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Vanadium, Niobium and Tantalum

22.1 Introduction

The discoveries of all three of these elements were made at the beginning of the nineteenth century and were marked by initial uncertainty and confusion due, in the case of the heavier pair of elements, to the overriding similarity of their chemistries. (See p. 1282 for element 105, dubnium.)

A. M. del Rio in 1801 claimed to have discovered the previously unknown element 23 in a sample of Mexican lead ore and, because of the red colour of the salts produced by acidification, he called it erythronium. Unfortunately he withdrew his claim when, 4 years later, it was (incorrectly) suggested by the Frenchman, H. V. Collett-Desotils, that the mineral was actually basic lead chromate. In 1830 the element was "rediscovered" by N. G. Sefström in some Swedish iron ore. Because of the richness and variety of colours found in its compounds he called it vanadium after Vanadis, the Scandinavian goddess of beauty. One year later F. Wöhler established the identity of vanadium and erythronium. The metal itself was isolated in a reasonably pure form in 1867 by H. E. Roscoe who reduced the chloride with hydrogen, and he was also responsible for much of the early work on the element.

In the same year that del Rio found his erythronium, C. Hatchett examined a mineral which had been sent to England from Massachusetts and had lain in the British Museum since 1753. From it he isolated the oxide of a new element which he named columbium, and the mineral columbite, in honour of its country of origin. Meanwhile in Sweden A. G. Ekeberg was studying some Finnish minerals and in 1802 claimed to have identified a new element which he named tantalum because of the difficulty he had had in dissolving the mineral in acids.[†] It was subsequently thought that the two elements were one and the same, and this view persisted until at least 1844 when H. Rose examined a columbite sample and showed that two distinct elements were involved.

[†] The classical allusion refers to Tantalus, the mythical king of Phrygia, son of Zeus and a nymph, who was condemned for revealing the secrets of the gods to man: one of his punishments was being made to stand in Tartarus up to his chin in water, which constantly receded as he stooped to drink. As Ekeberg wrote (1802): "This metal I call *tantalum* ... partly in allusion to its incapacity, when immersed in acid, to absorb any and be saturated."

One was Ekeberg's tantalum and the other he called niobium (Niobe was the daughter of Tantalus). Despite the chronological precedence of the name columbium, IUPAC adopted niobium in 1950, though columbium is still sometimes used in US industry. Impure niobium metal was first isolated by C. W. Blomstrand in 1866 by the reduction of the chloride with hydrogen, but the first pure samples of metallic niobium and tantalum were not prepared until 1907 when W. von Bolton reduced the fluorometallates with sodium.

22.2 The Elements

22.2.1 Terrestrial abundance and distribution

The abundances of these elements decrease by approximately an order of magnitude from V to Nb and again from Nb to Ta. Vanadium has been estimated to comprise about 136 ppm (i.e. 0.0136%) of the earth's crustal rocks, which makes it the nineteenth element in order of abundance (between Zr, 162 ppm, and Cl, 126 ppm); it is the fifth most abundant transition metal after Fe, Ti, Mn and Zr. It is widely, though sparsely, distributed; thus although more than 60 different minerals of vanadium have been characterized, there are few concentrated deposits and most of it is obtained as a coproduct along with other materials. Its major commercial source is the titanoferrous magnetites of South Africa, the former USSR and China. One of its important minerals is the polysulfide, patronite, VS_4, but, being a class-a metal, it is more generally associated with oxygen. For example, vanadinite approximates to lead chloride vanadate, $PbCl_2.3Pb_3(VO_4)_2$, and carnotite to potassium uranyl vanadate, $K(UO_2)(VO_4).1.5H_2O$. Vanadium is also found in some crude oils, in particular those from Venezuala and Canada, and can be recovered from the oil residues and from flue dusts after burning.

The crustal abundances of niobium and tantalum are 20 ppm and 1.7 ppm, comparable to N (19 ppm), Ga (19 ppm), and Li (18 ppm), on the one hand, and to As (1.8 ppm) and Ge (1.5 ppm), on the other. Of course, in view of their chemical similarities. Nb and Ta usually occur together, and their most widespread mineral, $(Fe,Mn)M_2O_6$ (M = Nb, Ta), is known as columbite or tantalite, depending on which metal preponderates. Until the 1950s, this was the major source of both metals, with significant amounts obtained also as a byproduct of the extraction of tin in SE Asia and Nigeria. The discovery of a huge, high grade (2.5% Nb_2O_5) deposit of pyrochlore, $NaCaNb_2O_6F$, in Brazil totally changed the pattern. Nb is now obtained chiefly from Brazil; Ta from Australia, Canada and SE Asia but its production is heavily dependent on demand for Sn.

22.2.2 Preparation and uses of the metals

Because it is usually produced along with other metals, the availability of vanadium and the economics of its production[1] are intimately connected with the particular coproduct involved.

The usual extraction procedure is to roast the crushed ore, or vanadium residue, with NaCl or Na_2CO_3 at 850°C. This produces sodium vanadate, $NaVO_3$, which is leached out with water. Acidification with sulfuric acid to pH 2–3 precipitates "red cake", a polyvanadate, which, on fusing at 700°C, gives a black, technical grade vanadium pentoxide. Reduction is then necessary to obtain the metal, but, since about 80% of vanadium produced is used as an additive to steel, it is usual to effect the reduction in an electric furnace in the presence of iron or iron ore to produce ferrovanadium, which can then be used without further refinement. Carbon was formerly used as the reductant, but it is difficult to avoid the formation of an intractable carbide, and so it has been superseded by aluminium or, more commonly, ferrosilicon (p. 330) in which case lime is also added to remove the silica as a slag of calcium silicate. If pure vanadium metal is required it can

[1] C. K. GUPTA and N. KRISHNAMURTHY, *Extractive Metallurgy of Vanadium*, Elsevier, Amsterdam, 1992, 689 pp.

be obtained by reduction of VCl_5 with H_2 or Mg, by reduction of V_2O_5 with Ca, or by electrolysis of partially refined vanadium in fused alkali metal chloride or bromide.

The benefit of vanadium as an additive in steel is that it forms V_4C_3 with any carbon present, and this disperses to produce a fine-grained steel which has increased resistance to wear and is stronger at high temperatures. Such steels are widely used in the manufacture of springs and high-speed tools. In 1995, world consumption of vanadium metal, alloys and concentrates exceeded 33 000 tonnes of contained vanadium.

Production of niobium and tantalum is on a smaller scale and the processes involved are varied and complicated. Alkali fusion, or digestion of the ore with acids can be used to solubilize the metals, which can then be separated from each other. The process originally developed by M. C. Marignac in 1866 and in use for a century utilized the fact that in dil HF tantalum tends to form the sparingly soluble K_2TaF_7, whereas niobium forms the soluble $K_3NbOF_5.2H_2O$. Nowadays it is more usual to employ a solvent extraction technique. For instance, tantalum can be extracted from dilute aqueous HF solutions by methyl isobutyl ketone, and increasing the acidity of the aqueous phase allows niobium to be extracted into a fresh batch of the organic phase. The metals can then be obtained, after conversion to the pentoxides, by reduction with Na or C, or by the electrolysis of fused fluorides. In 1995, world production of contained metal was in the region of 18 000 tonnes for Nb and 1000 tonnes for Ta.

Niobium finds use in the production of numerous stainless steels for use at high temperatures, and Nb/Zr wires are used in superconducting magnets. The extreme corrosion-resistance of tantalum at normal temperatures (due to the presence of an exceptionally tenacious film of oxide) leads to its application in the construction of chemical plant, especially where it can be used as a liner inside cheaper metals. Its complete inertness to body fluids makes it the ideal material for surgical use in bone repair and internal suturing.

It is widely used by the electronics industry in the manufacture of capacitors, where the oxide film is an efficient insulator, and as a filament or filament support. Indeed, it was for a while widely used to replace carbon as the filament in incandescent light bulbs but, by about 1911, was itself superseded by tungsten.

22.2.3 Atomic and physical properties of the elements

Some of the important properties of Group 5 elements are summarized in Table 22.1. Having odd atomic numbers, they have few naturally occurring isotopes; Nb only 1 and V and Ta 2 each, though the second ones are present only in very low abundance (^{50}V 0.250%, ^{180}Ta 0.012%). As a consequence (p. 17) their atomic weights have been determined with considerable precision. On the other hand, because of difficulties in removing all impurities, reported values of their bulk properties have often required revision.

All three elements are shiny, silvery metals with typically metallic bcc structures. When very pure they are comparatively soft and ductile but impurities usually have a hardening and embrittling effect. When compared to the elements of Group 4 the expected trends are apparent. These elements are slightly less electropositive and are smaller than their predecessors, and the heavier pair Nb and Ta are virtually identical in size as a consequence of the lanthanide contraction. The extra d electron again appears to contribute to stronger metal–metal bonding in the bulk metals, leading in each case to a higher mp, bp and enthalpy of atomization. Indeed, these quantities reach their maximum values in this and the following group. In the first transition series, vanadium is the last element before some of the $(n-1)$d electrons begin to enter the inert electron-core of the atom and are therefore not available for bonding. As a result, not only is its mp the highest in the series but it is the last element whose compounds in the group oxidation state (i.e. involving all $(n-1)$d and ns electrons) are not strongly oxidizing. In the second and

Table 22.1   Some properties of Group 5 elements

Property		V	Nb	Ta
Atomic number		23	41	73
Number of naturally occurring isotopes		2	1	2
Atomic weight		50.9415(1)	92.90638(2)	180.9479(1)
Electronic configuration		[Ar]$3d^34s^2$	[Kr]$4d^35s^2$	[Xe]$4f^{14}5d^36s^2$
Electronegativity		1.6	1.6	1.5
Metal radius (12-coordinate)/pm		134	146	146
Ionic radius (6-coordinate)/pm	V	54	64	64
	IV	58	68	68
	III	64	72	72
	II	79	—	—
MP/°C		1915	2468	2980
BP/°C		3350	4758	5534
ΔH_{fus}/kJ mol^{-1}		17.5	26.8	24.7
ΔH_{vap}/kJ mol^{-1}		459.7	680.2	758.2
ΔH_f (monoatomic gas)/kJ mol^{-1}		510 ($\pm$29)	724	782 ($\pm$6)
Density (20°C)/g cm^{-3}		6.11	8.57	16.65
Electrical resistivity (20°C)/μohm cm		~25	~12.5	(12.4)

third series the entry of $(n-1)$d electrons into the electron core is delayed somewhat and it is molybdenum and tungsten in Group 6 whose mps are the highest.

22.2.4 Chemical reactivity and trends

The elements of Group 5 are in many ways similar to their predecessors in Group 4. They react with most non-metals, giving products which are frequently interstitial and nonstoichiometric, but they require high temperatures to do so. Their general resistance to corrosion is largely due to the formation of surface films of oxides which are particularly effective in the case of tantalum. Unless heated, tantalum is appreciably attacked only by oleum, hydrofluoric acid or, more particularly, a hydrofluoric/nitric acid mixture. Fused alkalis will also attack it. In addition to these reagents, vanadium and niobium are attacked by other hot concentrated mineral acids but are resistant to fused alkali.

The most obvious factor in comparing the chemistry of the three elements is again the very close similarity of the second and third members although, in this group, slight differences can be discerned as will be discussed shortly. The

stability of the lower oxidation states decreases as the group is descended. As a result, although each element shows formal oxidation states from +5 down to −3, the most stable one in the case of vanadium under normal conditions is the +4, and even the +3 and +2 oxidation states (which are admittedly strongly reducing) have well-characterized cationic aqueous chemistries; by contrast most of the chemistries of niobium and tantalum are confined to the group oxidation state +5. Of the halogens, only the strongly oxidizing fluorine produces a pentahalide of vanadium, and the other vanadium(V) compounds are based on the oxohalides and the pentoxide. The pentoxide also gives rise to the complicated but characteristic aqueous chemistry of the polymerized vanadates (isopolyvanadates) which anticipates the even more extensive chemistry of the polymolybdates and polytungstates; this is only incompletely mirrored by niobium and tantalum.

The +4 oxidation state, which for Nb and Ta is best represented by their halides, is most notable for the uniquely stable VO^{2+} (vanadyl) ion which retains its identity throughout a wide variety of reactions and forms many complexes. Indeed it is probably the most stable diatomic ion known. The M^{IV} ions have only slightly smaller radii

Table 22.2 Oxidation states and stereochemistries of compounds of vanadium, niobium and tantalum

Oxidation state	Coordination number	Stereochemistry	V	Nb/Ta
-3 (d^8)	5	—	$[V(CO)_5]^{3-}$	$[M(CO)_5]^{3-}$
-1 (d^6)	6	Octahedral	$[V(CO)_6]^-$	$[M(CO)_6]^-$
0 (d^5)	6	Octahedral	$[V(CO)_6]$	—
1 (d^4)	6	Octahedral	$[V(bipy)_3]^+$	—
	7	Capped octahedral	—	$[TaH(CO)_2(diphos)_2]$
2 (d^3)	4	Square planar	—	NbO
	6	Octahedral	$[V(CN)_6]^{4-}$	TaO(?)
		Trigonal prismatic	VS	NbS
3 (d^2)	3	Planar	$[V\{N(SiMe_3)_2\}_3]$	—
	4	Tetrahedral	$[VCl_4]^-$	
	5	Trigonal bipyramidal	$[VCl_3(NMe_3)_2]$	
	6	Octahedral	$[V(C_2O_4)_3]^{3-}$	$[Nb_2Cl_9]^{3-}$
		Trigonal prismatic	—	LiNbO$_2$
	7	Complex	—	$[Ta(CO)Cl_3(PMe_2Ph)_3].EtOH$
	8	Dodecahedral	—	$[Nb(CN)_8]^{5-}$
4 (d^1)	4	Tetrahedral	VCl$_4$	$[Nb(NEt_2)_4]$ (not Ta)
	5	Trigonal bipyramidal	$[VOCl_2(NMe_3)_2]$	
		Square pyramidal	$[VO(acac)_2]$	
	6	Octahedral	$[VCl_4(bipy)]$	$[MCl_6]^{2-}$
	7	Pentagonal bipyramidal	—	$[NbF_7]^{3-}$
	8	Dodecahedral	$[VCl_4(diars)_2]$	$[NbCl_4(diars)_2]$ (not Ta)
		Square antiprismatic	$[V(S_2CMe)_4]^{(a)}$	$[Nb(\beta\text{-diketonate})_4]$
5 (d^0)	4	Tetrahedral	VOCl$_3$	ScNbO$_4$
	5	Trigonal bipyramidal	VCl$_5$(g)	MF$_5$(g)
		Square pyramidal	$[VOF_4]^-$	$[M(NMe_2)_5]$
	6	Octahedral	$[VF_6]^-$	$[MF_6]^-$
		Trigonal prismatic	—	$[M(S_2C_6H_4)_3]^-$
	7	Pentagonal bipyramidal	$[VO(S_2CNEt_2)_3]$	$[TaS(S_2CNEt_2)_3]$
		Capped trigonal prismatic	—	$[MF_7]^{2-}$
	8	Dodecahedral	$[V(O_2)_4]^{3-}$	$[M(O_2)_4]^{3-}$
				$[Ta(S_2CNMe_2)_4]^+$
		Square antiprismatic	—	$[MF_8]^{3-}$

[a]Tetrakis(dithioacetato)vanadium(IV) was originally classified as dodecahedral. Re-examination has shown that its unit cell in fact contains two independent metal sites. One is indeed dodecahedral but the other is square antiprismatic; C. W. HAIGH, *Polyhedron* **14**, 2871–8 (1995).

than those of Group 4, and, again, coordination numbers as high as 8 are found. In the +5 state, however, only Nb and Ta are sufficiently large to achieve this coordination number with ligands other than bidentate ones with very small "bites", such as the peroxo group. Table 22.2 illustrates the various oxidation states and stereochemistries of compounds of V, Nb and Ta.

Niobium and tantalum provide no counterpart to the cationic chemistry of vanadium in the +3 and +2 oxidation states. Instead, they form a series of "cluster" compounds based

on octahedral M_6X_{12} units. The occurrence of such compounds is largely a consequence of the strength of metal–metal bonding in this part of the periodic table (as reflected in high enthalpies of atomization), and similar cluster compounds are found also for molybdenum and tungsten.

Compounds containing M–C σ-bonds are frequently unstable and do not give rise to an extensive chemistry (p. 999). Vanadium forms a neutral (paramagnetic) hexacarbonyl which, though not very stable, contrasts with that of titanium in that it can at least be prepared in

quantity. All three elements give a number of η^5-cyclopentadienyl derivatives.

22.3 Compounds of Vanadium, Niobium and Tantalum[2,3]

The binary hydrides (p. 67), borides (p. 148), carbides (p. 299), and nitrides (p. 418) of these metals have already been discussed and will not be described further except to note that, as with the analogous compounds of Group 4, they are hard, refractory and nonstoichiometric materials with high conductivities. The intriguing cryo-compound $[V(N_2)_6]$ has been isolated by cocondensing V atoms and N_2 molecules at $20-25$ K; it has an infrared absorption at 2100 cm^{-1} and its d–d and charge-transfer spectra are strikingly similar to those of the isoelectronic 17-electron species $[V(CO)_6]$.

22.3.1 Oxides

Table 22.3 gives the principal oxides formed by the elements of this group. Besides the 4 oxides of vanadium shown, a number of other phases of intermediate composition have been identified and the lower oxides in particular have wide ranges of homogeneity. V_2O_5 is orange yellow when pure (due to charge transfer) and is the final product when the metal is heated in an excess of oxygen, but contamination with lower oxides is then common and a better method is to heat

ammonium "metavanadate":

$$2NH_4VO_3 \longrightarrow V_2O_5 + 2NH_3 + H_2O$$
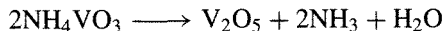
On the basis of simple radius ratio arguments, vanadium(V) is expected to be rather large for tetrahedral coordination to oxygen, but rather small for octahedral coordination. It is perhaps not surprising therefore that, though the structure of V_2O_5 is somewhat complicated, it consists essentially of distorted trigonal bipyramids of VO_5 sharing edges to form zigzag double chains. Another, metastable, form has been prepared which differs from the normal one in the relative dispositions of adjacent parallel chains.[4] V_2O_5 is homogeneous over only a small range of compositions but loses oxygen reversibly on heating, which is probably why it is such a versatile catalyst. For instance, it catalyses the oxidation of numerous organic compounds by air or hydrogen peroxide, and the reduction of olefins (alkenes) and of aromatic hydrocarbons by hydrogen, but most importantly it catalyses the oxidation of SO_2 to SO_3 in the contact process for the manufacture of sulfuric acid (p. 708). For this purpose it replaced metallic platinum which, besides being far more expensive, was also prone to "poisoning" by impurities such as arsenic. V_2O_5 is amphoteric. It is slightly soluble in water, giving a pale yellow, acidic solution. It dissolves in acids producing salts of the pale-yellow dioxovanadium(V) ion, $[VO_2]^+$, and in alkalis producing colourless solutions which, at high pH, contain the orthovanadate ion, VO_4^{3-}. At intermediate pHs a series of hydrolysis-polymerization reactions occur yielding the isopolyvanadates to be discussed in the next section. It is also a mild oxidizing agent and in aqueous solution is reduced by, for instance, hydrohalic acids to vanadium(IV). In the solid, mild reduction with CO, SO_2, or fusion with oxalic acid gives the deep-blue VO_2.

At room temperature VO_2 has a rutile-like structure (p. 961) distorted by the presence of pairs of vanadium atoms bonded together. Above 70°C, however, an undistorted rutile

Table 22.3   Oxides of Group 5 metals

Oxidation state:	+5	+4	+3	+2
V	V_2O_5	VO_2	V_2O_3	VO
Nb	Nb_2O_5	NbO_2	—	NbO
Ta	Ta_2O_5	TaO_2	—	(TaO)

[2] D. L. KEPERT, *The Early Transition Metals*, Chap. 3, V, Nb, Ta, pp. 142–254, Academic Press, London, 1972.

[3] R. J. H. CLARK, Chap. 34, pp. 491–551, and D. BROWN, Chap. 35, pp. 553–622, in *Comprehensive Inorganic Chemistry*, Vol. 3, Pergamon Press, Oxford, 1973.

[4] J. M. COCCIANTELLI, P. GRAVEREAU, M. POUCHARD and P. HAGENMULLER, *J. Solid State Chem.*, **93**, 497–502 (1991).

structure is adopted as the atoms in each pair separate, breaking the localized V–V bonds and releasing the bonding electrons, so causing a sharp increase in electrical conductivity and magnetic susceptibility. It is again amphoteric, dissolving in non-oxidizing acids to give salts of the blue oxovanadium(IV) (vanadyl) ion$[VO]^{2+}$, and in alkali to give the yellow to brown vanadate(IV) (hypovanadate) ion $[V_4O_9]^{2-}$, or at high pH $[VO_4]^{4-}$. Like the vanadium(V) system, a number of polyanions are produced at intermediate pH. Between V_2O_5 and VO_2 is a succession of phases V_nO_{2n+1} of which V_3O_7, V_4O_9 and V_6O_{13} have been characterized.

Further reduction with H_2, C or CO produces a series of discrete chemical-shear phases (Magnéli phases) of general formula V_nO_{2n-1} based on a rutile structure with periodic defects (p. 961), before the black, refractory sesquioxide V_2O_3 is reached. Examples are V_4O_7, V_5O_9, V_6O_{11}, V_7O_{13} and V_8O_{15}. The oxides VO, V_2O_3 and V_3O_5 also conform to the general formula V_nO_{2n-1}, but this is a purely formal relation and their structures are not related by chemical-shear to those of the Magnéli phases.

V_2O_3 has a corundum structure (p. 243) and is notable for the transition occurring as it is cooled below about 170 K when its electrical conductivity changes from metallic to insulating in character. Chemically it is entirely basic, dissolving in aqueous acids to give blue or green vanadium(III) solutions which are strongly reducing. On still further reducing the oxide system, the corundum structure is retained down to compositions as low as $VO_{1.35}$, after which the grey metallic monoxide VO, with a defect rock-salt structure, is formed. This too is markedly nonstoichiometric with a composition range from $VO_{0.8}$ to $VO_{1.3}$. In all, therefore, at least 13 distinct oxide phases of vanadium have been identified between $VO_{\sim 1}$ and V_2O_5.

Niobium and tantalum also form various oxide phases but they are not so extensive or well characterized as those of vanadium. Their pentoxides are relatively much more stable and difficult to reduce. As they are attacked by conc HF and will dissolve in fused alkali, they may perhaps

be described as amphoteric, but inertness is the more obvious characteristic. Their structures are extremely complicated and Nb_2O_5 in particular displays extensive polymorphism. It is interesting to note that the polymorphs of Nb_2O_5 and Ta_2O_5 are by no means all analogous.

High temperature reduction of Nb_2O_5 with hydrogen gives the bluish-black dioxide NbO_2 which has a distorted rutile structure. As in VO_2 the distortion is caused by pairs of metal atoms evidently bonded together, but the distortion is in a different direction. Between Nb_2O_5 and NbO_2 there is a homologous series of structurally related phases of general formula $Nb_{3n+1}O_{8n-2}$ with $n = 5$, 6, 7, 8 (i.e. Nb_8O_{19}, $Nb_{19}O_{46}$, $Nb_{11}O_{27}$ and $Nb_{25}O_{62}$). In addition, oxides of formula $Nb_{12}O_{29}$ and $Nb_{47}O_{116}$ have been reported: the numerical relationship to Nb_2O_5 is clear since $Nb_{12}O_{29}$ is $(12Nb_2O_5-2O)$ and $2Nb_{47}O_{116}$ (or $Nb_{94}O_{232}$) is $(47Nb_2O_5-3O)$. Further reduction produces the grey monoxide NbO which has a cubic structure and metallic conductivity but differs markedly from its vanadium analogue in that its composition range is only $NbO_{0.982}$ to $NbO_{1.008}$. The structure is a unique variant of the rock-salt NaCl structure (p. 242) in which there are vacancies (Nb) at the eight corners of the unit cell and an O vacancy at its centre (Fig. 22.1). The structure could therefore be described as a vacancy-defect NaCl structure $Nb_{0.75}\boxminus_{0.25}O_{0.75}\boxminus_{0.25}$, but as all the vacancies are ordered it is better to consider it as a new structure type in which both Nb and O form 4 coplanar bonds. The central feature is a 3D framework of Nb_6 octahedral clusters (Nb–Nb 298 pm, cf. Nb–Nb 285 pm in Nb metal) and this accounts for the metallic conductivity of the compound. The structure is reminiscent of the structure-motif of the lower halides of Nb and Ta (p. 992) and the retention of the Nb_6 clusters rather than the adoption of the ionic NaCl-type structure can similarly be related to the high heats of sublimation of Nb and neighbouring metals. (For a fuller discussion of the bonding, see ref. 5.)

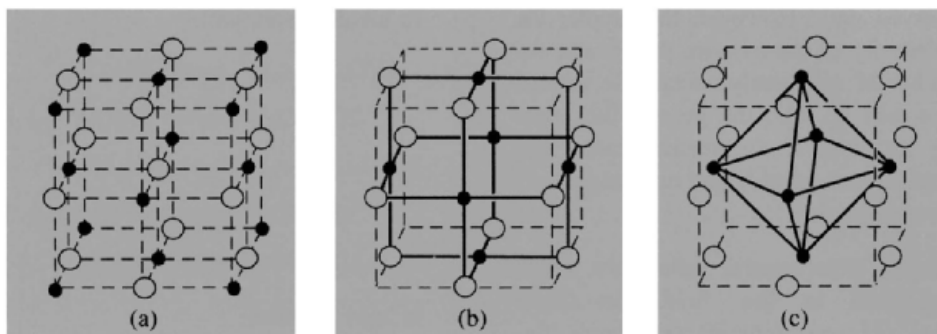[5] J. K. BURDETT and T. HUGHBANKS, *J. Am. Chem. Soc.* **106**, 3101–13 (1984).

Figure 22.1 (a) NaCl (MgO) showing all sites occupied by M(●) and O(○). (b) NbO showing planar coordination of Nb (and O) and vacancies at the cube corners (Nb) and centre (O). (c) NbO as in (b), but emphasizing the octahedral Nb_6 cluster (joined by corner sharing to neighbouring unit cells).

The heavier metal tantalum is distinctly less inclined than niobium to form oxides in lower oxidation states. The rutile phase TaO_2 is known but has not been studied, and a cubic rock-salt-type phase TaO with a narrow homogeneity range has also been reported but not yet fully characterized. Ta_2O_5 has two well-established polymorphs which have a reversible transition temperature at 1355°C but the detailed structure of these phases is too complex to be discussed here.

22.3.2 Polymetallates [6-8b]

The amphoteric nature of V_2O_5 has already been noted. In fact, if the colourless solution produced by dissolving V_2O_5 in strong aqueous alkali such as NaOH is gradually acidified, it first deepens in colour, becoming orange to red as the neutral point is passed; it then darkens further and, around pH 2, a brown precipitate of hydrated V_2O_5 separates and redissolves at still lower pHs to give a pale-yellow solution. As a result of spectrophotometric studies there is general agreement that the predominant species in the initial colourless solution is the tetrahedral VO_4^{3-} ion and, in the final pale-yellow solution, the angular VO_2^+ ion. In the intervening orange to red solutions a complicated series of hydrolysis-polymerization reactions occur, which have direct counterparts in the chemistries of Mo and W and to a lesser extent Nb, Ta and Cr. The polymerized species involved are collectively known as isopolymetallates or isopolyanions. The determination of the equilibria involved in their formation, as well as their stoichiometries and structures, has been a confused and disputed area, some aspects of which are by no means settled even now. That this is so is perfectly understandable because:

(i) Some of the equilibria are reached only slowly (possibly months in some cases) and it is likely that much of the reported work has been done under non-equilibrium conditions.

(ii) Often in early work, solid species were crystallized from solution and their stoichiometries, quite unjustifiably as it turns out, were used to infer the stoichiometries of species in solution.

(iii) When a series of experimental measurements has been made it is usual to see what combination of plausible ionic species will best account for the

[6] M. T. POPE, Iso- and Hetero-polyanions, Chap. 38 in *Comprehensive Coordination Chemistry*, Vol. 3, pp. 1028–58, Pergamon Press, Oxford, 1987.

[7] M. T. POPE, *Heteropoly and Isopoly Oxometalates*, Springer Verlag, Berlin, 1983, 180 pp.

[8] M. T. POPE and A. MÜLLER, *Angew. Chem. Int. Edn. Engl.* **30**, 34–48 (1991).
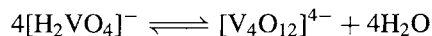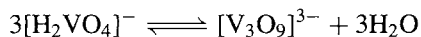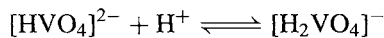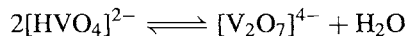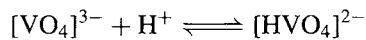
[8a] G. M. MAKSIMOV, *Russ. Chem. Rev. (Engl. Transl.)* **64**, 445–61 (1995).

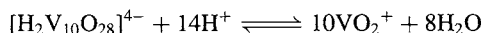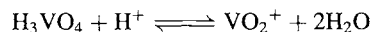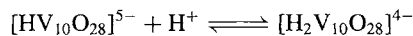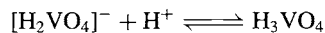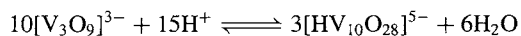[8b] M. I. KHAN and J. ZUBIETA, *Prog. Inorg. Chem.* **43**, 1–149 (1995).

observed data. However, the greater the complexity of the system, the greater the number of apparently acceptable models there will be, and the greater the accuracy required if the measurements are to distinguish reliably and unambiguously between them.

Of the many experimental techniques which have been used in this field, the more important are: pH measurements, cryoscopy, ion-exchange and ultraviolet/visible spectroscopy for studying the stoichiometry of the equilibria, and infrared/Raman and nmr spectroscopy for studying the structures of the ions in solution, where oxygen-17 and metal atom nmr spectroscopy are playing an increasingly important role. Probably the best summary of our current understanding of the vanadate system is given by Fig. 22.2. This shows how the existence of the various vanadate species depends on the pH and on the total concentration of vanadium.[7] Their occurrence can be accounted for by protonation and condensation equilibria such as the following:

In alkaline solution:

$$[VO_4]^{3-} + H^+ \rightleftharpoons [HVO_4]^{2-}$$
$$2[HVO_4]^{2-} \rightleftharpoons [V_2O_7]^{4-} + H_2O$$
$$[HVO_4]^{2-} + H^+ \rightleftharpoons [H_2VO_4]^-$$
$$3[H_2VO_4]^- \rightleftharpoons [V_3O_9]^{3-} + 3H_2O$$
$$4[H_2VO_4]^- \rightleftharpoons [V_4O_{12}]^{4-} + 4H_2O$$

In acid solution:

$$10[V_3O_9]^{3-} + 15H^+ \rightleftharpoons 3[HV_{10}O_{28}]^{5-} + 6H_2O$$
$$[H_2VO_4]^- + H^+ \rightleftharpoons H_3VO_4$$
$$[HV_{10}O_{28}]^{5-} + H^+ \rightleftharpoons [H_2V_{10}O_{28}]^{4-}$$
$$H_3VO_4 + H^+ \rightleftharpoons VO_2^+ + 2H_2O$$
$$[H_2V_{10}O_{28}]^{4-} + 14H^+ \rightleftharpoons 10VO_2^+ + 8H_2O$$

In these equilibria the site of protonation in the species $[HVO_4]^{2-}$, $[H_2VO_4]^-$ etc., is an oxygen atom (not vanadium); a more precise representation would therefore be $[VO_3(OH)]^{2-}$, $[VO_2(OH)_2]^-$ etc. However, the customary formulation is retained for convenience (cf. HNO_3, HSO_4^-, H_2SO_4, etc.).
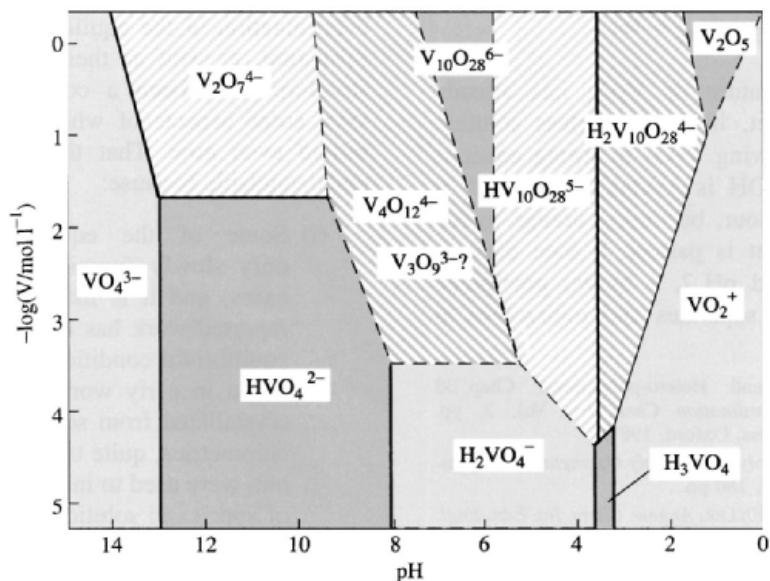

Figure 22.2   Occurrence of various vanadate and polyvanadate species as a function of pH and total concentration of vanadium.

It is evident from Fig. 22.2 that only in very dilute solutions are monomeric vanadium ions found and any increase in concentrations, particularly if the solution is acidic, leads to polymerization. ^{51}V nmr work indicates that, starting from the alkaline side, the various ionic species are all based on 4-coordinate vanadium(V) in the form of linked VO_4 tetrahedra until the decavanadates appear. These evidently involve a higher coordination number, but whether or not it is the same in solution as in the solids which can be separated is uncertain. However, it is interesting to note that similarities between the vanadate and chromate systems cease with the appearance of the decavanadates which have no counterpart in chromate chemistry. The smaller chromium(VI) is apparently limited to tetrahedral coordination with oxygen, whereas vanadium(V) is not.

More information is of course available on the structures of the various crystalline vanadates which can be separated from solution. Traditionally, the colourless salts obtained from alkaline solution were called ortho-, pyro-, or meta-vanadates by analogy with the phosphates of corresponding stoichiometry. "Ortho"-vanadates, $M_3^I VO_4$(aq), apparently contain discrete, tetrahedral, $VO_4{}^{3-}$ ions; "pyro"-vanadates, $M_4^I V_2O_7$ (aq), contain dinuclear $[V_2O_7]^{4-}$ ions consisting of 2 VO_4 tetrahedra sharing a corner; the structures of "meta"-vanadates depend on the state of hydration (Fig. 22.3) but in no cases do they involve discrete $VO_3{}^-$ ions. Anhydrous metavanadates such as NH_4VO_3 contain infinite chains of corner-linked VO_4 tetrahedra, while hydrated metavanadates, such as $KVO_3.H_2O$, contain infinite chains of approximately trigonal bipyramidal VO_5 units, not unlike those in V_2O_5. From the bright orange, acidic solutions, orange, crystalline decavanadates such as $Na_6V_{10}O_{28}.18H_2O$ are obtained: the anion $[V_{10}O_{28}]^{6-}$ is made up of 10 VO_6 octahedra, two representations of which are shown in Fig. 22.3. ^{51}V and ^{17}O nmr evidence shows that this is present in solution, and it can be isolated with a variety of counter cations — indeed it occurs naturally in at least three minerals. Other compounds such as $(PyH)_4[V_{10}O_{28}H_2]$

can also be crystallized[9] in which outer oxygen atoms of the polyanion are protonated[†], while refluxing the tetra-*n*-butyl ammonium salt of the decavanadate in acetonitrile has been shown[10] to yield the dark-red inclusion compound $[(n\text{-}C_4H_9N)]_4[MeCN \subset (V_{12}O_{32})^{4-}]$ in which the MeCN molecule sits inside the now basket-shaped polyanion.

Because of potential applications in catalysis and in providing convenient models for biological systems (for example, the chemical similarities of VO^{n+} and Fe^{n+} may be harnessed to study iron storage and transport proteins), a more diverse chemistry has so far been developed for reduced polyvanadates exhibiting a whole range of V^V to V^{IV} ratios. At the reduced extreme of this range, prolonged heating (4 days at 200°C) of NH_4VO_3 and $EtC(CH_2OH)_3$ produces black crystals of the V^{IV} compound[11] $(NH_4)_4[V_{10}O_{16}\{EtC(CH_2O)_3\}_4].4H_2O$, in the anion of which, twelve of the oxygen atoms in the $V_{10}O_{28}$ cluster are provided by bridging alkoxy groups. The same research workers have also used this hydrothermal technique to prepare another decavanadate(IV) material which contains chiral, interpenetrating double helices of vanadium phosphate units.[12] Still higher nuclearity is found in the dark brown $M_{12}^I[V_{18}O_{42}].nH_2O$ crystallized from alkaline solutions of VO_2. The anion consists this time of VO_5 square pyramids, the bases of which by corner- and edge-sharing form an almost spherical cavity of diameter ~450 pm (Fig. 22.3f). It has the extraordinary ability to encapsulate *negatively* charged ions, as in

[†] Although protonation usually occurs on outer oxygen atoms (Fig. 22.3e), an exception is provided by $[NH_3(C_6H_{13})][V_{10}O_{28}H_2]$ in which the protons have been located on triply linked, inner oxygen atoms. See P. ROMAN, A. ARANZABE, A. LUQUE, J. M. G.-ZORILLA and M. M.-RIPOLL, *J. Chem. Soc., Dalton Trans.*, 2225–31 (1995).

[9] J. M. ARRIETA, *Polyhedron* **11**, 3045–68 (1992).

[10] V. W. DAY, W. G. KLEMPERER and O. M. YAGHI, *J. Am. Chem. Soc.* **111**, 5959–61 (1989).

[11] M. I. KHAN, Q. CHEN and J. ZUBIETA, *J. Chem. Soc., Chem. Commun.*, 305–6 (1992).

[12] V. SOGHOMONIAN, Q. CHEN, R. C. HAUSHALTER, J. ZUBIETA and C. J. CONNOR, *Science* **259**, 1596–9 (1993).

(a) Anhydrous metavanadates, (e.g. NH_4VO_3) consisting of infinte chains of corner-shared VO_4 tetrahedra.

(b) Hydrated metavanadates, (e.g. $KVO_3 \cdot H_2O$) consisting of infinite chains of edge-shared VO_5 trigonal bipyramids.

(c) The $[M_6O_{19}]^{8-}$ (M = Nb, Ta) ions made up of 6 MO_6 octahedra (one is obscured).

(d) The decavanadate, $[V_{10}O_{28}]^{6-}$, ion made up of 10 VO_6 octahedra (2 are obscured).

(e) An alternative representation of $[V_{10}O_{28}]^{6-}$ emphasizing the V–O bonds.

(f) Polyhedral cavity of $[V_{18}O_{42}]^{12-}$. Each square represents the base of a VO_5 unit whose apex points outwards; and the triangles are "gaps" between pyramids.
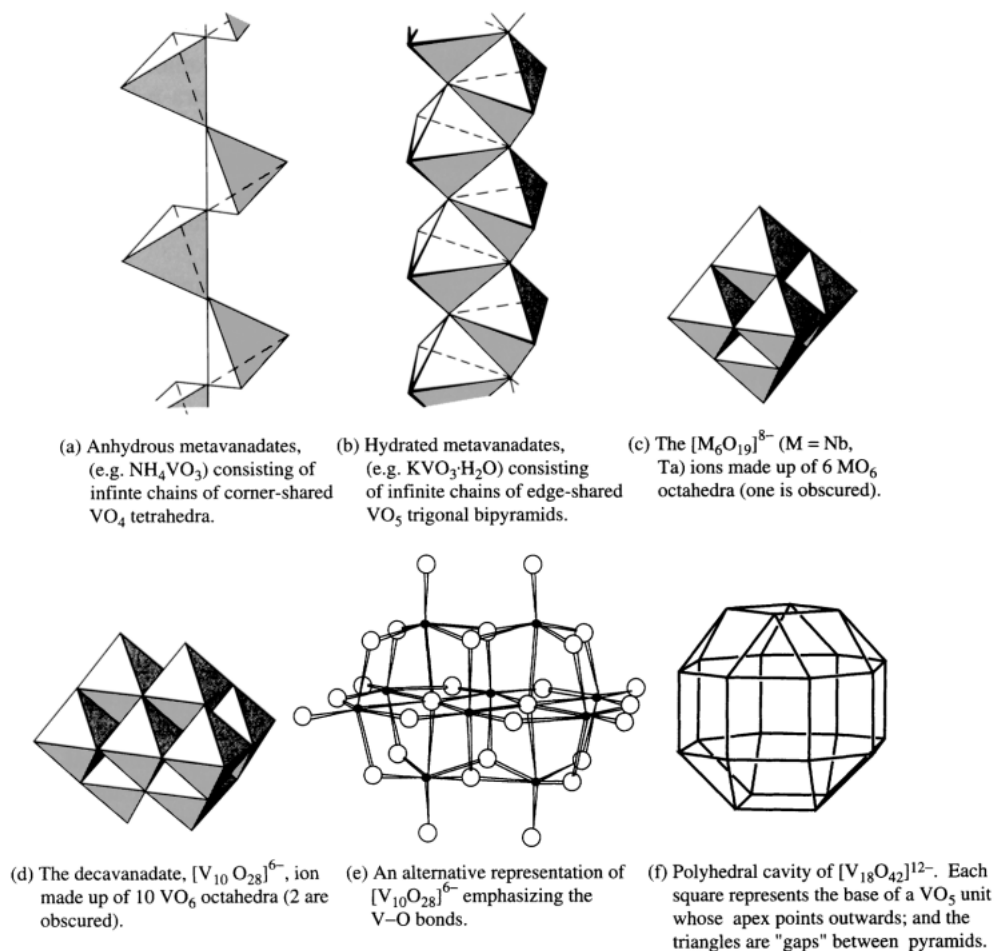
Figure 22.3 The structures of some isopoly-anions in the solid state using, where relevant, the conventional representation in which each polyhedron contains a metal atom and each vertex of a polyhedron represents an oxygen atom.

the compounds,[13] $M_9[H_4V_{18}O_{42}X] \cdot nH_2O$ (M = Cs, $n = 12$, X = Br, I; M = K, $n = 16$, X = Cl). Amongst the mixed, V^V, V^{IV} polyvanadates nuclearities up to 34 have been attained,[14] as in $K_{10}[V_{34}O_{82}] \cdot 20H_2O$. In these materials the coordination of the metal can be octahedral (V^V, V^{IV}), square pyramidal (V^V, V^{IV}), trigonal bipyramidal (V^V) and tetrahedral (V^V), and the

magnetic moment per V^{IV} atom decreases as the proportion of V^{IV} atoms increases (indicating increasing M–M interaction). To rationalize this rich variety of structures it has been suggested[15] that they may be conceptually derived from that of V_2O_5.

Heteropolyanions, in which an atom of a different element is incorporated, usually at the centre of a cage-like structure, are most abundant in Group 6 (p. 1013) but increasing numbers are to

[13] A. MÜLLER, M. PENK, R. ROHLFING, E. KRICKEMEYER and J. DÖRING, *Angew. Chem. Int. Edn. Engl.* **29**, 926–7 (1990).
[14] A. MÜLLER, R. ROHLFING, J. DÖRING and M. PENK, *Angew. Chem. Int. Edn. Engl.* **30**, 588–60 (1991).

[15] W. KLEMPERER, T. A. MARQUART and O. M. YAGHI, *Angew. Chem. Int. Edn. Engl.* **31**, 49–51 (1992).

be found in this group also. For vanadium(V) the $[XV_{14}O_{42}]^{9-}$ ions (X = P, As) are composed of an X atom tetrahedrally coordinated to four oxygen atoms at the centre of a "Keggin" anion (p. 1014) which is capped by two VO groups.[16] Reduced species, because of their lower overall anionic charge, allow the formation of clusters of higher nuclearity and several of these have been reported.[8]

Fusion of Nb_2O_5 and Ta_2O_5 with an excess of alkali hydroxides or carbonates, followed by dissolution in water, produces solutions of isopolyanions but not in the variety produced with vanadium. It appears that, down to pH 11, $[M_6O_{19}]^{8-}$ ions are present; in the case of niobium protonation occurs at lower pH to give $[HNb_6O_{19}]^{7-}$. The presence of discrete MO_4^{3-} ions in strongly alkaline solutions is uncertain. Below pH ~ 7 for Nb and pH ~ 10 for Ta, precipitation of the hydrous oxides occurs. Salts such as $K_8M_6O_{19}.16H_2O$ can be crystallized from the alkaline solutions and contain $[M_6O_{19}]^{8-}$ ions which are made up of octahedral groupings of 6 MO_6 octahedra (Fig. 22.3). A decaniobate, exactly analogous to the decavanadate, has also been isolated and it is possible that such species exist also in solution at low pH.

Most niobates and tantalates, however, are insoluble and may be regarded as mixed oxides in which the Nb or Ta is octahedrally coordinated and with no discrete anion present. Thus KMO_3, known inaccurately (since they have no discrete MO_3^- anions) as metaniobates and metatantalates, have the perovskite (p. 963) structure. Several of these perovskites have been characterized and some have ferroelectric and piezoelectric properties (p. 57). Because of these properties, $LiNbO_3$ and $LiTaO_3$ have been found to be attractive alternatives to quartz as "frequency filters" in communications devices.

A number of nonstoichiometric "bronzes" are also known[17] which, like the titanium bronzes

already mentioned (p. 964) and the better known tungsten bronzes (p. 1016), are characterized by very high electrical conductivities and characteristic colours. For instance, Sr_xNbO_3 ($x = 0.7-0.95$) varies in colour from deep blue to red as the Sr content increases. Fusion of mixtures of appropriate oxides of niobium and alkali metals produces black powders (shiny, golden *single crystals*) of $NaNb_{10}O_{18}$ (metallic conductance)[18] and KNb_8O_{14} (semiconductor),[19] both of which are made up of Nb^VO_6 octahedra and Nb_6O_{12} clusters analogous to the M_6X_{12} halide cluster (p. 992). Li_xNbO_2 ($x \sim 0.5$) has been shown[20] to be a superconductor below 5 K, and is notable as the first superconductor involving an early transition metal oxide which has a layered rather than a 3D structure. It is, indeed, the search for better superconductors and battery electrode materials which is responsible for the upsurge in interest in early transition metal oxides, and further expansion of this area of chemistry is to be expected.

22.3.3　Sulfides, selenides and tellurides

All three metals form a wide variety of binary chalcogenides which frequently differ both in stoichiometry and in structure from the oxides. Many have complex structures which are not easily described, and detailed discussion is therefore inappropriate. The various sulfide phases are listed in Table 22.4: phases approximating to the stoichiometry MS have the NiAs-type structure (p. 556) whereas MS_2 have layer lattices related to MoS_2 (p. 1018), CdI_2, or $CdCl_2$ (p. 1212). Sometimes complex layer-sequences occur in which the 6-coordinate metal atom is alternatively octahedral and trigonal prismatic. Most of the phases exhibit

[16] G.-Q. Huang, S.-W. Zhang, Y.-G. Wei and M.-C. Shao, *Polyhedron* **12**, 1483–5 (1993).

[17] P. Hagenmuller, Chap. 50 in *Comprehensive Inorganic Chemistry*, Vol. 4, pp. 541–605, Pergamon Press, Oxford, 1973.

[18] J. Köhler and A. Simon, *Z. anorg. allg. Chem.* **572**, 7–17 (1989).

[19] J. Köhler, R. Tischtan and A. Simon, *J. Chem. Soc., Dalton Trans.*, 829–32 (1991).

[20] M. Geselbracht, T. J. Richardson and A. M. Stacy, *Nature* **345**, 324–6 (1990).

Table 22.4   Sulfides of vanadium, niobium and tantalum

V_3S	$Nb_{21}S_8$	Ta_6S	V_2S_3	—	—
—	—	Ta_2S	V_5S_8	$Nb_{1+x}S_2$	$Ta_{1+x}S_2$
V_5S_4	—	—	—	NbS_2	TaS_2
VS	NbS_{1-x}	TaS	—	NbS_3	TaS_3
V_7S_8	—	—	VS_4	—	—
V_3S_4	Nb_3S_4	—			

Table 22.5   Selenides and tellurides of vanadium, niobium and tantalum

V_2Se	—	—	—	—	—
V_5Se_4	Nb_5Se_4	—	V_5Te_4	Nb_5Te_4	—
VSe	$NbSe$	—	VTe_{1+x}	—	$TaTe$
V_7Se_8	—	—	—	—	—
V_3Se_4	Nb_3Se_4	—	V_3Te_4	Nb_3Te_4	—
(V_2Se_3)	Nb_2Se_3	Ta_2Se_3	V_2Te_3	—	—
V_5Se_8	—	—	V_5Te_8	—	—
—	$Nb_{1+x}Se_2$	$Ta_{1+x}Se_2$	$V_{1+x}Te_2$	$Nb_{1+x}Te_2$	$Ta_{1-x}Te_2$
VSe_2	$NbSe_2$	$TaSe_2$	VTe_2	$NbTe_2$	$TaTe_2$
—	—	$TaSe_3$	—	—	—
—	$NbSe_4$	—	—	$NbTe_4$	$TaTe_4$

metallic conductivity and magnetic properties range from diamagnetic (e.g. VS_4), through paramagnetic (VS, V_2S_3), to antiferromagnetic (V_7S_8). Selenides and tellurides show a similar profusion of stoichiometries and structural types (Table 22.5).

In addition to these binary chalcogenides, many of which exist over wide ranges of composition because of the structural relation between the NiAs and CdI_2 structure types (p. 556), several ternary phases have been studied. Some, like $BaVS_3$ and $BaTaS_3$ have three-dimensional structures in which the Ba and V(Ta) are coordinated by 12 and 6 S atoms respectively. Other compounds such as the easily hydrolysed $(NH_4)_3VS_4$, which has been known for over a century, and $M_3^IVS_4$ (M = Na, K, Tl) prepared by heating stoichiometric amounts of the elements under vacuum[21] contain the discrete, tetrahedral $[VS_4]^{3-}$ anion. The cluster chemistry of the thiometallates of this group, however, is not comparable to that of the oxometallates. It is very limited and whereas, for instance, $(Et_4N)_4[M_6S_{17}].3CH_3CN$ (M = Nb,

Ta) contains a discrete $[M_6S_{17}]^{4-}$ anion,[22] the stoichiometrically analogous $M_4^INb_6O_{17}0.3H_2O$ has an extended structure.

22.3.4 Halides and oxohalides

The known halides of vanadium, niobium and tantalum, are listed in Table 22.6. These are illustrative of the trends within this group which have already been alluded to. Vanadium(V) is only represented at present by the fluoride, and even vanadium(IV) does not form the iodide, though all the halides of vanadium(III) and vanadium(II) are known. Niobium and tantalum, on the other hand, form all the halides in the high oxidation state, and are in fact unique (apart only from protactinium) in forming pentaiodides. However in the +4 state, tantalum fails to form a fluoride and neither metal produces a trifluoride. In still lower oxidation states, niobium and tantalum give a number of (frequently nonstoichiometric) cluster compounds which can be considered to involve fragments of the metal lattice.

[21] A. T. HARRISON and O. W. HAWORTH, *J. Chem. Soc., Dalton Trans.*, 1405–9 (1986).

[22] J. SOLA, Y. DO, J. M. BERG and R. H. HOLM, *Inorg. Chem.* **24**, 1706–13 (1985).