

SOME IMPORTANT ASPECTS OF THE CHEMISTRY OF ISO- AND HETEROPOLYANIONS

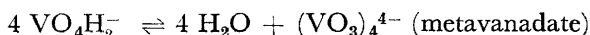
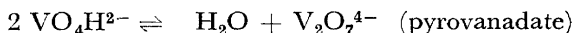
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THE ISOPOLYANIONS

Formation

The mild action of a strong acid upon the salt of a weak acid does not always yield the expected acid ion but a condensed ion, such as $\text{Cr}_2\text{O}_7^{2-}$, capable of coexistence in equilibrium with the acid ion:



This equilibrium may be displaced almost totally in favour of the condensed ion. Such is the case for the metavanadates, MVO_3 , whose ion is tetra-condensed even at very high dilutions.

Very often the polyanions thus formed have a more complex composition.

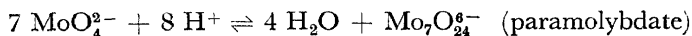
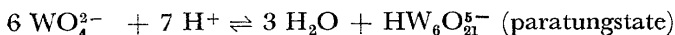


Figure 1 shows the different known ions of the polyvanadates; the number (x) of the equivalents of strong acid (per VO_4^{3-} ion) necessary to obtain their

<i>Equivalents</i>	<i>Species</i>	<i>Former denomination</i>
1	VO_4H^{2-} and $\text{V}_2\text{O}_7^{4-}$	Pyrovan $\text{V}_2\text{O}_7\text{M}_4$
2	$\text{V}_4\text{O}_{12}^{4-}$	Metavan VO_3M
2.4	$\text{V}_{10}\text{O}_{28}^{6-}$	Pentavan $5\text{V}_2\text{O}_5 \cdot 3\text{M}_2\text{O}$
2.5	$\text{V}_{10}\text{O}_{28}\text{H}^{5-}$	Hexavan $6\text{V}_2\text{O}_5 \cdot 3\text{M}_2\text{O}$
2.6	$\text{V}_{10}\text{O}_{28}\text{H}_2^{4-}$	Pentavan $5\text{V}_2\text{O}_5 \cdot 2\text{M}_2\text{O}$
3	$(\text{V}_2\text{O}_5)_n$ insoluble	

Figure 1

stoichiometric compositions is indicated. Figure 2 shows their correlation with the very distinct equivalent points of the potentiometric titration curve¹.

In this example, the degree of condensation increases with x , the final member of the series being the insoluble acid; a great many systems behave similarly, but for some others, particularly when the acid is weak and soluble, the proportion of condensed ions goes through a maximum. Such is the case

with the borates²: between the salt BO_3H_2^- ($x = 0$) and the acid BO_3H_3 ($x = 1$), neither of which are condensed, are the polyborates. The most

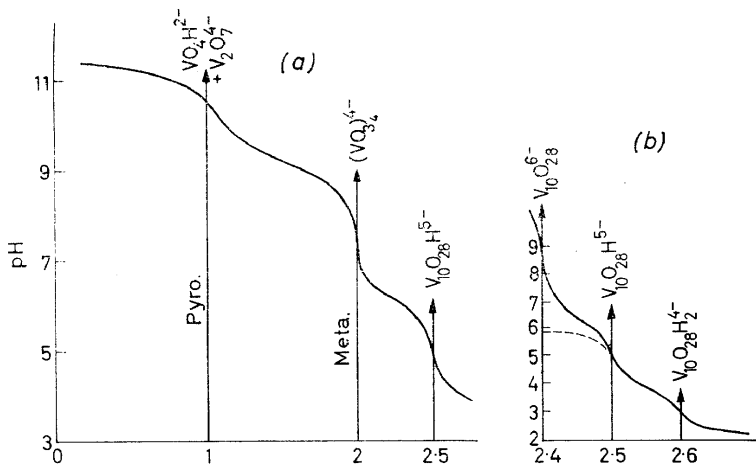


Figure 2

characteristic of these correspond to borax, $\text{B}_4\text{O}_7^{2-}$, and undergo degradation at high dilutions—

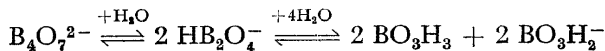


Figure 3 shows the ratio of the different species as a function of x , for a total

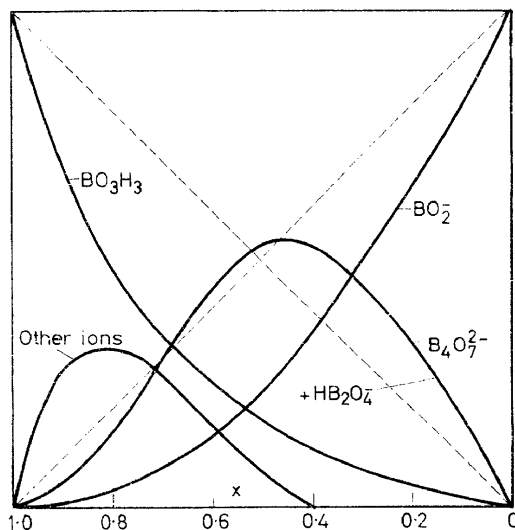


Figure 3

concentration $c = 0.4$ of B; when c is less than 0.02 mol/l, the polyborates are practically non-existent.

The ranges of pH in which the polyanions are stable differ from case to case: the polytungstates appear at $\text{pH} < 8$. Below this pH the niobic and silicic acids are precipitated, but their polyanions are stable even in alkaline medium. As for the polyborates, they are stable only between certain limiting values of pH (7.5 to 10.5), as already indicated.

Monomeric or metastable compounds

It thus seems that in a great many cases the acid ions, or the simple acids, are not stable and lead to the condensed species through the elimination of water between the hydroxyl groups belonging to two adjacent particles. The structures thus obtained will be specified later. It is, however, sometimes possible to demonstrate the existence of monomeric species. Thus, by mixing two fast streams of solutions of Na_2WO_4 and strong acid, and by placing a glass electrode immediately beyond the point of mixing of the two solutions, indications of the formation of WO_4H^- have been obtained³.

A notable example is that of monomeric metastable SiO_3H_2 , whose preparation was difficult for a long time since its rate of polymerization into a gel of silica shows a sharp minimum at about pH 3. The preparation of solutions as concentrated as 0.2 mol/l. can now be achieved by shaking powdered Na_2SiO_3 with a suspension of a cationic resin stabilized to pH 3 or by hydrolysing methyl silicate with $\text{N}/1000$ hydrochloric acid⁵.

Cases do exist, however, in which the intermediate compounds have a high degree of condensation. Thus, during the acidification of vanadic solutions in order to prepare the decavanadates ($x > 2$), a fugitive garnet-red colour appears, quite distinct from the yellow-orange colour of the decavanadates. It can be stabilized, either by the addition of glycol to the reaction medium and cooling to -20° in order to slow down the transformation of the compound, or by the precipitation of the tetrabutylammonium salt as an oil which can then be extracted with chloroform. The ion (not mentioned in *Figure 1*) should⁶ have the formula $\text{V}_{12}\text{O}_{33}^{6-}$.

Action of bases

The addition of bases should lead to the same series of transformations, but in the reverse order, as those observed on acidification. Indeed, reversibility is seen in many systems, but, due to the stability of some polyanions, the equilibrium is attained very slowly during the addition of alkali.

Thus, whereas the equilibria are attained rapidly with the polymolybdates, the addition of alkali to the orange solutions of decavanadates discolours them very slowly, even in 1N sodium hydroxide; the reaction has first order kinetics with respect to both decavanadate and hydroxyl ions.

The behaviour of the $\text{HV}_{10}\text{O}_{28}^{5-}$ ion during the potentiometric titration (*Figure 2(b)*, medium 1M sodium perchlorate) is easily explained. Starting with a solution of sodium decavanadate ($x = 2.5$), the addition of 1 equivalent of strong acid (one tenth per gatom V) leads to the formation of $\text{H}_2\text{V}_{10}\text{O}_{32}^{4-}$ ($x = 2.6$). On the other hand, the addition of 1 equivalent of base leads to the formation of $\text{V}_{10}\text{O}_{28}^{6-}$ ($x = 2.4$), when the titration is performed quite rapidly (full curve): yet, in the end, $\text{V}_{10}\text{O}_{28}^{6-}$ is decomposed partly into the

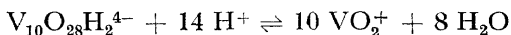
more acidic $\text{HV}_{10}\text{O}_{28}^{5-}$ ($x = 2.5$), and partly into the less acidic ($x = 2$) metavanadic ions. At the same time, the value of pH decreases (the final values are represented in the figure by the dotted line). Thus, the equilibria once attained, do coexist for $2 < x < 2.5$ not only with the meta and $\text{HV}_{10}\text{O}_{28}^{5-}$ ions, but also with $\text{V}_{10}\text{O}_{28}^{6-}$, which bears the usual acid-base relationship to the former¹.

The behaviour of the paratungstates is peculiar⁷: by an appropriate acidification of WO_4^{2-} , ($x = 7/6$), the $\text{HW}_6\text{O}_{21}^{5-}$ ion reacts easily with bases, but as the age of the solution increases, a small ratio is liable to a spontaneous reaction. Finally, after about one month, about one half of the two forms coexist. It seems that two forms of the paratungstic ion exist in equilibrium, one of these is more stable and less reactive than the other.

Behaviour in very acid medium

A certain number of acids or hydrated oxides corresponding to the poly-anions are amphoteric, but their weakly basic character manifests itself only in media of appreciable acidity. The cations thus formed are condensed (*e.g.* HMo_2O_6^+ , encountered in the molybdic reagent)⁸ or not condensed (*e.g.* VO_2^+), but their structure seems to be simpler than those of the poly-anions.

It has long been known that the orange colour of the decavanadates turns to light yellow on addition of a strong acid. Due to the strong dissociation of $\text{V}_{10}\text{O}_{28}\text{H}_6$, the anionic species $\text{V}_{10}\text{O}_{28}\text{H}_2^{4-}$ is converted directly into the cation VO_2^+ (ref. 8):



If the corresponding acid (*i.e.* hydrated V_2O_5) precipitates in the long run, this is due to its low solubility. The formation of cations is easier with V^{5+} than with Mo^{6+} ; at the total concentration (c) of the element noted in parenthesis, it requires a free acidity of 0.01 ($c = 0.01$) or 0.03 ($c = 0.05$) in the case of V^{5+} , and of 0.23 ($c = 0.01$) or 0.72 ($c = 0.1$) in that of Mo^{6+} , to obtain 50 per cent of the element as a cationic species. These cations may give complexes with the anion of the added strong acid: thus, hydrochloric acid solutions of Mo^{6+} contain the ether soluble chlorhydrin, MoO_2Cl_2 , which is formed quantitatively at hydrochloric acid concentrations higher than 5N; beyond 7N an anion is formed, as is shown by the nature of the salts isolated from a concentrated hydrochloric acid medium.

The metaphosphates

Instead of taking place spontaneously in acid media, the elimination of water molecules between the hydroxyl groups of the acid salts may require heating of the solid salts. In this way, the polyphosphates (*Figure 4(a)*) may be obtained with PO_4H^{2-} and PO_4H_2^- . When the relative proportion of the PO_4H^{2-} ions is low, long chain metaphosphates are formed, unless cyclization has occurred (cyclic metaphosphates with 3 or 4 elements, *Figure 4(b)*).

Although it does not lie within the scope of this paper, it is useful to recall the chemistry of the polyphosphates, since the simpler members of the series

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resemble the polyanions (they tend, however, to regenerate the usual acid ions in solution), and the higher members resemble the silicates, the chemistry

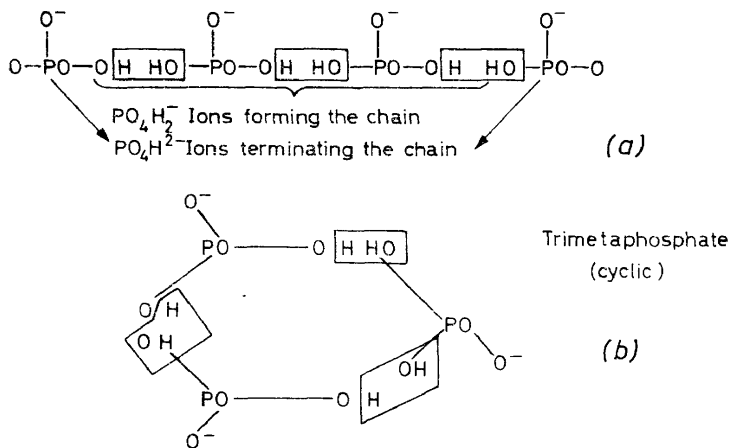
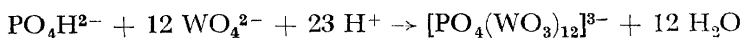


Figure 4

of which is solely concerned with the solid state of high polymers. Whenever a new structure is determined for the metaphosphates, it finds its equivalent in the silicates.

THE HETEROPOLYANIONS

In the previous examples, the condensation process involved identical molecules, but it can also occur in the presence of a group derived from another (hetero) atom: the radicals, as they unite, cluster around the hetero (central) atom and form heteropolyanions, *e.g.*

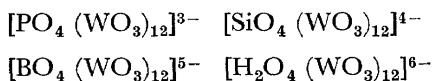


which are specified by a number equal to the ratio

$$\frac{\text{atoms W (or Mo)}}{\text{central atom}}$$

Metalloid as central atom

12 and 9 series—The first investigations (associated with such names as Marignac, Kehrman, Copaux and Rosenheim) were concerned primarily with compounds whose central atom was a metalloid; the most typical species belong to the “12 series”.



The last one cited (metatungstate) has no central atom, but as its properties are identical with those of the heteropolytungstates, and different from those

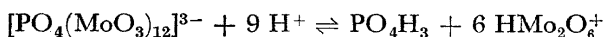
of the usual polytungstates, two hydrogen atoms derived from a constitutional water molecule are assumed to take the place of the central atom.

The acids display a noticeable affinity for oxygenated solvents, and the fact that they give a solution of high density with ether is utilized in their extraction; in acid medium, the acid is almost totally extracted and separated from the upper aqueous layer (Drechsel method).

With phosphorus and arsenic, a "9 series" exists, which in fact has a dimeric formula: $[(\text{PO}_4)_2(\text{WO}_3)_{18}]^{6-}$. It forms either in a warm concentrated medium or, in the case of the phosphomolybdates, on treatment of PO_4H_2^- with the 12 series in concentrated acid medium. Although they may have parallel properties, the 12 and 9 series have but little connection, especially in the case of the tungsten compounds.

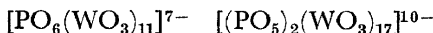
As far as the action of strong acids is concerned, the compounds of tungsten show outstanding stability, whereas those of molybdenum, especially the phospho-12-molybdic acid, do not. The decomposition yields PO_4H_3 and the molybdic compound, *viz.* the cation HMo_2O_6^+ , since the medium is acid. (p. 64).

These facts do not seem to be very consistent with the Drechsel method, or with the quantitative analysis of phosphorus with the molybdic reagent in acid medium. In fact, an equilibrium of the following type:



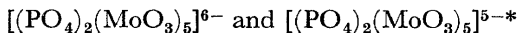
is displaced by extraction of the polyacid with ether (first case), and by the insolubility of the ammonium phosphomolybdate (second case).

Related series—The action of hydroxyl ions on the preceding series regenerates the reagents (*e.g.* PO_4H_2^- and WO_4^{2-}). If this action is performed with caution, one observes the loss of one tungsten (or molybdenum) atom and the 11 and $8\frac{1}{2}$ series are obtained:



The phospho-12-molybdic- (and tungstic-) series are so susceptible to this scission that it starts at a pH less than 2; in fact, the potentiometric titration curve for the addition of a base to the acid shows an equivalent point⁹ for 7 equivalents and not 3. This corresponds to the formation of the salt belonging to the 11 series and not, as is often claimed, to an acidity of the 12 acid higher than its normal acidity: the ratios Mo/P being close to each other make such an error easy.

In the case of the phosphomolybdates, the series 11, before its transformation into PO_4H_2^- and MoO_4^{2-} , undergoes an intermediate degradation into a $2\frac{1}{2}$ series.



Resulting from what has been previously stated, *Figure 5* represents the relations between the different phosphomolybdic compounds¹⁰; PO_4H_2^-

* Whereas this series is stable only in a certain pH range, a 3 series exists for the arseniomolybdates, with an equally low value for the Mo/As ratio, which is remarkably stable at all values of pH less than 9.

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and PO_4H^{2-} act in the same way as OH^- , since the successive reactions with OH^- yield series with an increasing proportion of phosphorus. Such equilibria are much slower for the tungsten derivatives; those between the 12 and 9 series cannot be realised under ordinary conditions.

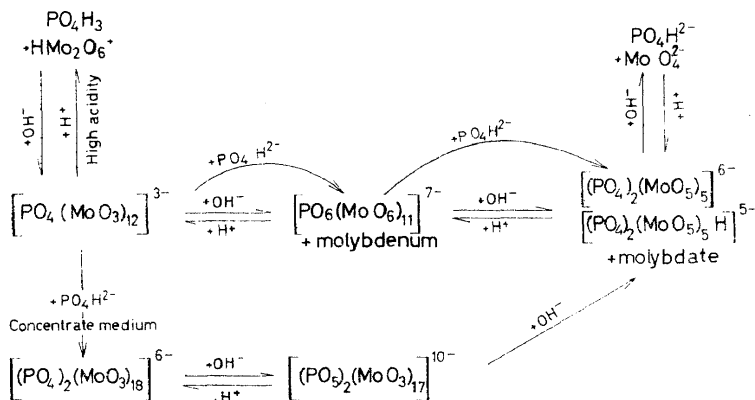
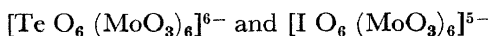


Figure 5

6 Series—The preceding series do not exist for metalloids with a valency higher than that of phosphorus; e.g. Te^{6+} and I^{7+} , which do not exhibit series higher than 6, *viz.*



with properties which are rather similar to those of the polyanions.

Examples of isomerism—In the preparation of the silico- and boro-tungstic acids, two isomers are obtained. One of these is always present in greater proportion than the other, but the factors favouring one at the expense of the other are not known. Their properties are very similar and there is no method for distinguishing them in solution; the acids or corresponding salts are not different hydrated species of the same compound since recrystallization always leads to the original product.

The preceding cases of isomerism have long been known (Marignac, 1864; Klein, 1883)¹¹. A new type was discovered later in the phospho-9-tungstates¹², and recently in the silico-12-molybdates. In this latter case acidification of silicate and molybdate solutions leads to a solution whose absorption spectrum differs from that of the usual silicomolybdates, but changes with time owing to the final formation of these compounds¹³.

Relation between iso- and heteropolyanions—Since the heteropolyanions are formed in a pH range in which isopolyanions are also formed, it might be concluded that the latter build up the structure of the heteropolyanions; in fact, it has been proved that the two classes are formed concurrently. Thus the heteropolyacids of tungsten are formed more slowly from the central anion and Na_2WO_4 , if these are kept for a sufficient time in an acid buffer. The isopolytungstic ions formed show great stability and no tendency to form of the heteropolyanion.

This dualism explains why the preparation of some heteropolytungstates is such a delicate operation. The isopolytungstates formed under the same conditions require time for degradation and reaction with the ion bringing in the central atom (prolonged boiling is necessary).

Metal as central atom

During recent years, evidence has been obtained for a large number of stable polyanions with a metal as central atom¹⁴.

Molybdic compounds—They are obtained by action of metallic ions upon molybdic solutions whose acidity is close to that of the paramolybdate. The addition of an oxidizing agent is necessary in the case of Mn^{4+} , Ni^{4+} and Co^{3+} .

The 12 series is of the following type: $\text{MO}_6(\text{MoO}_3)_{12}^{8-}$, where $\text{M} = \text{Ce}^{4+}$ or Th^{4+} (ref. 15); it is not analogous to those derived from the nonmetallic elements; the free acids are obtained from the salts by ion-exchange methods, and are not extractible with ether. At a pH greater than 10, a decomposition into hydroxide $\text{M}(\text{OH})_4$ and MoO_4^{2-} takes place.

The series 9 is of the type $\text{MO}_5(\text{MoO}_3)_9^{6+}$, where $\text{M} = \text{Ni}^{4+}$ (black) or Mn^{4+} (orange red)¹⁶; these compounds are strong oxidizing agents and are decomposed by hydrogen peroxide; they show weak stability towards acids and bases.

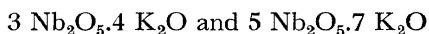
The 6 series belongs to the type $\text{MO}_3(\text{MoO}_3)_6^{3-}$, where $\text{M} = \text{Cr}$ (lilac-pink), Al , Fe^{3+} (colourless), Rh^{3+} , or Co^{3+} (bluish-green), and behaves much the same as the 12 series as far as the preparation of the acid and the action of bases are concerned¹⁷. The diamagnetism is a proof of the coordination number 6 for M , and is encountered in the other compounds belonging to the 6 series¹⁸.

Tungstic compounds—There should be two kinds of cobaltitungstic compounds with coordination number 6 (series 12 and 6) and 4 respectively. A cobaltic compound (yellow) and a cobaltous compound (green) belong to the 12 series; to the 6 series, which contains, in fact, two cobalt* and twelve tungsten atoms, belong a cobaltous compound (green) and a mixed compound (dark brown) with one Co^{3+} and one Co^{2+} . They are easily interconverted by oxidation–reduction or acid–base exchange processes¹⁹.

METHODS OF INVESTIGATION IN THE SOLID STATE

Thermogravimetry, differential thermal analysis

As their temperature is raised, the salts lose their water of crystallization, and the observed changes of mass indicate the different hydrates. However, the method is more useful for analysis when complex ratios of acid to base are involved and make the usual methods of quantitative analysis deceptive; thus, for the polyniobates, the choice can easily be made between the formulae:



Writing these as $\text{Nb}_2\text{O}_5 (1 + n\text{K}_2\text{O}) \cdot m\text{H}_2\text{O}$, it has been established²⁰ that above a temperature θ a decomposition takes place into metaniobate

* The coordination number is 4 for one Co and 6 for the other.

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$\text{Nb}_2\text{O}_5 \cdot n\text{K}_2\text{O}$ and K_2O which absorbs carbon dioxide in the ratio $n \text{CO}_2$ for $n\text{K}_2\text{O}$: n can be evaluated by the subsequent increase in weight. Moreover, around 800° , the meta compound reacts with K_2CO_3 and yields the ortho-compound: the loss of weight is then equal to the previous gain; if the dehydration process at θ was not total, the quantity of water still present at θ may be deduced from the difference of the two values.

Similarly, two isomeric borotungstic acids exist (p. 67); some authors have argued that the hexagonal acid was not an isomeric species of the quadratic acid, but that it belonged to a 14 series. However, its pyridinium salt loses 24.5 mg per g of sample between 260 and 320° ; assuming that this loss corresponds to the departure of 1 mole of pyridine per mole of salt, the theoretical loss is 24.3 or 20.8 mg, according to whether the formula contains 12 or 14 WO_3 . The hexagonal acid, therefore, belongs to the 12 series²¹.

Though less accurate than the previous method when the transformation is accompanied by a variation of weight, thermal analysis is more efficient when there is no change in weight. It has been used frequently in the investigation of the metaphosphates; as an example, *Figure 6* shows the curve

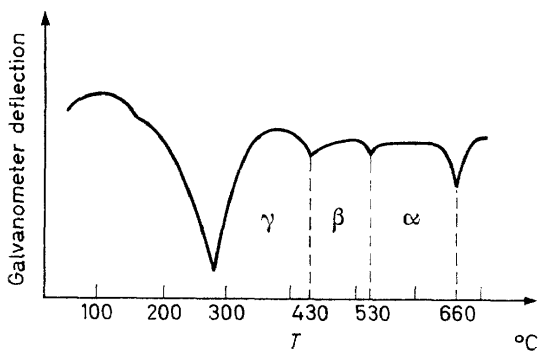


Figure 6

obtained with $\text{AsO}_4\text{H}_2\text{K}$ ²²: between 120 and 300° an important endothermic process corresponding to dehydration to give AsO_3K is observed; three subsequent phenomena are seen:

Transitions	{	γ - β	430°
		β - α	530°
Melting			660°

X-ray method

In addition to identifying the phases, the X-ray method can locate the atoms. Thanks to the remarkable research work performed by the Swedish School, the structures of the main types of isopolyanions have been elucidated during recent years. The first determination of this kind concerns the structure of phosphotungstic acid²³.

Due to the high value of their radii (≈ 0.62) molybdenum and tungsten may assume a coordination number 6 (octahedra WO_6); the central atom

adopts the coordination number 4 if its radius has a low value ($= 0.34\text{\AA}$ for P: PO_4 tetrahedra)* or 6 with the atoms of metallic character (Mn^{4+}) whose radius is higher. However, the relatively low proportion of the oxygen atoms implies the sharing of apices and edges of the WO_6 octahedron.

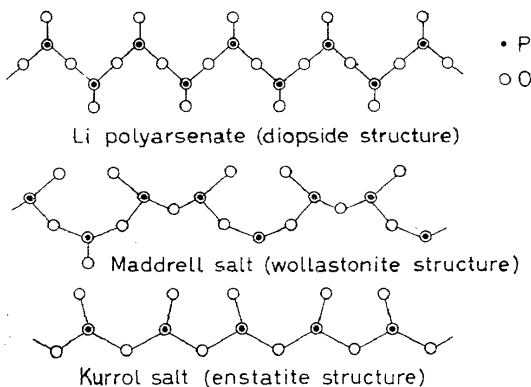
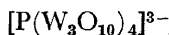
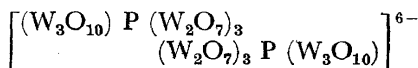


Figure 7

*Keggin's Model (1934)*²³—Figure 8 shows the structure of the phospho-12-tungstic ion: the central phosphorus atom is surrounded by four oxygens occupying the apices of a tetrahedron; the tungsten atoms are placed around the phosphorus atom in four groups of three octahedra; each octahedron of a group shares an edge with each of its two neighbours; moreover, each oxygen atom of the PO_4 group is common to three WO_6 (Figure 8(a)). Finally, the connections between the four groups of three WO_6 are such that each WO_6 belonging to a group has two oxygen atoms in common with a WO_6 belonging to the two groups closest to it. Figure 8(b) represents the connections between two groups, and Figure 8(c) the final aggregate. The formula can be written:



9 Series—The structure of the ion $[(\text{PO}_4)_2(\text{WO}_3)_{18}]^{6-}$ is easily inferred from the preceding one²⁴; a half-unit (one P and nine W) is obtained by keeping unaltered the whole of one of the four groups of three WO_6 and suppressing one W in each of the three remaining groups; the apices thus set free are then joined to those of an identical half-unit. The schematic notation is as follows:



* The grouping of the PO_4 tetrahedra (each PO_4 sharing an apex with its neighbour) leads to chain or ring structures. In the former case, the phosphorus atoms have a zig-zag arrangement, according to the units shown in Figure 7 (the projections of the phosphorus atom and of one of the oxygen atoms coincide). In the second case, the phosphorus and shared oxygen atoms form a planar hexagonal ring (trimetaphosphates) or a puckered octagonal ring (tetrametaphosphates).

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The structure of the maganimolybdates $[(\text{MnO}_5(\text{MoO}_3)_3)]^{6-}$ is different²⁵: manganese displays a coordination number of 6; three of the molybdenum atoms occupy the corners of a triangle coplanar with the

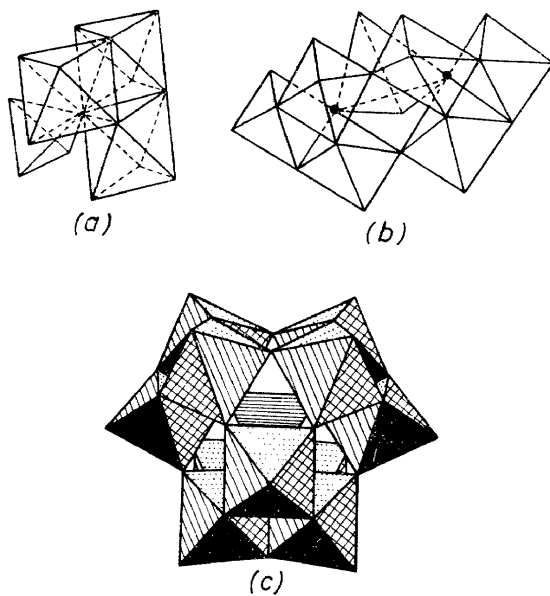


Figure 8

manganese atom; the other six atoms lie in planes parallel to the previous one, three above and three below (Figure 9; for clarity the two groups of 3 Mo which do not lie in the plane of the manganese atom have been spread out).

*Anderson's Model (1937)*²⁶—Six molybdenum atoms are arranged in a regular planar hexagon and each octahedron shares an edge with each of its two neighbours: the result is the unit $\text{Mo}_6\text{O}_{24}^{12-}$, which has a central cavity of the same form and volume as that in MoO_6 , and which may admit a cation with the same coordination number as molybdenum. With Te^{6+} the telluromolybdic ion (Figure 10(c)) is obtained which is written as $[\text{Te}(\text{MoO}_4)_6]^{6-}$ since the six molybdenum atoms play the same part²⁷. With Mo^{6+} itself, $[\text{Mo}(\text{MoO}_4)_6]^{6-}$ is obtained, which is none other than the paramolybdic anion. In fact the six molybdenum atoms are not coplanar: in Figure 10(b), the centre of the octahedra 1, 2, 3, and 4 lie in the plane of the figure, and those of the octahedra 5, 6, and 7 are displaced from it by a distance equal to $a/2$ (a = length of the octahedron edge)²⁸.

The analogy between the structures of the hetero- and isopolyanions will be apparent. These latter compounds must not be regarded as a structural basis for the former on the pretext that they are formed in very similar acidity ranges.

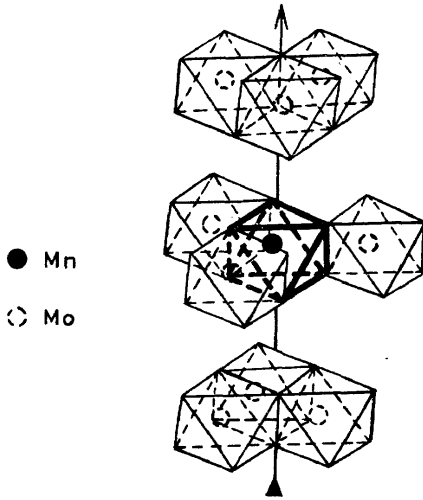


Figure 9

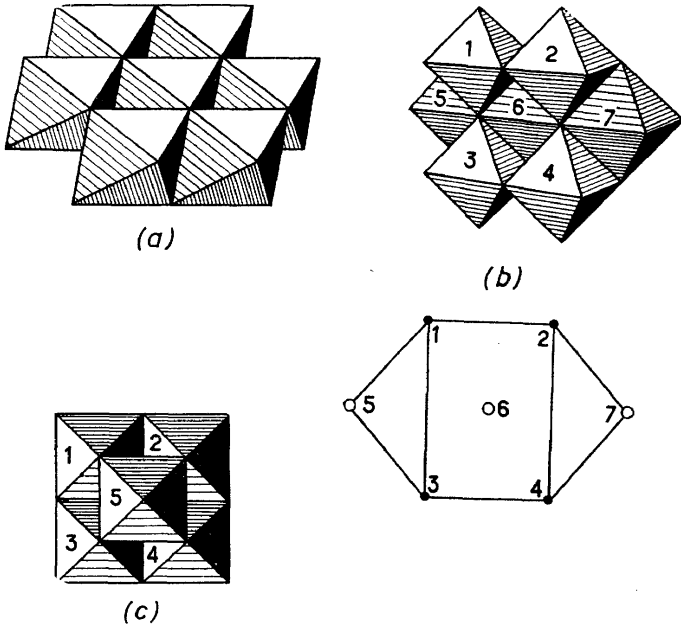


Figure 10

Similar structures—In the niobate $7 \text{Na}_2\text{O} \cdot 6 \text{Nb}_2\text{O}_5 \cdot 32 \text{H}_2\text{O}$, the anion contains six niobium and nineteen oxygen atoms, or $\text{HNb}_6\text{O}_{19}^{7-}$; the niobium atoms occupy the six apices of an octahedron, each niobium atom being itself at the centre of an octahedron NbO_6 (ref. 29). The resulting

ASPECTS OF THE CHEMISTRY OF ISO- AND HETEROPOLYANIONS

structure, shown in *Figure 10(c)* is associated with the structures of the paratungstates and of the tetramolybdates³⁰.

In the vanadic polyanions, the radius of the vanadium atom (in contrast to those of tantalum and niobium) is not large enough for the atom to assume a coordination number of 6. The arrangement of the oxygen atoms around the vanadium atom follows the coordination type 5 (triangular bipyramid or square based pyramid) or 4 (triangular based pyramid). Some structures display the two types of coordination alternatively; such is the case of $K_3V_5O_{14}$, which probably is a decavanadate $K_6V_{10}O_{28}$ (ref. 31).

The five vanadium atoms form a planar regular pentagon. The oxygen atoms are arranged around the vanadium atoms in pyramids: with a square base for three of the vanadium atoms and a triangular base for the other two. The figure is repeated so that all the oxygen atoms belonging to the bases lie in the same plane (below that of the vanadium) being shared by two pyramids (2 V), and the oxygen atoms occupying the apices, unshared, are themselves coplanar (above the plane of the vanadium atoms).

Figure 11 shows such a disposition: the oxygen atoms of the bases lie in

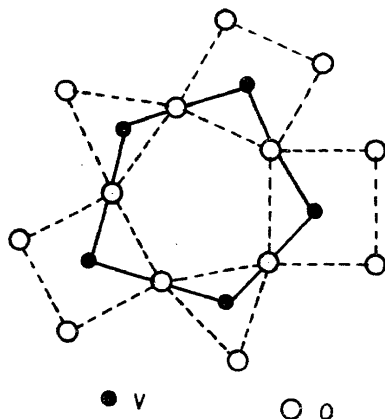


Figure 11

the plane of this figure; the vanadium atoms (upper plane) are projected on the plane taken as reference; the projections of the oxygen atoms placed at the apices coincide with those of the vanadium atoms.

METHODS OF INVESTIGATION IN SOLUTION

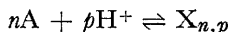
All the methods used in the study of complexes may be applied. Thus, polarography has been used to specify the dependence upon pH of the equilibria of heteropolytungstic ions either between themselves or with the polytungstates; the polarograms differ with each species³².

The light absorption coefficient of the decavanadates, in the region 350–400 $m\mu$ is much higher than that of the other polyvanadates and allows their proportion in mixtures to be estimated.

Lastly, chromatography, paper electrophoresis and ion-exchange methods allow the different classes of polyphosphates to be separated, whilst measurements of diffusion coefficients by Jander stimulated research on polyanions. Here, only those methods which, due to their generality, have attracted attention during the last few years will be discussed.

Potentiometry

The formation of polyanions from the initial simple ion may be written in a general way:



with
$$[X_{n,p}] = K_{n,p} [A]^n [\text{H}^+]^p \quad (1)$$

the brackets designate the concentrations, and the ionic strength is assumed to have a constant high value.

If C is the total concentration of the A ions, and x the number of equivalents of strong acid added per g ion of A for the formation of the polyanions, then the concentration Cx of H^+ ions added is either free or consumed in the formation of the polyanions:

$$Cx = [\text{H}^+] + \Sigma p[X_{n,p}]$$

An equivalent form of this expression is:

$$C\bar{x} = \Sigma p[X_{n,p}] \quad (2)$$

where $\bar{x} = x - [\text{H}^+]/C$ designates not the proportion of H^+ ions added, but the proportion combined, which is easily determined since $[\text{H}^+]$ is measurable.

Furthermore, if C represents the total concentration of species A either transferred or not, then

$$C = [A] + \Sigma_n [X_{n,p}]$$

or
$$\log \frac{C}{[A]} = \log \left(1 + \frac{\Sigma_n [X_{n,p}]}{[A]} \right) \quad (3)$$

Substituting the values of $[X_{n,p}]$ from equation (1) in equations (2) and (3), one obtains:

$$\log \frac{C}{[A]} = \log (1 + \Sigma_n K_{n,p} [A]^{n-1} [\text{H}^+]^p)$$

$$C\bar{x} = \Sigma p K_{n,p} [A]^n [\text{H}^+]^p$$

If, in addition to $[\text{H}^+]$ which is measurable, $[A]$ may be computed, one may gather a sufficient number of measurements and obtain as many equations as are needed for the determination of the variables n , p and $K_{n,p}$. The problem consists essentially in the evaluation of $[A]$; the methods generally make use of the slopes of the titration curves and of their alteration with a variation in the initial value of C (in a simple acid-base titration where $n = 1$, this shift is nil)³⁴.

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If the polyanions show sufficient stability, their existence is revealed by an equivalent point on the titration curve (*Figure 2*: vanadates) and the investigation of the system is thus simplified.

Finally, in the case of the heteropolyanions formed in equilibria of the following type:



new unknown quantities m intervene, and the network of the titration curves has to be enlarged by the use of different initial ratios $[Z]/[A]$.

Cryoscopy in salt medium

It is known that transition points of hydrated salts and eutectic points have their values lowered by dissolved salts, and that relations similar to those of cryoscopy apply. Moreover, the cation does not interfere if common with that of the solvent present in excess. This fact makes the interpretation easier. Since the drop in temperature is directly proportional to the number of dissolved particles, it is obvious that for an initial concentration C , the drop will be less as the degree of condensation of the ion increases. The method has been successfully applied to the molybdic³⁵, tungstic, meta- and decavanadic ions⁶.

When the equilibria are rapidly established, cryometric titration curves (Bye³⁵), similar to the potentiometric titration curves may be used. The cryoscopic lowering of temperature is plotted against x , and definite compounds are revealed by breaks, whose ordinates give the extent of condensation. These curves are related to the potentiometric curves: a simple relation exists, for a given value of x , between the slope and the shift in $(\Delta p\text{H})/(\Delta \log C)$ of the potentiometric curve for two different values of C .

Properties depending upon the mass and the shape of the ions

The constitution of the polyanions does not differentiate them from the ordinary complex ions, but from their high molar weights M (up to 4,000) they can be regarded as inferior terms of the macromolecular species. Thus, they constitute a link between simple and macro ions.

Research on the silico-12-tungstic ion shows³⁶ that its behaviour does not differ from that of particles with a high value of M , since M determined by sedimentation velocity measurements is practically equal to the value computed. Moreover, it is known that the ion is not hydrated and its shape must be spherical since Einstein's relation applies³⁷. The measurements make possible the determination of the ion's radius, and the values thus obtained are in good agreement with those resulting from X-ray studies. The interpretation of the results of the same methods are more involved with the ions of the 6 series, which are not spherical.

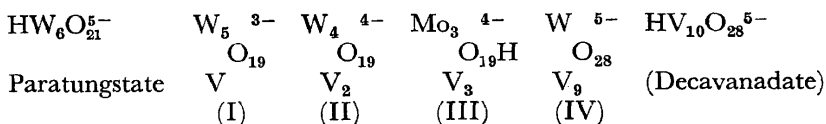
The studies on the sedimentation equilibria carried out on solutions of phospho-12-molybdic acid indicate that the anion belongs to the 11 series. This confirms the easy degradation of this acid, and studies on the orange vanadates support their decavanadic structure³⁸.

The same methods have been applied to the polyphosphates. For those with a long chain structure, the methods specific to the chemistry of macromolecules are also used: light diffusion (valid in the case of molecules, but

still applicable in the present case if there is an excess of electrolyte), viscosity and flow birefringence which allow the length of the chain to be determined and provide an indication of its more-or-less curled up shape.

SUBSTITUTION PRODUCTS

In the structure of a polyanion, the characteristic atoms can be substituted by other atoms also capable of forming polyanions. The two elements must then have very similar properties: the same ionic radius, as is the case for the V–Mo–W family; even when these conditions are satisfied, the structure assumed is that of the isopolyanion corresponding to the predominant element (hexatungstic or decavanadic).

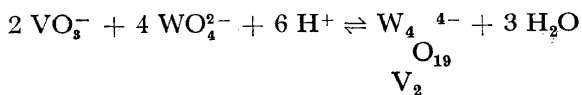


(Note the infrequency of species representative of the decavanadic type; (III) does not exist in the vanadotungstates).

Such a situation also leads to the possibility of mixed crystals between substituted salts, or between these and the unsubstituted salts. This additional possibility complicates the chemistry of these compounds in the solid state and explains the fact that, despite systematic investigations, there has been some disagreement in the past about the conclusions. The problem is simplified by working on solutions, since the second possibility is excluded but even this could only recently be undertaken since a precise knowledge of the ionic species of the isopolyanions was required.

Isopolyanions³⁹

Medium of low acidity—The most stable vanadotungstic ion is (II): it is revealed clearly by the acid titration curves of vanadate + tungstate mixtures:



Its colour is close to that of the decavanadates, but its absorption spectrum is nevertheless different. Bases degrade it rapidly, with discoloration, in a reaction that is the converse of its formation; the decomposition of the decavanadates on the other hand is slow.

Mixtures with a high proportion of vanadium—A more detailed study of the acid titration curve shows that even if the proportion of vanadium is higher than that required for the formation of (II), it is the compound (II) which is formed initially to the exclusion of any other mixed polyanion. The decavanadate is formed at pH less than 6, but appears only when the formation of (II) is practically complete*, and is accompanied by the species with a higher ratio of vanadium.

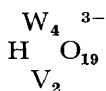
* In the case of the molybdates, the two regions are close to each other: the study of the solutions and the preparation of solid salts are thus made more difficult.

These latter species are investigated in the region of higher acidity about the equivalent point (pH 4.5–5), where they are in equilibrium with (II) and the decavanadic ions $\text{HV}_{10}\text{O}_{28}^{5-}$ present in excess. The concentration of the decavanadic ions is estimated by adding excess sodium hydroxide which does not discolour them. One can then plot $-\log [\text{HV}_{10}\text{O}_{28}^{5-}]$ against

$$\bar{n} = \frac{\text{conc. V introduced} - \text{conc. in the decavanadic state}}{\text{conc. W (or Mo) introduced}}$$

Analysis of this curve permits, by analogy with the titration curves, $\log [\text{H}^+] = f(\bar{n})$ of an acid, the knowledge of the possible different ions. (IV) and the corresponding vanadomolybdate, and (III) (only in the case of Mo) have been shown to exist.

Region of higher acidity—In the more acid region (pH \approx 3), (II) undergoes degradation into VO_2^+ less easily than the decavanadate and yields as an intermediate species the acid ion:



On the other hand, if the amount of tungsten is higher, (I) will form. It contains a higher ratio of tungsten and has a different absorption spectrum. It has been demonstrated that its formation from (II) and tungstate in excess requires time, since the solutions of vanadate and tungstate acidified to the appropriate pH behave as a mixture of (II) and isopolytungstates; it is only after the mixture has been kept that the spectrum of (I) appears.

Heteropolyanions

By introduction of vanadates during the preparation of tungstic or molybdic heteropolyacids, compounds belonging to the 12 series, partially substituted by vanadium, can be obtained^{40, 41}. Though it is alleged that substitution cannot affect more than two atoms (out of 12), we have been able to substitute three, but no more, in the case of the phosphomolybdic acid.

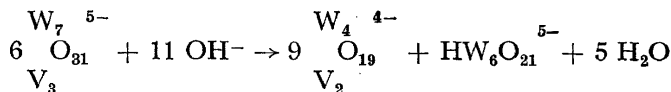
The preparation and properties of the products recall those of the usual heteropolyacids. They have a red-orange or ruby-red colour and display in general a greater stability in solution than the non-mixed compounds; they are more readily reduced and yield solutions characterized by a deep blue colour: for example, the phosphovanadomolybdic acid is reduced by Sb^{3+} at room temperature and the reaction can be used for the colorimetric quantitative analysis of the latter ion⁴².

Although they contain no hetero-atom, the metatungstates also fall in the heteropolyanion category. It is, therefore, possible to substitute partially vanadium for tungsten in their structures: such is the case with Rosenheim's "purple series"⁴³ which is of the following type: $\text{W}_7 \quad 5-*$.



* It should, however, be noted that the value of such a ratio does not correspond exactly to a metatungstic structure (with 12 atoms).

The conditions necessary for their preparation differ from those for the other vanadotungstates, and recall those for the metatungstates (prolonged boiling and high concentration of the reactant species). Like the polyanions referred to previously, this compound reacts with bases and the resulting irreversible degradation yields around pH 3-4 the isopolyanion (II) and the paratungstate:



(the reverse reaction is impossible under the conditions used).

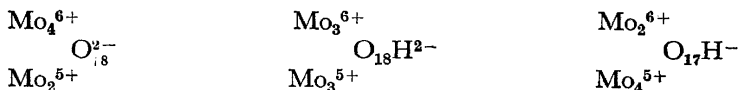
REDUCTION COMPOUNDS

One may consider these compounds as a particular case of the previous ones in which the substituent is the same element, but in a lower valency state. They are characteristic and important since they have deep colours, due to the enhanced possibilities of resonance between identical atoms of differing valencies, and afford an explanation of fractional valencies.

Isopolyanions derived from Molybdenum

Soluble compounds—They seem to be derived from a hexamolybdic type by a more-or-less extensive substitution of Mo^{6+} by Mo^{5+} .

The spectrophotometric titration of the molybdic solutions with Mo^{5+} is easy to follow since the compounds have characteristic spectra and clear breaks are obtained on plotting the optical density as a function of the proportion of Mo^{5+} added, provided that the acidity is suitable. The following compounds, whose spectra are given in *Figure 12* have been shown to exist⁴⁴.



blue (around pH 1.2) brown red (pH \sim 3) brown yellow (pH \sim 4)

In a medium of pH < 1, (I) (blue, soluble) precipitates the corresponding acid (blue, insoluble), which itself decomposes in a more acidic medium and yields cations of Mo^{6+} and Mo^{5+} , and consequently loses its colour. In a medium of pH greater than 5.5, (III) decomposes into molybdate and Mo^{5+} hydroxide which forms a brown precipitate. At intermediate values of pH, these compounds are easily converted into each other.

*Insoluble blue hydrated compounds of molybdenum**—Almost all these species are encountered only in the solid state since the corresponding ions do not exist in solution. They can be classified in the following way:

(a) The crystalline blue products which show X-ray diffraction patterns and whose structures are still unknown⁴⁵: These are obtained by reduction of suspensions of MoO_3 or $\text{MoO}_3 \cdot 2 \text{H}_2\text{O}$ in aqueous media; atomic hydrogen may also be used. The compounds can be represented as $\text{Mo O}_{x.n}\text{H}_2\text{O}$,

* The structures of the anhydrous blue compounds formed by the dry method are clearly outside the scope of this paper. It is, however, noteworthy that they are derived from the WO_3 type (WO_6 octahedra sharing their apices), but with a deficit of oxygen atoms.

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and are known where $x = 2.20, 2.50, 2.60, 2.75,$ and 2.87 . When they are heated, dehydration yields mixtures of MoO_3 and MoO_2 , and not the anhydrous blue compounds. With the exception of the compound corresponding to $x = 2.60$, they are stable to alkalis, except in the presence of air.

(b) Amorphous blue compounds⁴⁶: these are obtained by reduction of Mo^{6+} solutions with Mo^{5+} , Mo metal or by electrolysis. Bases decompose them into molybdate and Mo^{5+} hydroxide which precipitates; heating causes a progressive loss of water, which is not strongly bound as it is in the

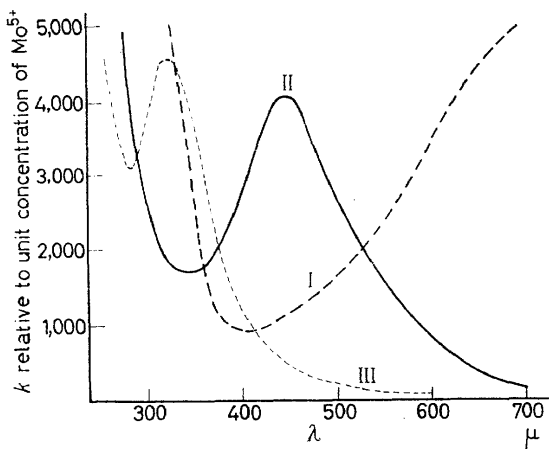


Figure 12

former compounds. They are diamagnetic and semi-conductors. x seems capable of a continuous variation between certain limits: for example, 2.88 to 2.93 while the ratio $\text{Mo}^{6+}/\text{Mo}^{5+}$ varies from 0.56 to 8.62. Compounds with $x = 2.75, 2.83, 2.87$ have been described⁴². It seems most likely that the compound with $x = 2.83$ constitutes the scarcely soluble acid derived from the blue anion previously mentioned.

Heteropolyanions

If a small part of the molybdenum (tungsten) atoms is reduced, the structure and the characteristic properties of the heteropolyanion are retained; the products thus obtained have a dark blue colour (ceruleo compounds or conjugated blue) and have properties similar to those of the non-reduced compounds: they can be extracted with ether, and some salts of alkali metals and organic bases exhibit a weak solubility. On further reduction the original structure is usually destroyed.

We have demonstrated that the reduction of more than four tungsten atoms (out of a total number of 12) to the pentavalent state is followed by a destruction of the silicotungstic structure. The intermediate step (2 W or Mo out of 12) may be characterized: thus the rate of the reduction by potassium iodide of the phospho-12-molybdic acid decreases abruptly when

about two molybdenum atoms have been reduced⁴⁸. The reduction of the phospho-12-tungstic acid on a platinum cathode also shows a change in rate (after 2 Faraday per mol. have been passed) at the same time as the cathodic potential increases⁴⁷.

Ammonium phospho-12-molybdates have been prepared, in which two or four Mo^{6+} have been replaced by Mo^{5+} , and 2- phospho-18-molybdates in which this substitution affects two, four and six molybdenum atoms¹².

The structure of the ceruleo compounds is not known with certainty. It must be very similar to that of the non-reduced compounds. The conversion of molybdenum (tungsten) atoms into the pentavalent state would take place either by the sharing apices of new octahedron summits, as is the case of reduced oxides, or by the addition of hydrogen atoms to the free apices of octahedra. Each substitution of one hydroxyl for one oxygen atom decreases the valency of one unit, and the original structure is kept unchanged.

Some cases of particular interest will now be considered.

*Silicomolybdic acid*⁴⁹—The heteropolyacids are more easily reduced than the isopolyanions. Their formation by action of the molybdic reagent on compounds of phosphorus, arsenic, silicon and germanium followed by reduction has been used for the colorimetric quantitative analysis of these latter elements, but the reduction process is not well defined. We have studied it by electrolytic reduction which allows the operating conditions to be strictly controlled. The problem is rendered more difficult by the coexistence in solution of two isomeric species; their existence was proved by Strickland⁵⁰, who also showed that the conversion $\beta \rightarrow \alpha$ is irreversible.

We have shown that the reduction of the usual form (α) yields successively two reduced compounds ($2e^-$ and $4e^-$ per ion). The oxidation of Mo^{5+} by the required quantity of KMnO_4 , in the presence of silica, yields the compounds with $4e^-$ and $2e^-$ which belong to the β series; a total oxidation gives the β -acid, identified by its spectrum.

In contrast to the non-reduced β -acid, the compound with $6e^-$ is stable; as for the compound with $2e^-$, it undergoes a partial dismutation into the compound with $4e^-$ and the non-reduced β acid. Since the latter is converted into the α -acid, the equilibrium is displaced, and finally the compound with $2e^-$ is converted totally into the compound with $4e^-$ and the non-reduced α -acid. Spectra are given in *Figure 13*.

*Metatungstate*⁵¹—As in the case of the other tungstic heteropolyanions, the reduction might be expected to yield the blue compounds with $2e^-$, then $4e^-$, and to result finally in a decomposition.

In fact, reduction may proceed as far as W^{3+} , *i.e.* $36e^-$ per $\text{H}_2\text{W}_{12}\text{O}_4^{66-}$ ion, without destruction of the structure, since re-oxidation gives back the metatungstic ion; the products obtained differ from those formed by reduction of the ordinary tungstic ions. By carrying out the reduction in dilute solutions (0.005 M) and by plotting the absorption coefficient at a given wavelength against the number of e^- involved, clear breaks at positions corresponding to 21, 26, 31, and 36 e^- are obtained. In more concentrated solution (0.05 M) and a weakly acid medium, the blue compounds with 2 and $4e^-$, which were not obtained under the previous conditions, are

ASPECTS OF THE CHEMISTRY OF ISO- AND HETEROPOLYANIONS

formed. They are unstable and disproportionate into metatungstate and more reduced compounds.

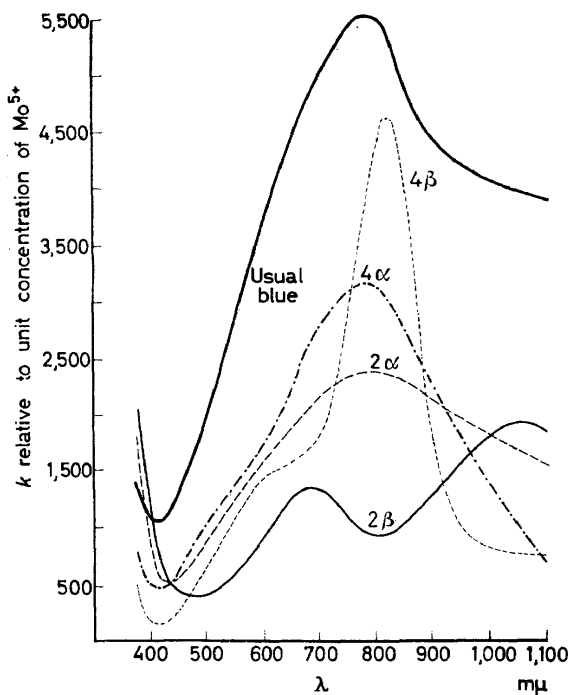


Figure 13

RELATIONS OF THE POLYANIONS WITH SOME OTHER COMPOUNDS

The general survey just given demonstrates the fact that the polyanions constitute an important and characteristic class in inorganic chemistry. The dehydration (either spontaneous or due to heating: polyphosphates) of the acid radicals introduces no new type of bonding, but leads to specific arrangements of the atoms which build up the structure. It follows from this remark that the alterations in the nature or number of the constitutional elements must be small if the structural type is to be preserved (see pp. 76-81). In this connection, the simplification of the structures displayed by other types of compounds is noteworthy; for example, the chemistry of the peroxidized anions is simple compared with that of the polyanions, compounds with a degree of condensation superior to two being unusual. The table of the pervanadates can be compared with *Figure 1*; these compounds have been recently investigated in our laboratory by spectrophotometric, cryometric and potentiometric methods⁵². The stable structures correspond to those of the most simple vanadates; one notices particularly the non-existence of a decavanadate type and the existence of a single bicondensed species: $V_2O_7H^{3-} \cdot 3O$, whose non-preoxidized analogue has only been

postulated; it must result from a combination of the perpyro with the permeta (*Figure 14*).

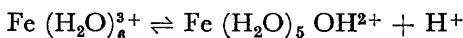
Equivalents of acid per Na_3VO_4	Species (the O active are written separately)	Colour	Name
0	VO_4^{3-} 3 $\bar{\text{O}}$	yellow	} . perortho
0	VO_4^{3-} 4 $\bar{\text{O}}$	violet	
1	VO_4H^{2-} 2 $\bar{\text{O}}$	light yellow	} . perpyro
1	VO_4H^{2-} 3 $\bar{\text{O}}$	light yellow	
1.5	$\text{V}_2\text{O}_7\text{H}^{3-}$ 4 $\bar{\text{O}}$	light yellow	. perpyro acid
2	VO_3^- 3 $\bar{\text{O}}$	yellow	. permeta
4	VO_2^- $\bar{\text{O}}$	red	. pervanadyl cation

Figure 14

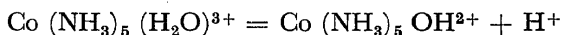
Similar investigations in the molybdc series show, besides $\text{MoO}_4^{2-} \cdot 4\text{O}$ (red), only the compounds $\text{Mo}_2\text{O}_7^{2-} \cdot 4\text{O}$ and $\text{Mo}_2\text{O}_7\text{H}_2 \cdot 4\text{O}$ (yellow); in contradiction to former claims, the pyromolybdc type Mo_2O_7 does not exist for the non-peroxidized molybdc polyanions⁵⁸.

Similarly, the chemistry of the fluoxy-molybdates-niobates-tantalates is simpler than that of the corresponding isopolyanions.

Parallelism with cationic species—A large number of salts derived from polyvalent cations, when dissolved in water, yield “basic cations” by loss of protons



The corresponding salts are very often insoluble or difficult to prepare. Those difficulties do not exist for the “ammine” cations. Consequently, their equilibria have long been familiar. The hydrolysis of the roseo salts has been known since the work of Jorgensen in 1892:



In fact, the reactions are very often more complicated, the hydroxy ions formed showing a tendency to condensation into polynuclear ions. Whereas in the polyanions the bonds between acid radicals are formed by sharing of oxygen atoms (oxygen bridging the two groups), here the strong disposition of the intervening hydroxyl groups to coordinate is responsible for bonding.

Besides the previously cited hydroxy compounds, it can bind itself to two metal atoms and give compounds devoid of any basic property.

Consequently, if basic ions can be prepared in solution for a polyvalent ion, an increase in the quantity of base added introduces more hydroxyl ions and they promote condensation. The result is the formation of species with a degree of condensation increasing from that of the simple solution to that of colloidal solutions, and ending up with a hydroxide suspension.

This illustrates the difficulties encountered in the investigation of such systems, but the methods employed are, nevertheless, similar to those used in the study of the polyanions. Some analogies also exist between the structures: thus, the sulphate which crystallizes from solutions of the $\text{Al}_6(\text{OH})_{15}^{3+}$ ion contains the $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ ion, in which twelve AlO_6 octahedral group

themselves around a central AlO_4 tetrahedron, adopting the same arrangement as in the phosphotungstic ion (p. 71). Taking into account a sufficient number of constitutional water molecules,

is obtained⁵⁴ which is similar to

$$\begin{array}{cccc} \text{Al} & \text{Al}_{12} & \text{O}_{40} & \text{H}_{48}^{7+} \\ \text{P} & \text{W}_{12} & \text{O}_{40}^{3-} & \end{array}$$

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