-ordination and a volatile compound results.

A comparison of the properties of the tertiary alkoxides of Group IVA elements with regard to their shielding requirements is very interesting. For example, tetra-*tert.*-butoxysilane has only recently been prepared owing to the difficulty of replacing four halogen atoms by tertiary butoxide groups around the small silicon atom. In the cases of titanium and zirconium the shielding by the *tert.*-butoxide groups is sufficient to produce monomeric compounds which are the most volatile alkoxides of these elements. Finally, the thorium atom is so large that screening by four *tert.*-butoxides does not prevent polymerisation so that thorium *tert.*-butoxide is complex and much less volatile than the titanium and zirconium compounds. In fact the higher tertiary alcohol (triethylcarbinol) is required to produce a monomeric thorium alkoxide. The behaviour of cerium resembles that of thorium in this respect although the lower complexity of the cerium derivative of 3-methylpentan-3-ol (diethylmethylcarbinol) suggests that cerium may have a smaller atomic radius than thorium. The order of shielding efficiency of different tertiary C₆ alkyloxide groups as judged by the molecular complexity of their thorium derivatives was found to be $(O·CMeEt_2) > (O·CMe_2Pr^i) > (O·CMe_2Pr^n)$. The same order obtains in the case of the cerium derivatives.

TABLE 7. *Boiling points (in °c/0·1 mm. Hg) and molecular complexities (in parentheses) of* M(O·CMeₙEt₃₋ₙ)₄.

n	Ti	Zr	Ce	Th
3	52° (1)	50° (1)	150° (2·4)	160° (3·4)
2	98° (1)	95° (1)	240° (2·3)	198° (2·8)
1	128° (1)	128° (1)	132° (1)	148° (1·8)
0	166° (1)	166° (1)	154° (1)	154° (1)

A comparison of the tertiary alkoxides $Ce(O·CMe_nEt_{3-n})_4$ with the analogous compounds of other elements of Group IVA is shown in Table 7. The data in this Table give a definite indication that the atomic radius of cerium may not be identical with that of thorium and is really a little smaller.

Another interesting feature is the behaviour of the monomeric tertiary C_7 alkyloxides of titanium, zirconium, cerium, and thorium. The relative volatility of the analogous monomeric *n*-heptyloxides is Ce = Th > Zr = Ti, whereas the molecular weights of these compounds are in the order Ti < Zr < Ce < Th. This order of volatility is, however, in conformity with the theory of the fundamental effect of mass on volatility. Nevertheless, it must be pointed out that the effect of molecular mass on volatility is very small compared with the part played by the latent heat of vaporisation, and it is still an open question whether the order of volatilities of these compounds is a result of differences in latent heats or molecular mass.

To ascertain how widely the stereochemical theory could be applied we thought it would be worth while to examine the properties of the alkoxides of some Group V elements. For this purpose we selected niobium and tantalum as they have identical atomic radii but very different atomic weights (93·3, 181·4). In their alkoxides the fundamental effect of mass on volatility might well be apparent.

Perusal of the literature showed that little attention had been given to the study of organic

FIG. 1.
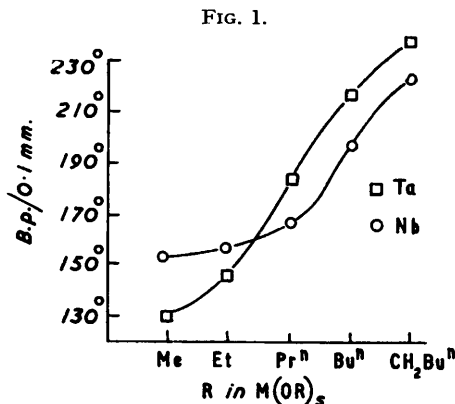
compounds of these elements. The reaction between ethyl alcohol and niobium or tantalum pentachloride was known to take place according to the equation :

$$MCl_5 + 3EtOH = MCl_2(OEt)_3 + 3HCl$$
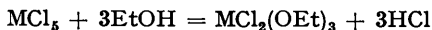
However no mention was made in the literature of niobium or tantalum penta-alkoxides. Recently Miss A. Whitley and B. N. Chakravarti have shown that a range of such alkoxides can be made by the general reaction :

$$MCl_5 + 5ROH + 5NH_3 = M(OR)_5 + 5NH_4Cl$$
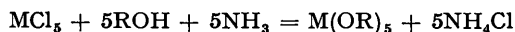
(where M = Nb, Ta; R = Me, Et, Pr^n, or Bu^n).

The method of alcohol interchange was particularly useful in the preparation of pure normal alkoxides. However, we found that a fully substituted secondary or tertiary alkoxide of niobium or tantalum cannot be prepared by the alcohol-interchange process. Only four out of the five primary alcohol groups can be replaced by a secondary alcohol acting upon niobium and tantalum alkoxides. Four tertiary groups can be introduced by alcohol interchange into tantalum penta-primary or penta-secondary alkoxides. Such compounds of tantalum, $Ta(OR)(OR')_4$ where R = a primary or secondary group and R' = a tertiary group, are quite stable and volatile. When a primary alkoxide of niobium reacted with a tertiary alcohol, practically the whole of the primary alcohol group was replaced and the product had the composition $Nb_2O(OR^t)_8$. These experiments established the fact that the failure to obtain penta-tertiary alkoxides of niobium is due to some specific property of niobium itself.

Additional interest was centred on the relative volatilities of corresponding niobium and tantalum alkoxides because of the possibility that the fundamental effect of molecular weight on volatility might be apparent. The boiling points of niobium and tantalum alkoxides under reduced pressure are given in Table 8. The striking feature of these data is the dependence of the relative volatility of niobium and tantalum normal alkoxides on the length of the alkyl chain. Thus it is clear that for the methoxides and alkoxides the tantalum compound is the

more volatile, whilst for the higher normal alkoxides the niobium compound is the more volatile. Moreover this occurs in both the pressure ranges investigated. These results suggest that the separation of niobium and tantalum by distillation of the alkoxides should be relatively simple, and this is now being investigated. The molecular weights of the niobium and tantalum *n*-alkoxides were determined ebullioscopically in benzene, in toluene, and in the parent alcohols and the molecular complexities are given in Table 9.

TABLE 8.

| R in M(OR)$_5$ | M. p. | | Boiling point (°c/mm. Hg) | | | | Molecular complexity | |
| | | | Lower pressure | | Higher pressure | | | |
	Nb	Ta	Nb	Ta	Nb	Ta	Nb	Ta
Me	60°	50°	153°/0·12	130°/0·2	200°/5·5	189°/10	2·11	1·98
Et	Liq.	Liq.	156·5°/0·05	146·5°/0·15	207·5°/5·5	202°/10	2·02	1·98
Pr^n	,,	,,	166°/0·04	184°/0·15	218·5°/5·5	232°/10	2·02	1·95
Bu^n	,,	,,	197°/0·15	217°/0·15	230°/5·5	256°/10	2·01	2·02
Am^n	,,	,,	223°/0·15	239°/0·2	—	—	2·00	2·01

TABLE 9.

Molecular complexity

| R in M(OR)$_5$ | Benzene [a] | | Toluene [b] | | Parent alcohol | |
	Nb	Ta	Nb	Ta	Nb	Ta
Me	2·11	1·98	1·90	1·83	1·34 [c]	1·20
Et	2·02	1·98	1·89	1·83	1·52 [d]	1·78
Pr^n	2·02	1·95	1·79	1·83	1·29 [e]	1·70
Bu^n	2·01	2·02	1·74	1·83	1·13 [f]	1·40
Am^n	2·00	2·01	—	—	—	—

[a] Benzene: b. p. 80·3°, D.C. 2·28. [b] Toluene: b. p. 110°, D.C. 2·38. [c] Methyl alcohol: b. p. 64°, D.C. 33·1. [d] Ethyl alcohol: b. p. 78°, D.C. 24. [e] *n*-Propyl alcohol: b. p. 97°, D.C. 22·2. [f] *n*-Butyl alcohol: b. p. 117°, D.C. 17·7.

All the niobium and tantalum *n*-alkoxides are dimeric in boiling benzene and it seems likely that these metals are 6 co-ordinate. Evidence for the dissociation of these dimers at a higher temperature is apparent from the results in boiling toluene. However, there is a significant difference between the behaviour of niobium and of tantalum alkoxides in this solvent. Whilst the *n*-alkoxides of tantalum all have the same complexity, there is a distinct decrease in complexity with increase in alkyl-chain length for the niobium compounds. We infer from these results that the energy of depolymerisation is sensibly constant for the tantalum series but decreases with increase in the alkyl chain for the niobium *n*-alkoxides. Further, this explanation is quantitatively consistent with the dependence of relative volatility of niobium and tantalum *n*-alkoxides on the chain length of the alkyl group. Thus the energy of depolymerisation will be included in molar heat of vaporisation,

$$L_v = L_{mon.} + E$$

where L_v = molar heat of vaporisation, $L_{mon.}$ = hypothetical heat of vaporisation of " monomeric " alkoxide, and E = energy of depolymerisation. It seems reasonable to assume that $L_{mon.}$ for a niobium alkoxide will be close to that for a corresponding tantalum compound, and differences in E will therefore be reflected as differences in L_v.

If now $E\{Nb(OMe)_5\} > E\{Ta(OMe)_5\}$, then according to the view that E for tantalum *n*-alkoxides is constant whilst E for niobium *n*-alkoxides varies in the order : methoxide > > ethoxide > *n*-propoxide > *n*-butoxide > *n*-pentyloxide, it seems quite possible that the values of L_v will be Nb(OMe)$_5$ > Ta(OMe)$_5$, Nb(OEt)$_5$ > Ta(OEt)$_5$, and Nb(OR)$_5$ < Ta(OR)$_5$ where R = Pr^n, Bu^n, or *n*-C$_5$H$_{11}$. This postulated order of L_v's is in agreement with the order of boiling points given in Table 8. Some support for this argument is forthcoming from the complexities of the alkoxides in their parent alcohols. It has been suggested that the primary factors causing dissociation of tantalum *n*-alkoxides in their boiling parent alcohols are (1) boiling point of solvent (temperature effect) and (2) " donor " power of solvent (solvation effect). The same arguments must apply to niobium alkoxides, and hence it is deduced that $E\{Nb(OMe)_5\} > E\{Ta(OMe)_5\}$, and $E\{Nb(OR)_5\} < E\{Ta(OR)_5\}$, where R = Et, Pr^n, Bu^n. Only in the case of the ethoxide does the order of E's conflict with that suggested above for

L_v's. It is clear that vapour-pressure data will give valuable information concerning these phenomena.

Since the atomic radii of niobium and tantalum are the same (1·34 Å) these differences in the behaviour of their alkoxides must be ascribed to electronic factors. It is well known that niobium differs from tantalum in having a pronounced tendency to form any compounds containing the niobium–oxygen double bond, and hence there will be a greater tendency for covalency expansion involving " intramolecular " bonding as in $(RO)_4\overset{-}{Nb}{=}\overset{+}{O}R$ to compete with the intermolecular bonding which causes dimerisation. This will clearly lead to a readier depolymerisation with increase in temperature for the niobium compounds than for the tantalum derivatives. This ready double bonding between niobium and oxygen may also explain the lower thermal stability of the niobium alkoxides which will tend to split off carbonium ions : $Nb(OR)_5 = [(RO)_4\overset{-}{Nb}{=}O] + \overset{+}{R}$. This mechanism will be enhanced by the $(+I)$ electron-releasing tendency of the alkyl group and is in accord with the observed decrease in stability of niobium n-alkoxides with increase in chain length of the alkyl group.

According to current views on the effect of molecular weight on volatility, there should be a tendency for the heavier tantalum alkoxides to be more volatile than the corresponding niobium compounds although this effect is usually obscured by the differences in molar heats of vaporisation. However, we have already pointed out that the molecular complexities of the ethoxides in ethyl alcohol imply that $E\{Ta(OEt)_5\} > E\{Nb(OEt)_5\}$ and hence $L_v\{Ta(OEt)_5\} > L_v\{Nb(OEt)_5\}$ which would predict the order of volatilities $Nb(OEt)_5 > Ta(OEt)_5$. The observed order of volatilities $Ta(OEt)_5 > Nb(OEt)_5$ might well be due to the " mass effect " over-ruling the unfavourable order of latent heats. This problem should be resolved when vapour-pressure data are available.

It was evident that a study of the physicochemical properties of the alkoxides would be worth while, and with this in view measurements of the density, surface tension, vapour pressure, and viscosity of a range of alkoxides have been made. The parachor has been of great value in connection with the interpretation of structural abnormalities in compounds, especially as a result of recent work. It now seems well established that the volume contribution of any atom must vary with the nature of the other atoms to which it is attached. Consequently, the old idea of atomic parachors is severely restricted in application and, instead, Gibling has evaluated a set of group parachors. Thus, in hydrocarbons the methyl group when attached to carbon $CH_3{-}(C) = 55\cdot2$ units whilst the methylene group attached to two carbons $(C){-}CH_2{-}(C) = 39\cdot8$ units but methylene attached to carbon and to oxygen $(C){-}CH_2{-}(O) = 39\cdot4$. These are standard values used by us in evaluating the calculated $[P]$ of a substance. These values are corrected for various other structural factors which may obtain in a particular molecule. Thus there·is the correction for interference between non-bonded atoms which leads to a reduction in the parachor. Further corrections involve the bending of chains of atoms and also alignment of parallel chains. It appears from the data on organic compounds that there is an expansion effect in which the observed parachor is slightly greater than the calculated parachor to an extent which increases steadily with the size of the molecule.

Gibling's method may be illustrated by calculating the standard parachor for the group comprising a titanium atom and four oxygen atoms, the latter being joined to carbon atoms, *i.e.*, $[P]$ Ti$[O(C)]_4$. For this purpose the experimental $[P]$ for titanium *tert.*-butoxide is selected because this is a monomeric alkoxide. The experimental parachor $[P] = 842\cdot8$ and this must be corrected for the expansion effect. To arrive at the corrected standard value the experimental parachor is divided by $(1\cdot0004165)^n$ where $n =$ number of atoms other than hydrogen in the molecule. Thus the corrected standard value $= 842\cdot8/1\cdot0072 = 836\cdot7$. A summation of the standard parachors for four tertiary butyl groups attached to oxygen atoms is given as follows :

$$12 \times CH_3(C) = 662\cdot4 \text{ units}$$
$$4 \times \underset{(C)}{\overset{(C)}{(C)}}{>}C{-}(O) = 4\cdot8 \text{ units}$$
$$\overline{667\cdot2 \text{ units}}$$

After allowance for the correction $(-2\cdot8)$ for 4 carbon atoms attached to oxygen atoms, this gives a corrected standard value $= 664\cdot4$ units. Hence the standard value for Ti$[O{-}(C)]_4$ $= 836\cdot7 - 664\cdot4 = 172\cdot3$ units. This value has been used for the calculations in Table 10. The parachor data show in a striking way that the titanium n-alkoxides are exhibiting some structural abnormalities. The very considerable contraction of *ca.* 95 units in each compound

is entirely consistent with the view that these molecules are trimeric in the liquid state. The phenomena of evaporation, surface formation, and flow of pure liquids all involve the breaking of bonds between molecules. According to current theories it should be possible by comparing

TABLE 10.

Compound	$[P]$, experimental	$[P]$, calculated	$\Delta[P]$
$Ti(OEt)_4$	453·7	550·6	96·9
$Ti(OPr^n)_4$...............................	615·8	708·5	92·7
$Ti(OBu^n)_4$	768·2	863·6	95·4

the energy of vaporisation (E_v), the work of cohesion (W_c), and the energy of activation of viscosity ($E_{visc.}$) to obtain some insight into the structural aspects of the liquid alkoxides. Eyring has proposed an ingenious theory of the flow of liquids. He regards viscous flow as related to vaporisation, so that the energy required to create a hole of molecular dimensions inside a liquid is given by the energy of vaporisation defined as follows :

$$E_v = L_v - RT$$

L_v, the molar heat of vaporisation, is calculated from the relationship $\log_{10} P = $ constant $- L_v/2\cdot303RT$. RT is the molar work of expansion involved in the passage from liquid to vapour. It seems reasonable to suppose that the condition for movement is that molecules should possess sufficient kinetic energy to push others out of their way. This is the basis of Eyring's theory of viscous flow. He suggests that, although it is necessary for a hole to be present into which the flowing molecule may pass, this hole may only be a fraction of the full size of a molecular hole and hence the free energy of activation for viscous flow (ΔF^*) should be some fraction of the energy of vaporisation E_v. For a wide range of compounds, including associated liquids but excluding metals, the ratio of E_v to ΔF^* was found to be sensibly constant, *i.e.*, $E_v/\Delta F^* \cong 2\cdot45$. Thus it appears that the free energy of activation for viscous flow is approximately one-third of the energy of vaporisation. From the experimental determination of viscosity (η) at different temperatures the important quantities, $E_{visc.}$ and ΔF^*, may be deduced.

$$\log \eta = E_{visc.}/2\cdot303RT - \text{constant}$$

$$\eta = \left(\frac{hN}{v}\right) e^{\Delta F^*/RT}$$

The ratio $E_v/E_{visc.}$ is usually between 3 and 4 except for metals and long-chain hydrocarbons. Hence the energy of activation of viscosity is approximately one-quarter of the energy of vaporisation.

Some data for the metal alkoxides obtained by Dr. C. C. A. Prevedorou are presented in Table 11 together with the ratios $E_v/\Delta F^*$ and $E_v/E_{visc.}$. It is noticeable that for each alkoxide the ratios $E_v/\Delta F^*$ and $E_v/E_{visc.}$ are practically temperature-independent. The ratio $E_v/\Delta F^*$ is uniformly equal to 3 for all except the complex normal alkoxides and the " abnormal " derivatives of 2-methylpentan-2-ol (dimethyl-*n*-propylmethanol). This ratio is near to Eyring's value of 2·45, and the discrepancy is probably caused by the fact that his values of E_v were calculated at the temperatures of normal boiling points whilst the values in Table 11 were calculated from the latent heats at temperatures well below the boiling points. Similarly, the values of $E_v/E_{visc.}$ are close to 3 and are usually very close to $E_v/\Delta F^*$. It seems permissible to assume that the compounds in Table 11 with the ratios $E_v/\Delta F^*$ and $E_v/E_{visc.} \sim 3$ are behaving normally with a mechanism of flow involving the movement of a sinple molecule over a potential gradient into an available hole. On the other hand, the titanium and zirconium derivatives of 2-methylpentan-2-ol (dimethyl-*n*-propylcarbinol) gives the abnormally high values of $E_v/\Delta F^* \sim 3\cdot5$ and $E_v/E_{visc.} \sim 5$. This behaviour is consistent with the theory that in these compounds the unit of flow is smaller than a simple molecule. The data for the complex *n*-alkoxides of titanium are somewhat irregular. The values of $E_v/E_{visc.}$ less than 3 are consistent with the behaviour of complex molecules which have to dissociate either before evaporating or before engaging in viscous flow.

The viscosity data for the tertiary alkoxides are given in Table 12. All the tertiary alkoxides studied show values for the activation energy and free energy of viscosity which are independent of temperature over the range 25—40°.

TABLE 11.

Compound	Temp.	E_v (kcal./mol.)	$E_v/\Delta F^*$	$E_v/E_{visc.}$	$E_{visc.}/W_c$	E_v/W_c
Ti(OEt)$_4$	25°	21·01	3·55	2·50	2·95	7·39
	30	21·00	3·55	2·50	2·96	7·39
	35	21·00	3·55	2·49	2·98	7·44
	40	20·98	3·55	2·49	2·98	7·44
Ti(OPr^n)$_4$	25	15·11	2·18	1·71	2·33	3·99
	30	15·10	2·18	1·71	2·33	4·04
	35	15·10	2·18	1·70	2·40	4·10
	40	15·08	2·18	1·70	2·40	4·14
Ti(OBu^n)$_4$	25	19·51	3·00	2·71	1·63	4·44
	30	19·50	3·00	2·71	1·64	4·50
	35	19·49	2·99	2·70	1·68	4·55
	40	19·48	2·99	2·70	1·68	4·56
Ti(OBu^t)$_4$	25	14·00	2·91	3·41	0·83	3·00
	30	13·90	2·90	3·40	0·84	2·86
	35	13·89	2·90	3·39	0·85	2·90
	40	13·87	2·90	3·38	0·86	2·90
Zr(OBu^t)$_4$	25	14·61	3·04	3·32	0·98	3·27
	30	14·59	3·03	3·31	1·00	3·32
	35	14·58	3·03	3·31	1·01	3·39
	40	14·57	3·03	3·31	1·04	3·44
Ti(O·CMe$_2$Et)$_4$	25	16·11	2·98	3·10	0·86	2·67
	30	16·09	2·97	3·09	0·87	2·67
	35	16·09	2·97	3·09	0·87	2·72
	40	16·09	2·97	3·09	0·88	2·73
Zr(O·CMe$_2$Et)$_4$	25	15·71	2·90	2·91	0·98	2·88
	30	15·69	2·90	2·91	0·99	2·88
	35	15·68	2·90	2·90	1·00	2·90
	40	15·67	2·90	2·90	1·01	2·95
Ti(O·CPr^{n}Me$_2$)$_4$	25	18·91	3·63	4·97	0·57	2·73
	30	18·90	3·63	4·97	0·57	2·75
	35	18·89	3·63	4·97	0·57	2·78
	40	18·80	3·63	4·97	0·58	2·83
Zr(O·CPr^{n}Me$_2$)$_4$	25	18·41	3·54	4·60	0·64	2·93
	30	18·40	3·54	4·60	0·64	2·97
	35	18·39	3·54	4·60	0·65	3·00
	40	18·38	3·54	4·60	0·65	3·03
Ti(O·CEt$_2$Me)$_4$	25	18·41	2·92	3·01	0·88	2·66
	30	18·40	2·92	3·01	0·89	2·68
	35	18·39	2·91	3·01	0·91	2·70
	40	18·39	2·91	3·01	0·91	2·75
Zr(O·CEt$_2$Me)$_4$	25	18·41	2·96	2·80	1·05	2·92
	30	18·40	2·96	2·79	1·05	2·93
	35	18·39	2·96	2·78	1·05	2·94
	40	18·39	2·96	2·78	1·06	2·96

TABLE 12.

Alkoxide	η	ΔF^*	$E_{visc.}$	ΔS^*
Ti(OBu^t)$_4$	0·0352	4·8	4·1	$-2·4$
Zr(OBu^t)$_4$	0·0317	4·8	4·4	$-1·4$
Ti(O·CMe$_2$Et)$_4$	0·0808	5·4	5·2	$-0·7$
Zr(O·CMe$_2$Et)$_4$	0·0759	5·4	5·4	0
Sn(O·CMe$_2$Et)$_4$	0·1660	5·8	6·4	$+2·0$
Ti(O·CEt$_2$Me)$_4$	0·3453	6·3	6·1	$-0·7$
Zr(O·CEt$_2$Me)$_4$	0·2810	6·2	6·6	1·3
Ce(O·CEt$_2$Me)$_4$	1·0779	6·1	7·0	3·5
Sn(O·CEt$_2$Me)$_4$	0·4127	6·7	8·2	5·0
Ti(O·CPr^{n}Me$_2$)$_4$	0·0479	5·2	3·8	$-5·0$
Zr(O·CPr^{n}Me$_2$)$_4$	0·0464	5·2	4·0	$-4·0$
Ce(O·CPr^{n}Me$_2$)$_4$	8·1343	8·1	12·6	15·1
Sn(O·CPr^{n}Me$_2$)$_4$	0·0986	5·6	5·6	0
Ce(O·CEt$_3$)$_4$	0·5258	6·6	6·3	$-1·3$
Th(O·CEt$_3$)$_4$	0·4920	6·6	7·6	3·5

It is instructive to compare the behaviour of titanium tetra-*tert*.-butoxide with that of its long-chain isomer, the *n*-butoxide :

	Temp.	Viscosity	ΔF^* (kcal.)	$E_{visc.}$	ΔS^* (cal.)
Ti(OBu^n)$_4$	25°	0·6920	6·5	7·1	2·0

The remarkable effect of branching of the alkyl chain on physical properties is at once apparent. For example, the viscosity of the complex *n*-alkoxide is practically twenty times that of the *tert.*-alkoxide. This is reflected in the much greater free energy of activation of the *n*-butoxide, whilst its activation energy of viscosity approaches twice that of the *tert.*-isomer. By contrast, the difference in energies of cohesion is much smaller (*viz.*, *n*-butoxide $W_c = 4.39$ kcal./mole; *tert.*-butoxide $W_c = 4.92$ kcal./mole) and in the opposite sense. Clearly, the difference in $E_{\text{visc.}}$ is mainly the result of the depolymerisation energy requirements of the complex *n*-alkoxide and this is emphasised by the positive entropy of activation (2·0 cal./°/mole) for the *n*-isomer compared with the negative entropy of activation ($-2·4$ cal./°/mole) for the tertiary compound.

Some interesting features are immediately apparent if the data in Table 12 are considered from the viewpoint of the effect of changing the alkyl group in the case of a given metal atom. For example, the order of viscosities is $CEt_2Me > CEtMe_2 > CPr^nMe_2 > CMe_3$ for either
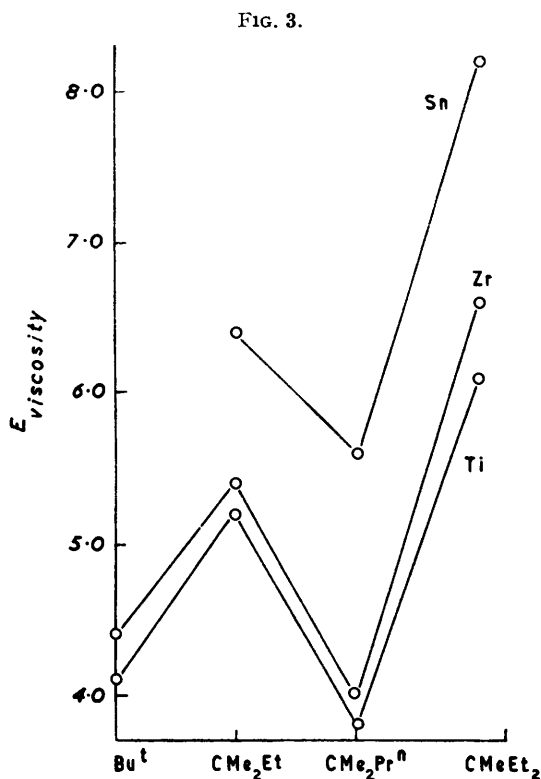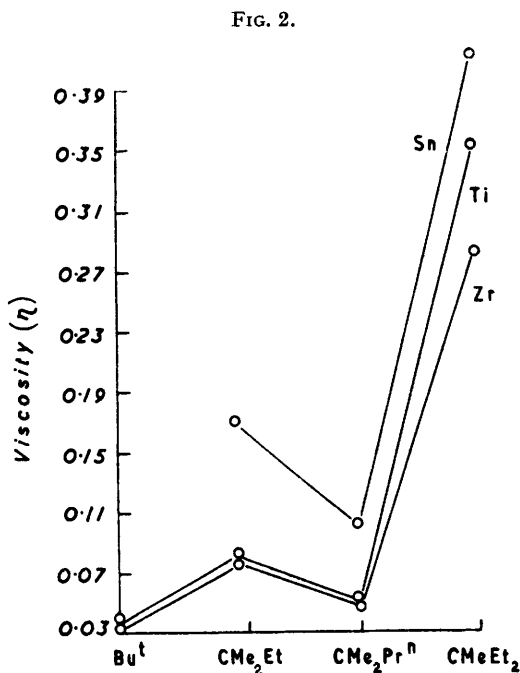
Fig. 2.

Fig. 3.

titanium or zirconium alkoxides. In the case of tin the order is the same but for the absence of data on the tertiary butoxide. The abnormal behaviour of the derivatives of 2-methylpentan-2-ol (dimethyl-*n*-propylcarbinol) is shown in Fig. 2. In Fig. 3 it is seen that the abnormality is also present in the values of $E_{\text{visc.}}$. The trend in positive entropy of activation is very similar. There is no doubt that these alkoxides are monomeric and that the behaviour is not due to metal–oxygen intermolecular bonding of the type involved in the complex normal alkoxides. Moreover, it is clear that the order of viscosities and of activation energies of viscosity $CEt_2Me > CEtMe_2 > CMe_3$ is that to be expected on the basis of molecular size. Finally, it has been found that the energies of cohesion for the derivatives of 3-methylpentan-3-ol and 2-methylpentan-2-ol (diethylmethyl- and dimethyl-*n*-propyl-carbinol) are quite close, and the inescapable conclusion is that the abnormal viscosity behaviour is caused by the abnormally low activation energy of viscosity. The possibility then arises that perhaps the mechanism of viscous flow is different for the derivatives of 2-methylpentan-2-ol from those of the other metal alkoxides. It has been implied throughout that the simple molecule is the unit of flow, but it appears that a smaller unit of flow may obtain for derivatives of this alcohol. This idea is not without precedent, since Eyring suggests that in long-chain hydrocarbons the unit

of flow is a segment of the simple molecule. In pictorial terms this means that viscous flow in the long molecules occurs by a mode of molecular " wriggling " rather than by molecular jumps.

Grunberg and Nissan [2] have also considered the structure of liquids by comparing the energies of vaporisation, viscosity, and cohesion. They found that for non-polar substances the activation energy of viscosity $E_{\text{visc.}}$ was equal to the energy of cohesion W_c. For polar associated liquids they found that $E_{\text{visc.}} > W_c$ and regarded the difference between these terms as a measure of the energy of dissociation. Moreover, with the aid of some assumptions concerning the number of intermolecular " bonds " broken in surface formation and in vaporisation, they suggested that the ratio E_v/W_c or $E_v/E_{\text{visc.}}$ for non-polar liquids is related to the " statistical structure " of the liquid as shown in Table 13.

It is clear from Table 11 that, with the exception of complex titanium n-alkoxides and the titanium and zirconium derivatives of 2-methylpentan-2-ol, the values are in good agreement. With regard to the complex titanium n-alkoxides, it is seen that the activation energies of viscosity are considerably in excess of the energies of cohesion, which confirms the early suggestion that these molecules are depolymerised before engaging in viscous flow. This is well shown by a comparison of the monomeric *tert.*-butoxide of titanium with its complex n-butyl isomer. Thus the energy of cohesion of the n-butoxide is close to the activation energy of viscosity and to the energy of cohesion of the *tert.*-butoxide. It is very interesting to find that the abnormal behaviour of the derivatives of 2-methylpentan-2-ol is confined to the process of viscous flow. Whereas the ratio $E_v/E_{\text{visc.}}$ is considerably higher for the titanium and zirconium derivatives of this carbinol than for the corresponding derivatives of 3-methylpentan-3-ol (diethylmethylcarbinol) yet the ratio E_v/W_c is practically the same in each case. This

TABLE 13.

Molecular configuration	Co-ordination number	Characteristic ratio, E_v/W_c or $E_v/E_{\text{visc.}}$
Tetrahedral	4	2
Octahedral	6	3
Cubic, body-centred	8	4
Cubic, close packing	12	4
Hexagonal close packing	12	4

proves that the " equilibrium configuration " is the same for each isomer and only the unit of flow is different. Returning to the monomeric alkoxides where $E_{\text{visc.}} \simeq W_c$ and applying Grunberg and Nissan's ideas that the ratio $E_v/E_{\text{visc.}}$ is related to the packing in the liquid state, it appears that in these liquids each molecule has on the average six near neighbours arranged octahedrally. In fact, the symmetry may be even higher than this because the values of E_v in Table 13 were deduced from latent heats appropriate to temperatures well above normal room temperature. Hence the true values of E_v are liable to be a little higher than those recorded in the table and this means that the ratio $E_v/E_{\text{visc.}}$ may be nearer to 4, corresponding to the co-ordination number of eight. In either case these liquid alkoxides have properties which are in accord with the behaviour to be expected from a close-packed assembly of spherically symmetrical molecules.

I have an uncomfortable feeling that I have stirred up far more questions than I have answered. I suppose this must always be the case when one seeks to explore fundamental principles. Indeed, I doubt if any fundamental principles are susceptible of precise formulation.

There are many voices raised today to impress on us the importance, the prime importance, of chemistry to industry, agriculture, medicine, and defence. It is most desirable that this should be said and said often. There is a real danger, however, that the practical applications of chemistry rather than its theoretical principles and fundamental discoveries should be uppermost in our esteem. Perhaps this is traditional. Alchemy was a very utilitarian pursuit of the elixir of life, whereby age and death might be defeated, and of the " philosopher's stone " which would transmute the elements into gold. No one can say what useful practical device may ultimately come from discoveries made purely in the pursuit of knowledge. Applied science draws its life-blood from pure science. Although we may be fascinated by applied science it must never weaken our allegiance to pure science.

[2] Grunberg and Nissan, *Trans. Faraday Soc.*, 1949, **45**, 125.