Isopoly-vanadates, -niobates, and -tantalates

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1 Introduction

In aqueous solution, vanadates, molybdates, tungstates, and, to a smaller extent, niobates, tantalates, and chromates, undergo complex hydrolysis–polymerisation reactions upon acidification. The major solute species generated by such reactions are the so-called *isopoly-anions*, of which dichromate, $[Cr_2O_7]^{2-}$, and heptamolybdate, $[Mo_7O_{24}]^{6-}$, are well-characterised examples. So far as they are known, the structures of isopolyanions, as well as those of *heteropoly*-anions such as $[SiW_{12}O_{40}]^{4-}$ and $[CrMo_6O_{24}H_6]^{3-}$, can be regarded as specific fragments of metal oxide lattices.[1] The metal atoms in all these compounds can be considered to be occupying interstices in close-packed arrays of oxide ions. In the oxides, mixed oxides, and some insoluble isopolyanions, the close-packed oxygen atoms form infinite chains, sheets, or three-dimensional lattices, whereas the structures of the soluble isopoly- and of the heteropoly-anions are discrete and usually of high symmetry. As well as behaving as conventional electrolytes, albeit often of high charge and large size, isopoly- and heteropoly-anions exhibit many of the properties of infinite lattices, *e.g.*, intraionic antiferromagnetism, and the ability to undergo partial reduction, forming soluble analogues of the tungsten and vanadium bronzes (heteropoly and isopoly 'blues'). For such reasons polyanions can be used to examine the redox, acid–base, and catalytic properties of metal oxides by methods which are inapplicable to solids, such as absorption spectroscopy and polarography. Further, these anions can be used as convenient models for testing theories of bonding and metal–metal interactions in oxide lattices.

A rationale of the formation, structures, and reactions of such a large fundamental category of compound is far from clear at present. In spite of considerable study during the past 50 years or so, it is probably fair to say that, of the six hydrolysis systems mentioned above, only the isopolychromates are reasonably well understood. Presumably the relative simplicity of chromate hydrolysis is related to the fact that while chromium(VI) appears to be limited to tetrahedral co-ordination in oxide structures, the larger sizes of V^{5+}, Nb^{5+}, Ta^{5+}, Mo^{6+}, and W^{6+} permit variable co-ordination numbers (4—6). Consequently the structural possibilities for isopolyanion formation are much greater with these elements.

In this Review we consider critically information on the structures, reactions,

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[1] L. C. W. Baker in 'Advances in the Chemistry of Co-ordination Compounds', ed. S. Kirschner, Macmillan, New York, 1961, p. 604.

and equilibria of those isopoly-vanadates, -niobates and -tantalates which may be present in aqueous solution. Polyanions obtained from melts and other non-aqueous media are specifically excluded. A brief reading of the literature, including some recent surveys, soon reveals serious differences between the results and interpretations of different research groups, particularly with regard to the vanadates.[2a–2e] [The subject has not been comprehensively and critically reviewed since Rosenheim's ambitious attempt[2f] to correlate the formulae and reactions of all isopoly- and heteropoly-anions in terms of the now abandoned 'Miolati–Rosenheim Theory'.] Some of these differences arise because the experimental conditions used are not strictly comparable, but many have been (and some still are) due to invalid or overambitious reasoning from experimental data, or to measurements inadvertently made under non-equilibrium conditions. In order to resolve some of the current debates, we find it necessary to preface our Review with a brief discussion of experimental difficulties, and the limitations of some commonly-used methods of investigation.

2 Experimental Problems

Table 1 lists those experimental methods which have most often been used for investigating isopolyanions in solution. A few less-common but potentially valuable methods such as n.m.r. are also included.

Table 1 *Methods for investigating isopolyanions in solution*

1. EMF (pH) measurements; equilibrium or rapid-flow
2. Salt cryoscopy
3. Light scattering
4. Equilibrium ultracentrifugation
5. Ion exchange
6. Ultraviolet and visible spectroscopy
7. Sedimentation ultracentrifugation
8. Infrared and Raman spectroscopy
9. Nuclear magnetic resonance (n.m.r.) spectroscopy
10. Diffusion and dialysis

The methods listed can roughly be divided into those which provide information concerning the stoicheiometry of the hydrolysis–polymerisation reactions (numbers 1—6), and those which may reveal ionic structures or sizes (7—10). At the outset it should be made clear that, in the opinion of the Reviewers, no single method is capable of providing an unambiguous answer, especially when the solution being investigated contains several solute species in comparable concentrations (*i.e.*, is polydisperse).

[2] (*a*) A. Morette and R. Rohmer, in 'Nouveau Traité de Chimie Minérale', ed. P. Pascal, Masson et Cie, Paris, 1958, vol. 12; (*b*) L. G. Sillén, *Quart. Rev.*, 1959, **13**, 146; (*c*) P. Souchay, 'Polyanions et Polycations', Gauthier-Villars, Paris, 1963; (*d*) K. F. Jahr, *Angew. Chem. Internat. Edn.*, 1966, **5**, 689; (*e*) Gmelins Handbüch der Anorganischen Chemie, System Nr. 48 'Vanadium', part B, section 1 and 2, Verlag Chemie, Weinheim, 1967; (*f*) A. Rosenheim, in Abeggs Handbüch der Anorganischen Chemie, vol. 4, part 1, Leipzig, 1921, p. 977.

Before discussing the limitations of the methods listed in Table 1, the possible complexities of the systems investigated must be considered. In a formal sense, hydrolysis of a metal oxyanion such as VO_4^{3-} involves reactions in which protons are consumed and the net anionic charge per metal atom, (Z), is reduced (*e.g.*, from 3 in VO_4^{3-} to 0·5 in $[HV_{10}O_{28}]^{5-}$). Since the neutral end-products of hydrolysis of metal oxyanions are the polymeric hydrous oxides ($Z = 0$), it is not surprising that polymeric anions are produced during the course of hydrolysis. What is perhaps surprising is that only a relatively small number of discrete isopolyanions seems to be formed, rather than the complete range of intermediates found in other polymerisations.

The various equilibria involved in anion hydrolysis may be formally divided into two categories, (1) and (2).

Protonation, *e.g.*, $VO_4^{3-} + H^+ \rightleftharpoons HVO_4^{2-}$;
$[HV_{10}O_{27}]^{5-} + H^+ \rightleftharpoons [H_2V_{10}O_{28}]^{4-}$ (1)
Condensation, *e.g.*, $2HVO_4^{2-} \rightleftharpoons V_2O_7^{4-} + H_2O$ (2)

Polymerisations that do not appear to involve condensations, such as (3) and (4) have been postulated in some systems.

$VO_3^- \rightleftharpoons V_3O_9^{3-}$ (3)
$[HW_6O_{21}]^{5-} \rightleftharpoons [H_2W_{12}O_{42}]^{10-}$ (4)

However the degree of solvation of such species is not known, and the mechanisms of these reactions could well involve condensation steps. It has been recognised for many years that these reactions can proceed at very different rates, and since the rapid-flow pH-measurements of Schwarzenbach,[3] more quantitative estimates of such differences can be made. Thus it appears that while protonations are very rapid ($< 10^{-4}$ sec.), some polymerisations, such as the formation of decavanadate from metavanadate, or $[H_2W_{12}O_{40}]^{6-}$ from $[HW_6O_{21}]^{5-}$, can be extremely slow and may take several days, weeks, or even months to reach equilibrium at room temperatures. There is no completely satisfactory explanation why some reactions should be so slow, although it will be noted that in the examples cited the reactions involve large increases in the degree of polymerisation and must involve gross structural changes. Solutions of isopolyanions may therefore contain species which are simultaneously reacting at several different rates. This situation leads to problems of irreversibility and the appearance of pseudo-equilibria.

Because of the wide variation of anionic charge and size encountered in solutions of isopolyanions, moderately concentrated solutions of supporting electrolytes (0·5—3·0M) have been used in those methods (1—4, 6—7) requiring essentially ideal-solution behaviour for valid interpretation of data. Light-scattering and ultracentrifugation[4,5] techniques have clearly demonstrated that

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[3] G. Schwarzenbach, *J. Inorg. Nuclear Chem.*, 1958, **8**, 302.

[4] W. H. Nelson and R. S. Tobias, *Canad. J. Chem.*, 1964, **42**, 731.

[5] W. H. Nelson and R. S. Tobias, *Inorg. Chem.*, 1963, **2**, 985; 1964, **3**, 643; J. Aveston and J. S. Johnson, *Inorg. Chem.*, 1964, **3**, 1051.

highly charged polyanions bind appreciable numbers of counterions from the supporting electrolytes. This is known to affect the position of equilibrium quite significantly in some cases.[6] Finally, many methods (2—4, 7) require extrapolation of data to infinite dilution. In those solutions where concentration-dependent equilibria are involved, such an extrapolation is clearly not possible.

Unfortunately, many investigators have not taken adequate account of the above complications. As a general rule, we have disregarded the conclusions of such studies, and we do not quote numerical results if no indication was provided concerning (*a*) the experimental attainment of equilibrium, (*b*) the temperature at which the measurements were made, or (*c*) the nature or concentration of the supporting electrolyte.

The most widely used method for investigating anion hydrolysis is through the interpretation of inflexions or breaks in pH or conductimetric titration curves. Although some of the earliest investigations of isopoly-vanadates[7] and -niobates[8] were made by such methods, in many cases the results obtained have not proved to be of much value for reasons such as those discussed above. In recent years, Sillén and his colleagues at Stockholm, aware of such difficulties, have significantly improved the technique of pH measurement and interpretation.[9] The method basically measures the number of protons or hydroxyl ions consumed following addition of a known amount of acid or base to a polyanion solution. The results, obtained at several different total concentrations of metal ion, are conventionally presented in the form of titration curves (Z against log $[H^+]$). In the general case, such curves are computer-fitted in terms of the formation constants of a limited number of solute species, each defined by its Z and N (number of metal atoms). Although in principle the interpretation of e.m.f. data should lead to an unambiguous result, this is true only for relatively simple systems. For polydisperse solutes, such as are often encountered with the vanadates, the choice of solute species to be included in the data analysis has usually been made on the basis of other experimental information. Recently, the Sillén group has developed a computer programme (LETAGROPVRID) which can systematically test a large number of solute species and discard those that are unsatisfactory. However, the ambiguities discussed here, still remain in complex systems. Consequently, the main limitation of the method appears when several species are required to fit the whole range of data, as for example in the 'metavanadate' region which is discussed more fully below (p. 536). In order to distinguish between several plausible multicomponent schemes, severe demands are made upon the accuracy and precision of the experimental data. Aveston *et al.*[10] have recently demonstrated the ambiguity which can arise in such cases. However, with the possible exception of the rapid-flow and n.m.r. methods mentioned below, the method is the only one which has proved capable of detecting individual components of a polydisperse solute.

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[6] G. Schwarzenbach and G. Geier, *Helv. Chim. Acta*, 1963, **46**, 906.
[7] P. Düllberg, *Z. phys. Chem.*, 1903, **45**, 129.
[8] P. Sué, *Ann. Chim.*, 1937, **7**, 493.
[9] L. G. Sillén, *Quart. Rev.*, 1959, **13**, 146.
[10] J. Aveston, E. W. Anacker, and J. S. Johnson, *Inorg. Chem.*, 1964, **3**, 735.

Recently Schwarzenbach has developed a technique of rapid-flow pH measurement for polyanion systems.[3] Besides determining stoicheiometries and formation constants of stable species, the method can detect short-lived intermediates and thereby provide mechanistic and, possibly, structural information. Specific applications are discussed later.

Salt cryoscopy is probably the second most often used method of investigation. It has recently received a thermodynamic treatment[11] and can certainly be regarded as a valid method. In a commonly used system, the transition point of reaction (5) is lowered by the presence of foreign ions. If sodium salts are used, only free H^+, HSO_4^-, and the isopolyanions are cryoscopically active, and since the medium furnishes its own concentrated supporting electrolyte, the behaviour is close to ideal. Difficulties arise (*a*) in making adequate allowance for free H^+ and HSO_4^- ions, particularly when their contributions to Δt are larger than those due to the polyanions, and/or when N is large, and (*b*) when concentration-dependent equilibria prevent extrapolation to infinite dilution.

$$Na_2SO_4, 10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O \qquad (5)$$

In spite of criticisms[12] the method is valuable, particularly for identifying or confirming the degree of polymerisation of essentially monodisperse solutes.

Light-scattering[13] and equilibrium ultracentrifugation[14] are complementary methods, providing the same information by independent means. Unambiguous results are obtained only if the solutions are monodisperse and if the degree of polymerisation of the solute is unaffected by dilution. The data yield self-consistent values for N and z^*, the effective ionic charge, which allows for the effects of counterion binding referred to above. In an analogous fashion, sedimentation ultracentrifugation[15] can give the effective ionic weight, M^*, of a monodisperse solute species. In each of these methods, extrapolation to infinite dilution is necessary.

Measurement of the number of metal ions bound by an anion-exchange resin, together with the number of equivalents of counterions liberated, can give a direct measure of Z. However, if moderately rapid depolymerisations can occur, or if the solution is polydisperse, the information obtained by this method is presumably of little value.

The remaining methods listed in Table 1 are of more limited scope, or have been less frequently used. Since most isopolyanions absorb in the near ultraviolet region, spectroscopy is not, in general, capable of differentiating between individual components of a polydisperse system. The method has, however, been used to investigate equilibria involving only two major solute species. The use of Raman spectroscopy to identify well-characterised ionic structures in solution by comparison with the solid-state spectra has been particularly valuable for

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[11] R. Fernandez-Prini and J. E. Prue, *J. Chem. Soc.* (*A*), 1967, 1974.

[12] R. S. Tobias, *J. Inorg. Nuclear Chem.*, 1961, **19**, 348; G. Schwarzenbach and G. Parissakis, *Helv. Chim. Acta*, 1958, **41**, 2425.

[13] R. S. Tobias and S. Y. Tyree, jun., *J. Amer. Chem. Soc.*, 1959, **81**, 6385.

[14] J. S. Johnson, K. A. Kraus, and G. Scatchard, *J. Phys. Chem.*, 1954, **58**, 1034.

[15] M. C. Baker, P. A. Lyons, and S. J. Singer, *J. Amer. Chem. Soc.*, 1955, **77**, 2011.

niobates and tantalates (see below). Direct vibrational analysis and interpretation of Raman and i.r. spectra is limited to simple, symmetrical species. High-resolution n.m.r. spectroscopy has many advantages for studying polydisperse systems, and can also give some structural information. So far, the technique has only been used on vanadate solutions by use of ^{51}V. The results were, on the whole, encouraging, and the method when further developed and tested with well-characterised solute species, could prove to be very useful. Measurements of diffusion and dialysis co-efficients, although they may be capable of revealing gross changes in the size, charge, or structure of the solute species as the pH of the solution is varied, can give no quantitative information.

3 Vanadates

A. Solution Properties.—Before a detailed discussion we give a brief overall picture of present knowledge regarding the chemistry of the vanadates in aqueous solution. Figure 1 shows the ranges of existence of the various vanadate species

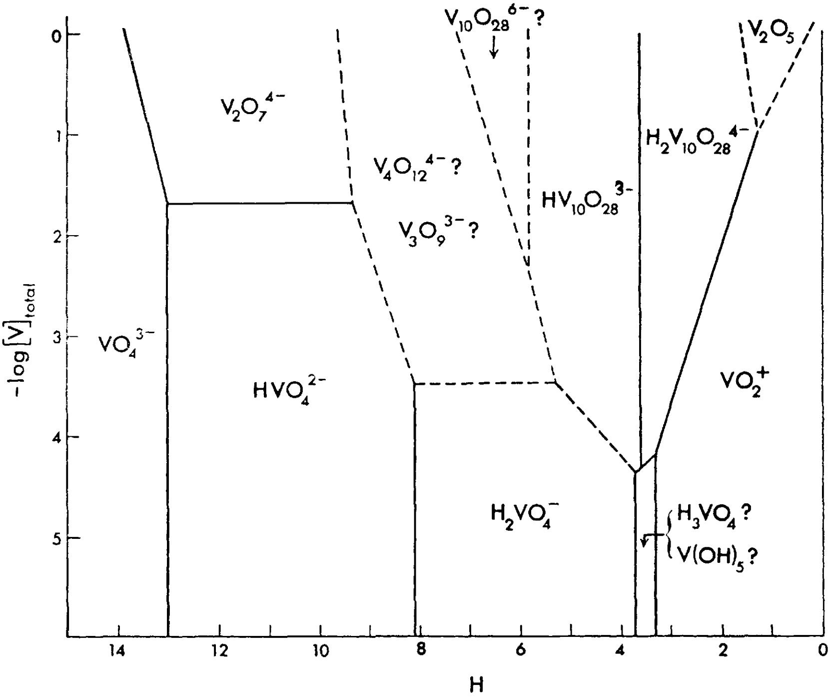

Figure 1 *The approximate conditions of* pH *and total vanadium concentration under which a given species would be the major solute component of a vanadate solution at 25°. Demarcations about which there is considerable doubt are represented by broken lines. The data used in the construction of this diagram were taken from: L. Newman, W. J. LaFleur, F. J. Brousaides, and A. M. Ross,* J. Amer. Chem. Soc., 1958, **80**, 4491; *N. Ingri and F. Brito,* Acta Chem. Scand., 1959, **13**, 1971; *D. Dyrssen and T. Sekine,* Acta Chem. Scand., 1961, **15**, 1399; *F. J. C. Rossotti and H. Rossotti,* Acta Chem. Scand., 1956, **10**, 957. *The data regarding the solubility of* V_2O_5 are *approximate*

as a function of pH and the total vanadium concentration. Such a diagram was first suggested for the vanadates by Schiller and Thilo,[16] but their version contained several errors. (For example, if the law of mass action is assumed to hold, all demarcation lines in the diagram should be straight. Also, all equilibria not involving the proton or the hydroxyl ion must be represented by horizontal lines.) We have, we hope, corrected the errors and brought the diagram up to date. Nevertheless, this diagram is intended as a visual aid, not as a definitive and accurate statement of fact. For example, the results quoted in the caption were not all obtained at the same ionic strength.

We now discuss each area of Figure 1, starting from the alkaline side. There seems to be little doubt that $[VO_4]^{3-}$ is the predominant species present in vanadate solutions at high pH. There is no evidence for the polymerisation of this ion, and no credible measurement of its degree of hydration. It is a moderately strong base, hydrolysing in solution to form $[HVO_4]^{2-}$. The hydrolysis constant, or alternatively, the pK_a of $[HVO_4]^{2-}$, has been determined by several workers; the most accurate measurements are listed in Table 2.

Evidence for the dimerisation of the $[HVO_4]^{2-}$ ion, to yield the species $[V_2O_7]^{4-}$ (and its protonated forms) now seems to be conclusive. Values for the dimerisation constant are given in Table 2. Ingri and Brito[17] in the original report of their work on alkaline vanadate solutions could find no evidence for the unprotonated dimer, although they postulated the existence of the protonated form $[HV_2O_7]^{3-}$. But in a later recalculation of their data[18] they concluded that there was evidence for both the protonated and the unprotonated form. Schwarzenbach and Geier[6] also found evidence for both forms, and report that $[V_2O_7]^{4-}$ is a stronger base than $[HVO_4]^{2-}$.

Protonation of $[HVO_4]^{2-}$ yields the ion $[H_2VO_4]^-$ (Schwarzenbach and Geier's work[6] indicates that the ion formed is a simple protonation product of $[HVO_4]^{2-}$, and we therefore write it as $[H_2VO_4]^-$ rather than $[VO_3]^-$), but this polymerises extensively if the vanadium concentration is greater than about 10^{-4} g.-atom/l. The simple protonation reaction can therefore be studied only in very dilute solution,[16] or by using a rapid-flow technique,[6] although Ingri and Brito[17] obtained a value for the hydrolysis constant by the analysis of equilibrium data obtained at vanadium concentrations in the range 6×10^{-4} to 8×10^{-2} g.-atom/l. The most reliable values for the hydrolysis constant of $[HVO_4]^{2-}$ and the pK_a of $[H_2VO_4]^-$ are listed in Table 2. The values depend quite strongly upon the nature of the medium employed. Schwarzenbach and Geier[6] have interpreted their results in terms of complex formation between $[HVO_4]^{2-}$ ions and the cations of the supporting electrolyte. There seems to be a case for using tetra-alkylammonium salts as supporting electrolytes for work on alkaline vanadate solutions.

The nature of the species formed by the polymerisation of $[H_2VO_4]^-$ is perhaps

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[16] K. Schiller and E. Thilo, *Z. anorg. Chem.*, 1961, **310,** 261.

[17] N. Ingri and F. Brito, *Acta Chem. Scand.*, 1959, **13,** 1971; F. Brito and N. Ingri, *Anales. Real. Soc. Esp. Fis. Quím.*, 1960, *B*, **56,** 165.

[18] F. Brito, N. Ingri, and L. G. Sillén, *Acta Chem. Scand.*, 1964, **18,** 1557.

Table 2 *Selected equilibrium data for aqueous vanadate solutions*

Equilibrium	*−Log* K	*Method*	*Temp.*	*Medium**	*Ref.*
$[HVO_4]^{2-} \rightleftharpoons H^+ + [VO_4]^{3-}$	13·2	Na_2SO_4 cryos.	32·4°	sat. Na_2SO_4	*a*
	13·0 ± 0·3	U.v.Spect.	25	0·5 (NaCl)	*b*
$[VO_4]^{3-} + H_2O \rightleftharpoons [HVO_4]^{2-} + OH^-$	1·01 ± 0·02	U.v.Spect.	25	3·0 ($NaClO_4$)	*c*
$2[HVO_4]^{2-} \rightleftharpoons [V_2O_7]^{4-} + H_2O$	−1·68 ± 0·04	U.v.Spect.	25	3·0 ($NaClO_4$)	*c*
$H_2O + 2[HVO_4]^{2-} \rightleftharpoons [HV_2O_7]^{3-} + OH^-$	3·18 ± 0·05	E.m.f.	25	0·5 (NaCl)	*b, d*
	3·16 ± 0·08	E.m.f.	25	0·5 (NaCl)	*e*
$[HVO_4]^{2-} + H_2O \rightleftharpoons [H_2VO_4]^- + OH^-$	6·0 ± 0·1	E.m.f.	25	0·5 (NaCl)	*b, d*
	5·89 ± 0·06	E.m.f.	25	0·5 (NaCl)	*e*
$[H_2VO_4] \rightleftharpoons H^+ + [HVO_4]^{2-}$	8·31	E.m.f. (rapid flow)	20	1·0 (T.M.A.Cl)†	*f*
	8·36	E.m.f. (rapid flow)	20	0·1 (T.M.A.Cl)†	*f*
	7·88	E.m.f. (rapid flow)	20	1·0 (NaCl)	*f*
	8·04	E.m.f. (rapid flow)	20	1·0 (KCl)	*f*
	8·23	E.m.f. (rapid flow)	20	0·1 ($NaClO_4$)	*f*
$HVO_3 \rightleftharpoons VO^{3-} + H^+$ ‡	3·70	Phase distr.	25	0·5 ($NaClO_4$)	*g*
$H_3VO_4 \rightleftharpoons H_2VO_4^- + H^+$	3·40	E.m.f. (rapid flow)	20	0·1 ($NaClO_4$)	*f*
$VO_2^+ + H_2O \rightleftharpoons HVO_3 + H^+$	3·30	Phase distr.	25	0·5 ($NaClO_4$)	*g*

Table 2—*continued*

Equilibrium	$-$*Log* K	*Method*	*Temp.*	*Medium**	*Ref.*
$10VO_2^+ + 8H_2O \rightleftharpoons [H_2V_{10}O_{28}]^{4-} + 14H^+$	6·75 ± 0·15	E.m.f.	25	1·0 ($NaClO_4$)	*h*
	5·5 ± 0·15	E.m.f.	25	3·0 ($NaClO_4$)	*h*
$[H_2V_{10}O_{28}]^{4-} \rightleftharpoons [HV_{10}O_{28}]^{5-} + H^+$	3·6 ± 0·3	E.m.f.	25	1·0 ($NaClO_4$)	*h*
	3·5 ± 0·3	E.m.f.	25	3·0 ($NaClO_4$)	*h*
	4·45	E.m.f. (rapid flow)	20	0·1 (T.M.A.Cl)†	*f* §
	4·34	E.m.f. (rapid flow)	20	0·1 ($NaClO_4$)	*f* §
	3·6	E.m.f. (rapid flow)	20	1·0 ($NaClO_4$)	*f* §
$[HV_{10}O_{28}]^{5} \rightleftharpoons [V_{10}O_{28}]^{6-} + H^+$	5·8	E.m.f.	25	1·0 ($NaClO_4$)	*h*
	7·52	E.m.f. (rapid flow)	20	0·1 (T.M.A.Cl)	*f* ‡
	6·94	E.m.f. (rapid flow)	20	0·1 ($NaClO_4$)	*f* ‡
	6·06	E.m.f. (rapid flow)	20	1·0 ($NaClO_4$)	*f* ‡

[a] P. Souchay and R. Schaal, *Bull. Soc. chim. France*, 1950, 842.
[b] F. Brito and N. Ingri, *Anales. Real. Soc. Esp. Fis. Quim.*, 1960, *B*, **56**, 165.
[c] L. Newman, W. J. LaFleur, F. J. Brousaides, and A. M. Ross, *J. Amer. Chem. Soc.*, 1958, **80**, 4491.
[d] N. Ingri and F. Brito, *Acta Chem. Scand.*, 1959, **13**, 1971.
[e] F. Brito, N. Ingri, and L. G. Sillén, *Acta Chem. Scand.*, 1964, **18**, 1557.
[f] A. Schwarzenbach and A. Geier, *Helv. Chim. Acta*, 1963, **46**, 906.
[g] D. Dyrssen and T. Sekine, *Acta Chem. Scand.*, 1961, **15**, 1399.
[h] F. J. C. Rossotti and H. Rossotti, *Acta Chem. Scand.*, 1956, **10**, 957.
* The magnitude of the ionic strength employed, and the supporting electrolyte used.
† T.M.A.Cl = tetra-methyl ammonium chloride.
‡ However, see text.
§ Values are also given for other media.

the most important unsolved problem in this field. Düllberg's original postulate,[7] based upon pH titrations and conductivity measurements, was that the major polymeric species in the pH range 6·5—8·2 was the trimer $[V_3O_9]^{3-}$, and he has been supported in this by several other workers.[16,19] On the other hand, a considerable body of reliable evidence has accumulated since 1953 to support the suggestion, originally made in 1933 by Jander and Jahr,[20] that the main product of polymerisation in this pH range is the tetramer, $[V_4O_{12}]^{4-}$. The fact that most of the evidence for the tetramer has come from cryoscopic measurements may, however, be significant; such measurements necessarily involve very high ionic strengths and, usually, high vanadium concentrations. The most reliable of these measurements are those of Jahr and his school,[21] and those of Naumann and Hallada.[22] The latter workers studied as large a concentration range as they found was compatible with accuracy, and also examined the equilibria on the acid side of the metavanadate region. This was to ensure that their results were not being distorted by the highly condensed polyvanadates known to be present in acidic vanadate solutions. Credible evidence for the $[V_3O_9]^{3-}$ ion is provided by Schiller and Thilo.[16] Using u.v. spectroscopy and very dilute solutions they obtained a set of consistent values for the trimerisation constant of $[H_2VO_4]^-$. Unfortunately, however, they did not work at constant ionic strength and they also failed to record the temperature of measurement.

The evidence provided by extensive e.m.f. measurements cannot yet be regarded as conslusive. Ingri and Brito, in their original report,[17] obtained a satisfactory theoretical fit for their experimental data on the assumption that the only important species in solution between pH 7 and pH 12 were $[HVO_4]^{2-}$, $[HV_2O_7]^{3-}$, $[H_2VO_4]^-$, and $[V_3O_9]^{3-}$. However, in a later recalculation[18] using the computer programme LETAGROP they found that the overall standard deviation could be reduced from 0·012 to 0·009 if the set of species was enlarged to include $[V_2O_7]^{4-}$, $[V_4O_{13}]^{6-}$, and $[V_4O_{12}]^{4-}$. This slight improvement in the standard deviation cannot, however, be considered to be positive evidence for a tetrameric 'metavanadate' in view of the almost two-fold increase in the number of species being considered. [The prefixes ortho-, pyro-, and meta-, with reference to vanadates and niobates, were originally introduced in the belief that these ions were analogous to the corresponding phosphates. The terms have no structural significance, but have been retained for convenience. They refer to anions with Z-values of 3(ortho), 2(pyro), and 1(meta).]

More recent work by Brito[23] on the acid side of the 'metavanadate' region (carried out at 40° to hasten the attainment of equilibrium), has also been interpreted in terms of a trimeric and a tetrameric 'metavanadate' in equilibrium with one another.[23,24] In this case it was found that a satisfactory fit could be achieved

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[19] R. A. Robinson and D. A. Sinclair, *J. Chem. Soc.*, 1934, 642; P. Souchay and G. Carpéni, *Bull. Soc. chim. France*, 1946, **13**, 160; P. Souchay, *ibid.*, 1947, **14**, 914.

[20] G. Jander and K. F. Jahr, *Z. anorg. Chem.*, 1933, **212**, 1.

[21] K. F. Jahr and L. Schoepp, *Z. Naturforsch.*, 1959, **14**b, 467; K. F. Jahr, H. Schroth, and J. Fuchs, *ibid.*, 1963, **18**b, 1133.

[22] A. W. Naumann and C. J. Hallada, *Inorg. Chem.*, 1964, **3**, 70.

[23] F. Brito, *Anales. Real. Soc. Esp. Fis. Quim.*, 1966, *B*, **62**, 123.

[24] F. Brito, *Acta Chem. Scand.*, 1967, **21**, 1968.

by assuming a set of five species, each of which had been postulated at various times by other workers. However, it was then found that a slightly better fit was obtained by the addition of several other, rather less likely species. It is clearly necessary, therefore, to have some independent way of deciding what constitutes an acceptable species. The method assumes that all species, having a given value of Z and N, have the same properties irrespective of the degree of counterion-binding. Such an assumption may have no validity. The measurements under discussion were all carried out in 0·5M-NaCl (although some preliminary measurements were made in 3·0M-NaCl). Schwarzenbach and Geier[6] have recently shown that there is appreciable complex formation between sodium ions and several vanadate species. Ingri, Brito, and Sillén do not seem to have adequately considered this point. Measurements made with a different supporting electrolyte seem to be very desirable in this complex system. These criticisms notwithstanding, the suggestion that trimeric and tetrameric 'metavanadates' are in equilibrium with one another in aqueous solution, is one which explains all known credible data on this problem, but the matter cannot yet be regarded as closed. (There is, of course, some inconsistency in criticising Ingri, Brito, and Sillén's evidence for the $[V_4O_{12}]^{4-}$ ion, while at the same time quoting their values for the hydrolysis constants of other species. However, the figures that we quote are ones that remain consistent within the given limits of error, irrespective of what other species are considered to be present in solution. We would regard such figures as valid.)

Simple protonation of $[H_2VO_4]^-$ yields the uncharged vanadic acid H_3VO_4. The second of these species is even more susceptible to polymerisation than the first, but Dyrssen and Sekine[25] were able to study this reaction under equilibrium conditions by working with exceedingly dilute solutions and extracting the uncharged vanadic acid into an organic solvent. The distribution of vanadium between the two phases was determined by a sensitive radioactive tracer method. Dyrssen and Sekine give a value of 3·7 for the pK_a of H_3VO_4 (Table 2). Schwarzenbach and Geier[6] have also been able to study this equilibrium, using their rapid-flow technique. They give a value of 3·3 for the first pK_a of H_3VO_4, and attach considerable importance to the difference between this value and that of Dyrssen and Sekine. We shall return to this point.

The nature of the species existing on the acid side of the 'metavanadate' region at ordinary concentrations is another subject that has provoked much discussion. Early workers based their conclusions almost entirely upon breaks and inflexions in conductimetric and pH-titration curves. They soon divided themselves into two camps; those who supported Düllberg[7] in his belief that the main species present in weakly acidic vanadate solutions was the hexavanadate $[V_6O_{17}]^{4-}$ and those who preferred the decavanadates suggested by Britton[26] and his co-workers. Very little real progress was made until 1956, when Rossotti

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[25] D. Dyrssen and T. Sekine, *Acta Chem. Scand.*, 1961, **15**, 1399.

[26] H. T. S. Britton and R. A. Robinson, *J. Chem. Soc.*, 1932, 1955; H. T. S. Britton and G. Welford, *ibid.*, 1940, 764.

and Rossotti[27] published the results of their work. They chose to start in the low pH region, where the predominant vanadium species is almost certainly the VO_2^+ ion,[28] and then studied the polymerisation that took place as the solution was made more basic. Using graphical methods, they were able to account for their e.m.f. and spectral data on the basis of four species: VO_2^+, $[H_2V_{10}O_{28}]^{4-}$, $[HV_{10}O_{28}]^{5-}$, and $[V_{10}O_{28}]^{6-}$. (They could not be completely unequivocal about this, but their results certainly could not be interpreted in terms of hexavanadate or other even less polymerised species.) Crysocopic measurements[22] and e.m.f. measurements in a rapid-flow apparatus[29] later provided independent verification of these results. However, recent papers[6,23,24] have cast doubt upon some of this work. The Rossottis made their measurements between pH 1 and pH 7. It seems probable, in the light of recent developments, that they did not in fact achieve true equilibrium in the upper part of this range although they reported that no electrode readings were recorded unless they had remained stable for at least 3 hr. Schwarzenbach and Geier[6] have shown that, although the monohydrogen decavanadate, $[HV_{10}O_{28}]^{5-}$ is quite stable in fairly concentrated solution ($[V]_{total} = 0{\cdot}5$ g.-atom/l.), it hydrolyses to the extent of about 4% in a more dilute solution ($[V]_{total} = 0{\cdot}15$ g.-atom/l.) with the evolution of protons. Equilibrium is only achieved after six months or so. A dilute solution of the unprotonated decavanadate $[V_{10}O_{28}]^{6-}$ disproportionates extensively, during 6 months, into the monoprotonated form and, presumably, 'metavanadate'. On the assumption that in both cases the hydrolysis product was indeed 'metavanadate' and further assuming that this was in the trimeric form, Schwarzenbach and Geier were able to obtain a value of 10^{-108} for K, the equilibrium constant

$$6H_2O + 3[HV_{10}O_{28}]^{5-} \rightleftharpoons 15H^+ + 10[V_3O_9]^{3-} \quad [\mu = 1{\cdot}0\ (NaClO_4);\ 20°c] \qquad (6)$$

of reaction (6). Now, by combining the Rossottis' results[27] with those of Ingri and Brito[17] and those of Dyrssen and Sekine,[25] we can obtain a value of 10^{-104} for K. This is surprisingly good agreement, in view of the large number of steps required to derive the second figure and the differences in ionic strength and temperature that are involved. Hence it should have been obvious for some time that the unprotonated decavanadate could not be a thermodynamically stable species at pH 6·5, as is implied by the Rossottis. This point has been underlined by recent work of Brito,[23,24] some of which we discussed earlier. By computer analysis of e.m.f. measurements made at 40° in the pH range 2—8 he concluded that the major vanadate species present under such conditions were $[V_3O_9]^{3-}$, $[V_4O_{12}]^{4-}$, $[HV_6O_{17}]^{3-}$, $[HV_{10}O_{28}]^{5-}$, and $[H_2V_{10}O_{28}]^{4-}$. He found no evidence for the unprotonated decavanadate $[V_{10}O_{28}]^{6-}$. We have commented previously upon the validity of results obtained by the type of analysis used by Brito and in our opinion his conclusions require independent verification before they can be regarded as well-established. Such verification is not, unfortunately, provided

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[27] F. J. C. Rossotti and H. S. Rossotti, *J. Inorg. Nuclear Chem.*, 1956, **2**, 201; *Acta Chem. Scand.*, 1956, **10**, 957.

[28] M. J. LaSalle and J. W. Cobble, *J. Phys. Chem.*, 1955, **59**, 519.

[29] G. Schwarzenbach, *Pure Appl. Chem.*, 1962, **5**, 377.

by Naumann and Hallada's cryoscopic work,[22] even though they did undertake a study of the metavanadate–decavanadate equilibrium. It is extremely unlikely that any cryoscopic measurement would be able to distinguish a direct metavanadate–decavanadate equilibrium from one going through an intermediate hexavanadate. However, Brito's results are obviously in good general agreement with those of Schwarzenbach and Geier. Both investigations indicate that $[V_{10}O_{28}]^{6-}$ has a very limited range of existence, if it is stable at all.

In Table 2 we have recorded the formation constant of $[H_2V_{10}O_{28}]^{4-}$ from VO_2^+, and also its two pK_a's as determined by Rossotti and Rossotti. Despite what has been said above about the instability of the $[V_{10}O_{28}]^{6-}$ ion, these figures are still valid. They are seen to agree quite well with those of Schwarzenbach and Geier, which are also shown.

B. The Structures of Vanadate Ions in the Solid State.—This aspect of the subject was last reviewed in 1961,[30] and we shall be concerned mainly with developments that have taken place since then.

On a simple radius-ratio argument the V^{5+} ion would be expected to be somewhat large for tetrahedral co-ordination to oxygen, somewhat small for octahedral co-ordination. The possibility of very irregular structures therefore arises. This point has been discussed by Orgel[31] and we shall confine ourselves to empirical observations here.

A detailed structure of a crystalline orthovanadate has yet to appear in the literature. Most of the present information comes from partial structural determinations, performed on the very insoluble orthovanadates of tervalent metal cations, or from the observed isomorphism of hydrated sodium ortho-vanadates, -phosphates, and -arsenates.[32] These studies indicate that such compounds contain discrete $[VO_4]^{3-}$ anions and that these are essentially tetrahedral, although slight distortions are sometimes found. The V—O bond lengths are reported to vary between 1·64 and 1·74 Å, although a value of *ca.* 1·66 Å could be regarded as typical.

The $[V_2O_7]^{4-}$ ion was shown to be isostructural with the $[P_2O_7]^{4-}$ ion by Peyronel[33] in 1942, and the complete structure of $Cd_2V_2O_7$ has recently been published by Au and Calvo.[34] The crystal contains discrete $[V_2O_7]^{4-}$ ions, which consist of two VO_4 tetrahedra sharing a corner. The vanadium ions are displaced slightly away from the centre of symmetry. However, the bridging oxygen shows a very high thermal motion, and it is not at all clear whether the V—O—V link should be regarded as linear or not.

No structure is yet known in which a discrete 'metavanadate' ion can be distinguished. All structures so far studied have been found to contain infinite

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[30] H. G. Bachmann and W. H. Barnes, *Z. Krist.*, 1961, **115**, 215.

[31] L. E. Orgel, *Discuss. Faraday Soc.*, 1958, **26**, 138.

[32] E. Broch, *Z. physik. Chem. (Leipzig)*, 1933, **20**, *B*, 345; R. W. G. Wyckoff, 'Crystal Structures', 2nd edn., Interscience, New York, vol. 3, 1965, pp. 17, 67; A. F. Wells, 'Structural Inorganic Chemistry, 3rd edn., Oxford Univ. Press, 1962, p. 686.

[33] G. Peyronel, *Gazzetta*, 1942, **72**, 83.

[34] P. K. L. Au and C. Calvo, *Canad. J. Chem.*, 1967, **45**, 2297.

chains of vanadium–oxygen polyhedra, linked either through corners or edges. Two distinctly different types of chain have so far been described. In the anhydrous metavanadates, of which we shall take KVO_3 and NH_4VO_3 as examples, since they have received the closest attention,[35,36] the vanadium atoms are quite definitely four-co-ordinate (Figure 2a). Of the four oxygen atoms surrounding each vanadium atom, two are responsible for linking the tetrahedra together and are therefore shared between two vanadium atoms. The V—O bond lengths in this case are quite long, 1·81 Å. The other two oxygen atoms are unshared and the bond lengths here are found to be 1·66 Å, close to the typical distance found in the pure tetrahedral co-ordination of the orthovanadates. After these

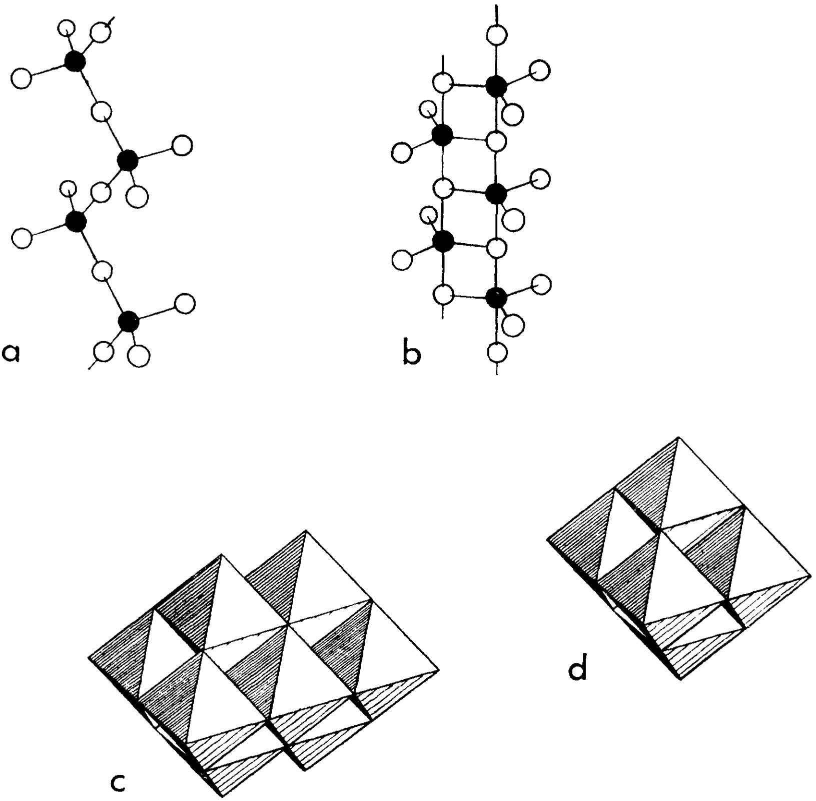

Figure 2 *The structures of some isopolyanions in the solid state.* (*a*) *The structure of the infinite chains of* VO_4 *tetrahedra found in anhydrous 'metavanadates'.* (*b*) *The structure of the infinite chains of* VO_5 *polyhedra found in hydrated 'metavanadates'.* (*c*) *The structure of the* $[V_{10}O_{28}]^{6-}$ *ion.* (*d*) *The structure of the* $[Nb_6O_{19}]^{8-}$ *and* $[Ta_6O_{19}]^{8-}$ *ions*
In (*a*) and (*b*), ● = V; ○ = O; in (*c*) and (*d*) each octahedron represents an MO_6 unit.

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[35] V. Syneček and F. Hanic, *Czech. J. Phys.*, 1954, **4**, 120.
[36] H. T. Evans, *Z. Krist.*, 1960, **114**, 257.

four, the next nearest oxygen atom is more than 3 Å away and is clearly not involved in the co-ordination around the vanadium. In the hydrated metavanadates, of which we take KVO_3, H_2O as an example,[36,37] the vanadium atoms are quite clearly five-co-ordinate. Again the oxygen atoms can be divided into two groups; those that are shared between two vanadium atoms and those that are unshared (Figure 2b). There are three of the former type per vanadium atom and again the V—O bond lengths here are long (1·93, 1·93, and 1·97 Å) while the two unshared oxygen atoms remain at 1·65 Å and 1·67 Å. The next nearest oxygen atom is 3·73 Å away. The co-ordination around the vanadium atom is approximately trigonal bipyramidal. The five-co-ordinate chain structure thus formed is very similar to that found in crystalline V_2O_5.[38]

As described in the previous section, slightly acidic vanadate solutions probably contain a great many different species at equilibrium. Moreover, there is an additional complication, in that equilibrium is reached very slowly. It is not surprising, therefore, to find that the nature of the solids that crystallise out of such solutions is very strongly dependent upon the exact conditions employed. When a vanadate solution is acidified beyond pH 6·5 it turns bright orange, and at suitable concentrations will yield crystalline salts of the decavanadate ions $[H_2V_{10}O_{28}]^{4-}$, $[HV_{10}O_{28}]^{5-}$, and $[V_{10}O_{26}]^{6-}$ in various degrees of hydration. However, if sufficient acid is added to make the Z-value exactly 0·6 (corresponding to $[V_{10}O_{28}]^{6-}$) and the solution is then kept at 60°, an almost insoluble light-orange product is obtained, having the empirical formula $M^{I}V_3O_8$.[39] But if a solution containing slightly less acid is rapidly evaporated at 40° dark red crystals of a pentavanadate $M^{I}_3V_5O_{14}$ are produced.[39] Of these products the most important, from a general point of view, are the decavanadates, because of the support they provide for the conclusions of Rossotti and Rossotti, and because of the strong possibility that these isopolyanions have the same structure in solution as they do in the solid state.

The structure of the decavanadate ion, $[V_{10}O_{28}]^{6-}$, was determined simultaneously and independently by Evans,[40] working with $K_2Zn_2V_{10}O_{28}$, $16H_2O$, by Swallow and Barnes,[40] using crystals of $Ca_3V_{10}O_{28}$, $16H_2O$, and by Pullman,[40] working with $Na_6V_{10}O_{28}$, $18H_2O$. The results of these three investigations are entirely consistent, and the structure of the decavanadate ion is as shown in Figure 2c. Six VO_6 octahedra are linked by edge-sharing into a 3 × 2 rectangular sheet. The other four octahedra are attached to this sheet, two to the upper side, two to the lower, by sharing of sloping edges. Evans[41] and Swallow, Ahmed, and Barnes[42] subsequently published refinements of their data which showed that all VO_6 octahedra were strongly distorted. The distortions can be

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[37] C. L. Christ, J. R. Clark, and H. T. Evans, *Acta Cryst.*, 1954, **7,** 801.

[38] A. Byström, K. A. Wilhelmi, and O. Brotzen, *Acta Chem. Scand.*, 1950, **4,** 119; H. G. Bachmann, F. R. Ahmed, and W. H. Barnes, *Z. Krist.*, 1961, **115,** 110.

[39] H. T. Evans and S. Block, *Inorg. Chem.*, 1966, **5,** 1808.

[40] H. T. Evans, A. G. Swallow, and W. H. Barnes, *J. Amer. Chem. Soc.*, 1964, **86,** 4209; N. Pullman, Ph.D. Thesis, Rutgers University, 1966 (Diss. Abs. 1967, **28,** *B*, 140).

[41] H. T. Evans, *Inorg. Chem.*, 1966, **5,** 967.

[42] A. G. Swallow, F. R. Ahmed, and W. H. Barnes, *Acta Cryst.*, 1966, **21,** 397.

described briefly by saying that all vanadium atoms are displaced away from the centre of the ion. Hence in each of the four octahedra that form the corners of the rectangular sheet and in each of the four that are on its top and bottom sides, the vanadium atom is displaced towards the outermost oxygen atom. The short V—O distances are found to be between 1·59 and 1·62 Å. In each of the two octahedra that are in the centre of the rectangular sheet, the vanadium atom is displaced towards the outside pair of oxygen atoms, and the short V—O bond lengths here are found to lie between 1·68 and 1·70 Å. There are further, less symmetric distortions, but these are probably due to hydrogen bonding in the crystal.

The structures of KV_3O_8 and CsV_3O_8 have been described by Evans and Block.[39] In contrast to the decavanadates, no discrete isopolyanion can be distinguished here. It is best first to consider the vanadium to be octahedrally co-ordinated. The octahedra then link together by sharing edges to form a buckled sheet. Adjacent sheets are held together entirely by the cations. However, within each octahedron the vanadium atom is strongly displaced towards one oxygen atom, and two types of vanadium can be distinguished, according to the extent of this distortion. In one case the short V—O distance is 1·624 Å and in the other it is 1·575 Å. This leaves correspondingly long V—O distances, 2·28 Å and 2·973 Å respectively, on the opposite sides of the octahedra. In the second case it is doubtful whether this oxygen atom can really be considered to be part of the vanadium co-ordination, which now might be regarded as five-fold (square pyramidal).

The structure of $K_3V_5O_{14}$ has not been reported in detail, but Byström and Evans[43] have shown that the vanadium-oxygen polyhedra are arranged in groups of five, so that the vanadium atoms lie roughly in a plane, forming an almost regular pentagon. Three of these vanadium atoms are in approximately square pyramidal co-ordination, while the other two are in approximately trigonal pyramidal co-ordination. In each case there is a short bond to one apex of the pyramid (1·5—1·6 Å) and a very long bond (*ca.* 3·4 Å) through the opposite side to an oxygen atom in another layer of V—O polyhedra.

C. The Structures of Vanadate Species in Solution.—Experimental techniques which are capable of providing unequivocal evidence for the structures of solute species are, at the moment, non-existent, except for the special case of highly symmetric molecules and ions. We therefore have very few hard facts regarding the structures of vanadate species in solution. In this situation it is very tempting to draw heavily on the few known crystal structures containing discrete vanadate ions. However, such an approach could prove to be misleading unless very careful note is taken of the precise conditions under which the crystals were obtained.

Infrared[44] and Raman[45] studies indicate that VO_4^{3-} is tetrahedral in solution,

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[43] A. M. Byström and H. T. Evans, *Acta Chem. Scand.*, 1959, **13**, 377.
[44] H. Siebert, *Z. anorg. Chem.*, 1954, **275**, 225.
[45] W. P. Griffiths and I. D. Wickins, *J. Chem. Soc. (A)*, 1966, 1087.

as it is in the solid state. This is supported by ^{51}V n.m.r. work;[46] the resonance corresponding to the VO_4^{3-} is very narrow, indicating that the symmetry around the vanadium atom is cubic.

According to Pauling's well-tested theory, the successive pK_a's of a polybasic acid, such as H_3VO_4, should be separated by equal increments, provided that the basic structure does not change. Schwarzenbach and Geier's values[6] for the first and second pK_a of H_3VO_4, obtained by protonation of $[HVO_4]^{2-}$ in a rapid-flow apparatus, are 3·4 and 8·23 [$\mu = 0{\cdot}1$M ($NaClO_4$): 25°]. The work of Newman[47] and his co-workers yields a value of 13·5 for the third pK_a, calculated on the assumption that the ionic product of water is $10^{-14{\cdot}22}$ in 3M-$NaClO_4$ at 25° and with correction of +0·3 in order to convert from 3M-$NaClO_4$ to 0·1M-$NaClO_4$.[10] The increments between these values are seen to be sensibly constant. Moreover, the parallel between these values and those for phosphoric acid H_3PO_4 (2·1, 6·71, and 11·8) is seen to be quite close. This strongly suggests that the species, $[VO_4]^{3-}$, $[HVO_4]^{2-}$, $[H_2VO_4]^-$, and H_3VO_4 are all based upon the same structure, *i.e.*, a tetrahedrally co-ordinated vanadium atom. Schwarzenbach and Geier's results were, however, obtained under non-equilibrium conditions, and it is necessary to ask whether these species are the same as those existing at equilibrium. In the case of $[HVO_4]^{2-}$ and $[H_2VO_4]^-$ they probably are; Newman's value for the third pK_a was the result of measurements made on equilibrated solutions, and values for the second pK_a determined from equilibrium measurements agree with those obtained by the rapid-flow technique when differences in ionic strength are taken into account. However, in the case of the first pK_a, there appears to be a genuine difference between the value obtained by the rapid-flow method and the equilibrium value obtained by Dyrssen and Sekine.[25] The latter employed an ionic strength of 0·5, and obtained a value of 3·7 (Schiller and Thilo,[16] presumably using solutions of very low ionic strength, found the first pK_a to be between 4·3 and 4·8 at equilibrium; which is consistent with the present argument). A positive correction must be made to Dyrssen and Sekine's value of 3·7 to make it comparable with Schwarzenbach and Geier's value of 3·4, obtained at an ionic strength of 0·1. When this is done, it is apparent that the two results do not agree, and this has been taken by Schwarzenbach and Geier to mean that 'vanadic acid' is not all in the form of H_3VO_4 at equilibrium. They suggest that some of it may exist as $V(OH)_5$, which would be expected to be a considerably less acidic species than H_3VO_4.

Howarth and Richards[46] have shown that when solutions containing the $[VO_4]^{3-}$ ion are progressively acidified, a plot of the ^{51}V chemical shift against average charge per vanadium atom (Z) is linear for all species up to and including 'metavanadate'. There is a definite discontinuity at decavanadate. Since the $[VO_4]^{3-}$ ion is tetrahedral these results suggest that the structures of the ions $[HVO_4]^{2-}$, $[HV_2O_7]^{3-}$, $[V_2O_7]^{4-}$, and $[V_3O_9]^{3-}$ (and/or $[V_4O_{12}]^{4-}$?) (these are the

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[46] O. W. Howarth and R. E. Richards, *J. Chem. Soc.*, 1965, 864.

[47] L. Newman, W. J. LaFleur, F. J. Brousaides, and A. M. Ross, *J. Amer. Chem. Soc.*, 1958, **80**, 4491.

only ions that would be present in appreciable amounts at the concentrations used by Howarth and Richards) are also based upon VO_4 tetrahedra, while the structure of the decavanadate ion is based upon some other co-ordination. If this is correct there could be quite a close parallel between the structures of these ions in solution and the corresponding structures in the solid state, although the vanadium atoms in solid 'metavanadates' can, of course, be either four- or five-co-ordinate.

Before the work of Howarth and Richards,[46] Ingri and Brito[17] had put forward a different theory. Noting that in solid hydrated 'metavanadates' the vanadium atoms can be considered to be five-co-ordinate, they pointed out that the species thought to be present in vanadate solutions under various conditions could all be based upon VO_5 units rather than VO_4 tetrahedra. However, given that $[VO_4]^{3-}$ is tetrahedral, it is significantly more difficult to account for the above evidence on the basis of a pentaco-ordinate vanadium species, although neither the thermodynamic nor the n.m.r. evidence can be regarded as conclusive. An experiment performed by Schwarzenbach and Geier[6] is very interesting in this context. To a solution in which VO_2^+ ions were the predominant vanadium-containing species they added sufficient hydroxide ion to give a mixture of $[HVO_4]^{2-}$ and $[H_2VO_4]^-$ in equal proportions (*i.e.*, 2·5 moles of hydroxide per mole of VO_2^+ more than required to neutralise the free acid present). After 10^{-2} sec. the pH of the solution was 4·5; only after 10^{-1} sec. did it rise to 8·2. A possible interpretation of these results would be that the first-formed species were $[VO_2(OH)_3]^{2-}$ and $[VO_2(OH)_2]^-$ which then had to undergo rearrangement in order to yield $[HVO_4]^{2-}$ and $[H_2VO_4]^-$. At present, however, this can only be regarded as an attractive hypothesis.

It is noteworthy that, in solution, there seems to be evidence for both trimeric and tetrameric forms of metavanadate, while there is no evidence whatever for a dimer. This suggests that polymeric metavanadates are cyclic. This possibility was first put forward by Ingri and Brito[17] in the case of $[V_3O_9]^{3-}$ and by Simon and Jahr[48] in the case of $[V_4O_{12}]^{4-}$.

As pointed out earlier, a plot of the ^{51}V chemical shift against the average charge per vanadium atom shows a discontinuity at the metavanadate–decavanadate transition. This probably indicates a pronounced difference in the co-ordination around the vanadium atoms in these two species. As was also pointed out earlier, the reaction of metavanadate with acid to form decavanadate is extremely slow. This could be taken as evidence for a change in the co-ordination number of the vanadium atoms, although the corresponding reaction in the case of the molybdates, where a change in co-ordination is known to occur, has been reported[3] to be fast. (In the case of the molybdates a monomer reacts with acid to form a polymer. In the case of the vanadates, both reactant and product are polymers.) In the solid state, of course, there is a pronounced difference between co-ordination around the vanadium in the metavanadates as opposed to the decavanadates, and it is very tempting to suppose that the

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[48] J. Simon and K. F. Jahr, *Z. Naturforsch.*, 1964, **19b**, 165.

$[V_{10}O_{28}]^{6-}$ ion and its protonated forms have the same structure in solution as they do in the solid state. However, what little evidence there is on this point, all of it from n.m.r. measurements, seems to point to a different conclusion. Howarth and Richards[46] report that the n.m.r. spectra of weakly acid vanadate solutions consist of two broad resonances and one narrow one, having respective intensity ratios of 1:3:1. These features are practically independent of the total vanadium concentration. Such results seem to be quite incompatible with the supposition that the decavanadate ion has the same structure in solution as it does in the solid state, since this would require intensity ratios of 2:2:1 (not necessarily in that order). However Hatton *et al.*,[49] who have also studied ^{51}V n.m.r. spectra of vanadate solutions, come to some quite different conclusions. The chemical shifts they report are, unfortunately, quoted relative to the resonance given by an aqueous solution of ammonium metavanadate, but they seem to agree roughly with those of Howarth and Richards. However, the line-widths and intensities are quite different in the two papers. While the more careful and extensive work of Howarth and Richards seems to be preferable, there is considerable scope for a reinvestigation here. It would also be advantageous to test the n.m.r. technique on a well-established system.

The rather elaborate cage structure suggested for the decavanadate anion by Jahr, Fuchs, and Preuss[50] is almost certainly wrong. The structure was suggested to account for the complexes that are formed between the decavanadate anion and alkaline earth cations, and it consists of three interlocking rings of VO_4 tetrahedra. Such complexity is not required in order to account for the observed complex formation, since it is now known that the hexaniobate anion which, as we shall see later, is structurally related to the decavanadate ion, forms complexes with metal cations by accommodating them in the octahedral pockets that exist on its outer faces.[51]

Now that suitable laser sources are available, there seems to be no reason why Raman spectroscopy could not be used to investigate the structure of the decavanadate ion in solution. This technique has proved to be very successful in determining the structure of heptamolybdate, and also, as we shall see, hexaniobate and hexatantalate ions in solution.

4 Niobates and Tantalates

We shall discuss the properties and structures of niobates and tantalates together, since, as far as they are known, these are very similar. In contrast to the situation with the vanadates, the hydrolyses of these anions appear to be quite simple and the literature is both less extensive and less controversial.

A. Solution Properties.—Niobium and tantalum pentoxides are considerably more inert than vanadium pentoxide. Aqueous solutions of niobates and

[49] J. V. Hatton, Y. Saito, and W. G. Schneider, *Canad. J. Chem.*, 1965, **43**, 47.

[50] K. F. Jahr, J. Fuchs, and F. Preuss, *Chem. Ber.*, 1963, **96**, 556.

[51] B. W. Dale and M. T. Pope, *Chem. Comm.*, 1967, 792; G. D. Stucky and C. M. Flynn, jun., American Crystallographic Association Meeting, Minneapolis, Minn., 1967, Paper R10.

tantalates can only be prepared by fusion of the oxides with excess of alkali-metal hydroxide or carbonate, and subsequent dissolution of the melt in water. [Although freshly precipitated hydrous Nb_2O_5 (but not Ta_2O_5) is soluble in concentrated alkali, the precipitate ages very rapidly and becomes inert.] The pH of the resulting very alkaline solutions cannot be lowered by the direct addition of acid, as this always results in the irreversible precipitation of the hydrous oxides. Indirect acidification, such as addition of ammonium chloride and removal of ammonia with a current of nitrogen,[52] or slow addition of carbon dioxide,[53] must be used. By such methods, the pH of niobate solutions can be reduced to *ca.* 7, and that of tantalates to *ca.* 10, before the onset of precipitation.

There now seems little doubt that over these limited pH-ranges, with the possible exception of the very alkaline region (to be discussed below), niobate and tantalate solutions contain a single polymeric species. Although both pentamers and hexamers have been suggested, recent experimental evidence is overwhelmingly in favour of the hexamers $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$. Such evidence is provided by e.m.f. measurements,[4,5,52] equilibrium ultracentrifugation,[4,5] light-scattering,[4,5] and Raman spectroscopy[54,55] of both niobate and tantalate solutions. Claims[56] for the pentameric tantalate anion $[Ta_5O_{16}]^{7-}$ were based upon ionic weights derived from diffusion coefficients, a procedure now known to have no empirical or theoretical validity.[57] Shortly after this work, Lehné and his co-workers,[58] on the basis of e.m.f. measurements and salt cryoscopy in potassium chloride at −10·7°, suggested that an analogous pentaniobate existed in the pH range 11—13·5. Later publications from the same laboratory favour the hexamer, however.[59]

Several workers[4,52,53] have noted the protonation of $[Nb_6O_{19}]^{8-}$, although the only quantitative measurements of equilibrium constants are (7) and (8), derived from e.m.f. measurements in 3M-KCl at 25°.[52]

$$[H_2Nb_6O_{19}]^{6-} \rightleftharpoons [HNb_6O_{19}]^{7-} + H^+ \qquad pK_1 = 10{\cdot}88 \pm 0{\cdot}05 \qquad (7)$$

$$[HNb_6O_{19}]^{7-} \rightleftharpoons [Nb_6O_{19}]^{8-} + H^+ \qquad pK_2 = 13{\cdot}8 \pm 0{\cdot}2 \qquad (8)$$

There was no evidence for any further protonation at pH *ca.* 10·7, the most acid solution studied. Somewhat similar measurements,[5] in 0·5M-KCl at 25°, showed no protonation of $[Ta_6O_{19}]^{8-}$ in the pH range 10—13.

In the course of his e.m.f. measurements of niobate solutions, Neumann[52] observed irreversible behaviour above pH 12·5, accompanied by some precipitation. Previously, from salt cryoscopy, Lehné and his co-workers,[58] had suggested that the species $[H_2Nb_2O_7]^{2-}$, $[HNb_2O_7]^{3-}$, and $[NbO_4]^{3-}$ were predominant in solutions above pH 13·5. However, in such solutions, 80% or more of the cryo-

[52] G. Neumann, *Acta Chem. Scand.*, 1964, **18**, 278.
[53] G. Jander and D. Ertel, *J. Inorg. Nuclear Chem.*, 1960, **14**, 71, 77, 85.
[54] J. Aveston and J. S. Johnson, *Inorg. Chem.*, 1964, **3**, 1051.
[55] R. S. Tobias, *Canad. J. Chem.*, 1965, **43**, 1222.
[56] G. Jander and D. Ertel, *J. Inorg. Nuclear Chem.*, 1956, **3**, 139.
[57] L. C. W. Baker and M. T. Pope, *J. Amer. Chem. Soc.*, 1960, **82**, 4176.
[58] M. Lehné and H. Goetz, *Bull. Soc. chim. France*, 1961, 334; J. Leicht, M. Lehné, and R. Rohmer, *ibid.*, 1963, 213.
[59] Y. Dartiguenave, M. Lehné, and R. Rohmer, *Bull. Soc. chim. France*, 1965, 62.

scopic depression is due to free OH^- ions. Consequently, interpretation of the results depends upon precise $[OH^-]$ measurement in 1—2M-KOH and is open to serious doubt. Moreover it seems unlikely that equilibrium was reached in these measurements. Very recently, the Raman spectrum of a saturated solution of potassium niobate in 12M-KOH has been found[45] to be similar to that in 1M-KOH, suggesting that the hexamer still predominates in the more basic solution. Unfortunately, since the report gave no indication of attempts to reach equilibrium, the question of the nature of niobate species in very alkaline solution must remain open, for there is no reason to believe that the depolymerisation of hexaniobate will be other than very slow at room temperature.

B. Structures.—With the exception of a few insoluble lanthanon niobates and tantalates, $M^{III}XO_4$ (X = Nb, Ta), which have the scheelite ($CaWO_4$) structure and discrete tetrahedral oxyanions, the co-ordination number of Nb and Ta in all known oxide structures is restricted[60] to 6. (The high-temperature form of Nb_2O_5 has one Nb atom in 28 occupying a tetrahedral site, the remainder being[61] octahedrally co-ordinated.) This is to be expected from simple radius-ratio considerations, and argues against the likelihood of species such as NbO_4^{3-} in aqueous solutions. Consequently, although many niobates and tantalates are often formulated as salts containing XO_4^{3-}, XO_3^-, and $X_2O_7^{4-}$ anions, they actually have infinite mixed oxide structures with octahedrally co-ordinated Nb and Ta. Common structures are perovskite for M^IXO_3, cassiterite for $M^{II}(XO_3)_2$ and $M^{III}XO_4$, and atopite for $M_2^{II}X_2O_7$.[60]

Apart from such mixed oxides, which are generally prepared from melts, several soluble alkali-metal niobates can be crystallised or precipitated from aqueous solutions. Only two, incomplete, *X*-ray structural investigations have been carried out on such compounds; $Na_{14}Nb_{12}O_{37},32H_2O$[62] and $K_8Ta_6O_{19},16H_2O$[63] were both found to contain octahedral groupings of six Nb or Ta atoms. From the metal–metal distances (3·3 Å) the positions of the oxygen atoms were inferred, and the symmetrical $[M_6O_{19}]^{8-}$ structure illustrated in Figure 2*d* was suggested. This structure is closely related to that of the decavanadate ion. The niobate is therefore more realistically formulated as an acid salt, $Na_7HNb_6O_{19}$, aq. A normal salt, $K_8Nb_6O_{19},16H_2O$ can be isolated from more alkaline solutions and is isomorphous with the tantalate.[64] Crystals of both $K_8Nb_6O_{19}$ and $K_8Ta_6O_{19}$ may contain excess of alkali in the range K/Nb,Ta = 4·0—4·2 without changes being detected in the *X*-ray powder patterns,[64] and this has been responsible for some confusion in the early literature.

The Raman spectra of solid $K_8Ta_6O_{19},16H_2O$ and $K_7HNb_6O_{19},13H_2O$ are

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[60] R. W. G. Wyckoff, 'Crystal Structures', 2nd edn., Interscience, New York, vol. 1, 1963, p. 252; vol. 3, 1965, pp. 23, 361, 439.

[61] B. M. Gatehouse and A. D. Wadsley, *Acta Cryst.*, 1964, **17**, 1545.

[62] I. Lindqvist, *Arkiv Kemi*, 1952, **5**, 247.

[63] I. Lindqvist and B. Aronsson, *Arkiv Kemi*, 1954, **7**, 49.

[64] F. Windmaisser, *Z. anorg. Chem.*, 1941, **248**, 283; F. Halla, A. Neth, and F. Windmaisser, *Z. Krist.*, 1952, **104**, *A*, 1961.

relatively simple, and are virtually identical to the spectra of saturated solutions of these salts in 1M-KOH.[54,55] There is little doubt, therefore, that the structures of these ions in solution are identical with those in the solid state.

Soluble 'metaniobates' of potassium and sodium can be crystallised from weakly basic solutions[8,65] (*e.g.*, by evaporation under an atmosphere of carbon dioxide). Although usually formulated as $MNbO_3$, aq. they are probably more correctly regarded as salts of $[H_2Nb_6O_{19}]^{6-}$, in view of what is now known about the protonation of $[Nb_6O_{19}]^{8-}$. In this connection we may note that (*a*) the corresponding 'soluble metatantalates' have not been reported, and (*b*) complete dehydration of a metaniobate renders it insoluble, suggesting the presence of constitutional water in the anion. Anhydrous alkali-metal niobates have the perovskite structure.[60]

A soluble sodium orthoniobate, Na_3NbO_4, has been prepared by fusing Nb_2O_5 with a large excess of NaOH, and extracting unused alkali with absolute alcohol.[53] The resulting crystals are said to be yellow and to hydrolyse immediately and irreversibly in solution, yielding the hexaniobate anion. No structural investigation of this material has been reported.

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[65] R. Rohmer and J. E. Guerchais, *Bull. Soc. chim. France*, 1961, 324.