Figure 24.1   Plot of volt-equivalent versus oxidation state for Mn, Tc and Re.

only are high oxidation states possible, but back donation of electrons from metal to ligand is also facilitated with resulting stabilization of low oxidation states.

A further point of interest is the noticeably greater tendency of rhenium, as compared to either manganese or technetium, to form compounds with high coordination numbers.

24.3 Compounds of Manganese, Technetium and Rhenium[3]

Binary borides (p. 145), carbides (p. 297), and nitrides (p. 417) have already been mentioned.

Manganese, like chromium (and also the succeeding elements in the first transition series), is too small to accommodate interstitial carbon without significant distortion of the metal lattice. As a consequence it forms a number of often readily hydrolysed carbides with rather complicated structures.

Hydrido complexes are well-known but simple binary hydrides are not, which is in keeping with the position of these metals in the "hydrogen gap" portion of the periodic table (p. 67).

24.3.1 Oxides and chalcogenides

All three metals form heptoxides (Table 24.4) but, whereas Tc_2O_7 and Re_2O_7 are the final products formed when the metals are burned in an excess of oxygen, Mn_2O_7 requires prior oxidation of the manganese to the $+7$ state. It separates as a reddish-brown explosive oil from the green

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[3] R. D. W. KEMMITT, Chap. 37, pp. 771–876; R. D. PEACOCK Chap. 38, pp. 877–903 and Chap. 39, pp. 905–78, in *Comprehensive Inorganic Chemistry*, Vol. 3, Pergamon Press, Oxford, 1973. (See also nine reviews devoted to the chemistry of Tc and Re in *Topics in Current Chemistry* **176**, 1996, 291 pp.)

Table 24.3 Oxidation states and stereochemistries of manganese, technetium and rhenium

| Oxidation state	Coordination number	Stereochemistry	Mn	Tc/Re
-3 (d^{10})	4	Tetrahedral	$[Mn(NO)_3(CO)]$	$[M(CO)_4]^{3-}$
-2 (d^9)	4	Square planar	$[Mn(phthalocyanine)]^{2-}$	—
-1 (d^8)	5	Trigonal bipyramidal	$[Mn(CO)_5]^-$	$[M(CO)_5]^-$
	4	Square planar	$[Mn(phthalocyanine)]^-$	—
0 (d^7)	6	Octahedral	$[Mn_2(CO)_{10}]$	$[M_2(CO)_{10}]$
1 (d^6)	6	Octahedral	$[Mn(CN)_6]^{5-}$	$[M(CN)_6]^{5-}$
2 (d^5)	2	Linear	$[Mn\{C(SiMe_3)_3\}_2]^{(a)}$	
	4	Tetrahedral	$[MnBr_4]^{2-}$	
		Square planar	$[Mn(phthalocyanine)]$	
	5	Trigonal bipyramidal	$[MnBr\{N(C_2H_4NMe_2)_3\}]^+$	$[ReCl(dppe)_2]^+$
		Square pyramidal	$[Mn(CS_4)_2Cl]^{3-(b)}$	
	6	Octahedral	$[Mn(H_2O)_6]^{2+}$	$[M(diars)_2Cl_2]$
	7	Capped trigonal prismatic	$[Mn(edta)(H_2O)]^{2-}$	
	8	Dodecahedral	$[Mn(NO_3)_4]^{2-}$	
		Distorted square prismatic	$[MnL]^{2+(c)}$	
3 (d^4)	5	Trigonal bipyramidal	$[Mn(PMe_3)_2I_3]$	
		Square pyramidal	$[MnCl_5]^{2-}$	$[Re_2Cl_8]^{2-}$
	6	Octahedral	$K_3[Mn(CN)_6]$	$[M(diars)_2Cl_2]^+$
	7	Pentagonal bipyramidal	$[Mn(NO_3)_3(bipy)]$	$[M(CN)_7]^{4-}$
	11	See Fig. 24.11a	—	$[Re(\eta^5\text{-}C_5H_5)_2H]$
4 (d^3)	5	—	—	$[(Me_3SiCH_2)_4Re(N_2)\text{-}Re(CH_2SiMe_3)_4]$
	6	Octahedral	$[MnF_6]^{2-}$	$[MI_6]^{2-}$
5 (d^2)	4	Tetrahedral	$[MnO_4]^{3-}$	—
	5	Trigonal bipyramidal (?)	—	ReF_5
		Square pyramidal	—	$[MOCl_4]^-$
	6	Octahedral	—	$[Tc(NCS)_6]^-$, $[ReNCl_2(PEt_2Ph)_3]$
	8	Dodecahedral	—	$[M(diars)_2Cl_4]^+$
6 (d^1)	4	Tetrahedral	$[MnO_4]^{2-}$	$[ReO_4]^{2-}$
	5	Square pyramidal		$ReOCl_4$
	6	Trigonal prismatic		$[Re(S_2C_2Ph_2)_3]$ (see p. 1055)
		Octahedral		ReF_6
	8	Dodecahedral		$[ReMe_8]^{2-}$
		Square antiprismatic		$[ReF_8]^{2-}$
7 (d^0)	4	Tetrahedral	$[MnO_4]^-$	$[MO_4]^-$
	5	Trigonal bipyramidal		$[ReO_2Me_3]$
	6	Octahedral		$[ReO_3Cl_3]^{2-}$
	7	Pentagonal bipyramidal		ReF_7
	9	Tricapped trigonal prismatic		$[ReH_9]^{2-}$

[a] N. H. BUTTRUS, C. EABORN, P. B. HITCHCOCK, J. D. SMITH and A. C. SULLIVAN *J. Chem. Soc., Chem. Commun.* 1380–1 (1985).
[b] S.-B. YU and R. H. HOLM, *Polyhedron* **12**, 263–6 (1993).
[c] L = 1,4,7,10-tetrakis(pyrazol-1-ylmethyl)-1,4,7,10-tetraazacyclododecane. See M. DI VAIRA, F. MANI and P. STOPPIONI, *J. Chem. Soc., Dalton Trans.*, 1127–30 (1992).

Table 24.4   Oxides of Group 7

Ox. state	+7	+6	+5	+4	+3	+2
Mn	Mn_2O_7			MnO_2	Mn_2O_3 Mn_3O_4	MnO
Tc	Tc_2O_7	$TcO_3(?)$		TcO_2		
Re	Re_2O_7	ReO_3	Re_2O_5	ReO_2		

solutions produced by the action of conc H_2SO_4 on a manganate(VII) salt. On standing, it slowly loses oxygen to form MnO_2 but detonates around 95°C and will explosively oxidize most organic materials. The molecule is composed of 2 corner-sharing MnO_4 tetrahedra with a bent Mn–O–Mn bridge. The liquid solidifies at 5.9°C to give red crystals in which the dimeric units persist with an Mn–O–Mn angle[4] of 120.7°. The other 2 heptoxides are yellow solids whose volatility provides a useful means of purifying the elements and, as has been pointed out, is a crucial factor in the commercial production of rhenium (Tc_2O_7: mp 119.5°, bp 310.6°; Re_2O_7: mp 300.3°, bp 360.3°). In the vapour phase both consist of corner-sharing MO_4 tetrahedra but, whereas this structure is retained in the solid phase by Tc_2O_7 (linear Tc–O–Tc), solid Re_2O_7 has an unusual structure consisting of polymeric double layers of corner-sharing ReO_4 tetrahedra alternating with ReO_6 octahedra. The same basic unit, though this time discrete, is found in the dihydrate which is therefore best formulated as $[O_3Re-O-ReO_3(H_2O)_2]$ and is obtained by careful evaporation of an aqueous solution of the heptoxide. The structure breaks down, however, if the solution is kept for a period of months. Crystals of perrhenic acid monohydrate, $HReO_4.H_2O$, are deposited and consist of fairly regular ReO_4^- tetrahedra and H_3O^+ ions linked by hydrogen bridges.[5]

Only rhenium forms a stable trioxide. It is a red solid with a metallic lustre and is obtained by the reduction of Re_2O_7 with CO. ReO_3 has a structure in which each Re is

Oxygen

Rhenium
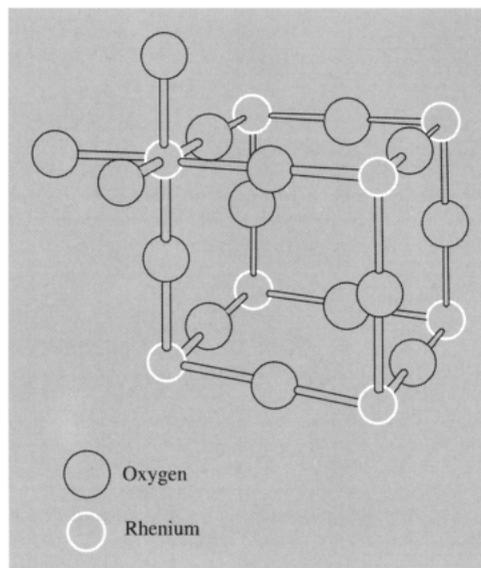
Figure 24.2   The structure of ReO_3. Note the similarity to perovskite (p. 963) which can be understood as follows: if the Re atom, which is shown here with its full complement of 6 surrounding O atoms, is imagined to be the small cation at the centre of Fig. 21.3(a), then the perovskite structure is obtained by placing the large cations (Ca^{II}) into the centre of the cube drawn above and in the 7 other equivalent positions around the Re.

octahedrally surrounded by oxygens (Fig. 24.2). It has an extremely low electrical resistivity which decreases with decrease in temperature like a true metal: ρ_{300K} 10 μohm cm, ρ_{100K} 0.6 μohm cm. It is clear that the single valency electron on each Re atom is delocalized in a conduction band of the crystal. ReO_3 is unreactive towards water and aqueous acids and alkalis, but when boiled with conc alkali it disproportionates into ReO_4^- and ReO_2. A blue pentoxide Re_2O_5 has been reported but is also prone to disproportionation into +7 and +4 species.

The +4 oxidation state is the only one in which all three elements form stable oxides, but only in the case of technetium is this the most stable oxide. TcO_2 is the final product when any Tc/O

[4] R. DRONSKOWSKI, B. KREBS, A. SIMON, G. MILLER and B. HETTICH, *Z. anorg. allg. Chem.* **558**, 7–20 (1988).

[5] G. WLTSCHEK, I. SVOBODA and H. FUESS, *Z. anorg. allg. Chem.* **619**, 1679–81 (1993).

Applications of Manganese Dioxide[6]

Although the primary use of manganese is in the production of steel it also finds widespread and important uses in non-metallurgical industries. These frequently use the manganese as MnO_2 but even where this is not the case the dioxide is invariably the starting material.

The largest non-metallurgical use of MnO_2 is in the manufacture of dry-cell batteries (p. 1204) which accounts for about half a million tonnes of ore annually. The most common dry batteries are of the carbon-zinc Leclanché type in which carbon is the positive pole. MnO_2 is incorporated as a depolarizer to prevent the undesirable liberation of hydrogen gas on to the carbon, probably by the reaction

$$MnO_2 + H^+ + e^- \longrightarrow MnO(OH)$$

Only the highest quality MnO_2 ore can be used directly for this purpose, and "synthetic dioxide", usually produced electrolytically by anodic oxidation of manganese(II) sulfate, is increasingly employed.

The brick industry is another major user of MnO_2 since it can provide a range of red to brown or grey tints. In the manufacture of glass its use as a decolourizer (hence "glassmaker's soap") is its most ancient application. Glass always contains iron at least in trace amounts, and this imparts a greenish colour; the addition of MnO_2 to the molten glass produces red-brown Mn^{III} which equalizes the absorption across the visible spectrum so giving a "colourless", i.e. grey glass. In recent times selenium compounds have replaced MnO_2 for this application, but in larger proportions the latter is still used to make pink to purple glass.

The oxidizing properties of MnO_2 are utilized in the oxidation of aniline for the preparation of hydroquinone which is important as a photographic developer and also in the production of dyes and paints.

In the electronics industry the advantages of higher electrical resistivity and lower cost of ceramic ferrites ($M^{II}Fe_2O_4$) (p. 1081) over metallic magnets have been recognized since the 1950s and the "soft" ferrites (M^{II} = Mn, Zn) are the most common of these. They are used on the sweep transformer and deflection yoke of a television set and, of course, MnO_2, either natural or synthetic, is required in their production.

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system is heated to high temperatures, but ReO_2 disproportionates at 900°C into Re_2O_7 and the metal. Hydrated TcO_2 and ReO_2 may be conveniently prepared by reduction of aqueous solutions of MO_4^- with zinc and hydrochloric acid and are easily dehydrated. TcO_2 is dark brown and ReO_2 is blue-black: both solids have distorted rutile structures like MoO_2 (p. 1008).

It is MnO_2, however, which is by far the most important oxide in this group, though it is not the most stable oxide of manganese, decomposing to Mn_2O_3 above about 530°C and being a useful oxidizing agent. Hot concentrated sulfuric and hydrochloric acids reduce it to manganese(II):

$$2MnO_2 + 2H_2SO_4 \longrightarrow 2MnSO_4 + O_2 + 2H_2O$$

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$
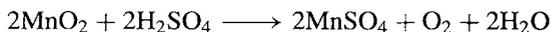
the latter reaction being formerly the basis of the manufacture of chlorine. It is, however, extremely insoluble and, as a consequence, often unreactive. As pyrolusite it is the most plentiful ore of

manganese and it finds many industrial uses (see Panel).

The structural history of MnO_2 is complex and confused due largely to the prevalence of nonstoichiometry and the fact that in its hydrated forms it behaves as a cation-exchanger. Many of the various polymorphs which have been reported are probably therefore simply impure forms. The only stoichiometric form is the so-called β-MnO_2, which is that of pyrolusite and possesses the rutile structure (p. 961), but even here a range of composition from $MnO_{1.93}$ to $MnO_{2.0}$ is possible. β-MnO_2 can be prepared by careful decomposition of manganese(II) nitrate but, when precipitated from aqueous solutions, for instance by reduction of alkaline MnO_4^-, the hydrated MnO_2 has a more open structure which exhibits cation-exchange properties and cannot be fully dehydrated without some loss of oxygen.

Apart from the black $Re_2O_3.2H_2O$ (which is readily oxidized to the dioxide and is prepared by boiling $ReCl_3$ in air-free water) oxides of oxidation states below +4 are known only for manganese. Mn_3O_4 is formed when any

6 *Ulmann's Encyclopedia of Industrial Chemistry*, Vol. A16, pp. 123–43, VCH, Weinheim, 1990.

oxide of manganese is heated to about 1000°C in air and is the black mineral, hausmannite. It has the spinel structure (p. 247) and as such is appropriately formulated as $Mn^{II}Mn_2^{III}O_4$, with Mn^{II} and Mn^{III} occupying tetrahedral and octahedral sites respectively within a ccp lattice of oxide ions; there is, however, a tetragonal distortion due to a Jahn–Teller effect (p. 1021) on Mn^{III}. A related structure, but with fewer cation sites occupied, is found in the black γ-Mn_2O_3 which can be prepared by aerial oxidation and subsequent dehydration of the hydroxide precipitated from aqueous Mn^{II} solutions. If MnO_2 is heated less strongly (say <800°C) than is required to produce Mn_3O_4, then the more stable α-form of Mn_2O_3 results which has a structure involving 6-coordinate Mn but with 2 Mn–O bonds longer than the other 4. This is no doubt a further manifestation of the Jahn–Teller effect expected for the high-spin d^4 Mn^{III} ion and is presumably the reason why Mn_2O_3, alone among the oxides of transition metal M^{III} ions, does not have the corundum (p. 242) structure.

Reduction with hydrogen of any oxide of manganese produces the lowest oxide, the grey to green MnO. This is an entirely basic oxide, dissolving in acids and giving rise to the aqueous Mn^{II} cationic chemistry. It has a rock-salt structure and is subject to nonstoichiometric variation ($MnO_{1.00}$ to $MnO_{1.045}$), but its main interest is that it is a classic example of an antiferromagnetic compound. If the temperature is reduced below about 118 K (its Néel point), a rapid fall in magnetic moment takes place as the electron spins on adjacent Mn atoms pair-up. This is believed to take place by the process of "superexchange" by which the interaction is transferred through intervening, non-magnetic, oxide ions. (MnO_2 is also antiferromagnetic below 92 K whereas the alignment in Mn_3O_4 results in ferrimagnetism below 43 K.)

The sulfides are fewer and less familiar than the oxides but, as is to be expected, favour lower oxidation states of the metals. Thus manganese forms MnS_2 which has the pyrite structure (p. 680) with discrete Mn^{II} and S_2^{-II} ions and is converted on heating to MnS and sulfur. This green MnS is the most stable manganese sulfide and, like MnO, has a rock-salt structure and is strongly antiferromagnetic ($T_N - 121°C$). Less-stable red forms are also known and the pale-pink precipitate produced when H_2S is bubbled through aqueous Mn^{II} solutions is a hydrated form which passes very slowly into the green variety. The corresponding selenides are very similar: $Mn^{II}Se_2$ (pyrite-type), and MnSe (NaCl-type), antiferromagnetic with $T_N - 100°C$.

Technetium and rhenium favour higher oxidation states in their binary chalcogenides. Both form black diamagnetic heptasulfides, M_2S_7, which are isomorphous and which decompose to $M^{IV}S_2$ and sulfur on being heated. These disulfides, unlike the pyrite-type $Mn^{II}S_2$, contain monatomic S^{-II} units. The diselenides are similar. TcS_2, $TcSe_2$ and ReS_2 feature trigonal prismatic coordination of M^{IV} by S (or Se) in a layer-lattice structure which is isomorphous with a rhombohedral polymorph of MoS_2. $ReSe_2$ also has a layer structure but the Re^{IV} atoms are octahedrally coordinated.

Lower formal oxidation states are stabilized, however, by M–M bonding in ternary chalcogenides such as $M_4^I M_6 Q_{12}$, $M_4^I M_6 Q_{13}$ (M^I = alkali metal; M = Re, Tc; Q = S, Se) and the recently reported[7] $M_{10}^I M_6 S_{14}$. Their structures are all based on the face-capped, octahedral $M_6 X_8$ cluster unit found in Chevrel phases (p. 1018) and in the dihalides of Mo and W (p. 1022).

24.3.2 Oxoanions

The lower oxides of manganese are basic and react with aqueous acids to give salts of Mn^{II} and Mn^{III} cations. The higher oxides, on the other hand, are acidic and react with alkalis to yield oxoanion salts, but the polymerization which was such a feature of the chemistry of the preceding group is absent here.

[7] W. Bronger, M. Kanert, M. Lovenich and D. Schmitz, *Z. anorg. allg. Chem.* **619**, 2015–20 (1993).

Fusion of MnO_2 with an alkali metal hydroxide and an oxidizing agent such as KNO_3 produces very dark-green manganate(VI) salts (manganates) which are stable in strongly alkaline solution but which disproportionate readily in neutral or acid solution (see Fig. 24.1):

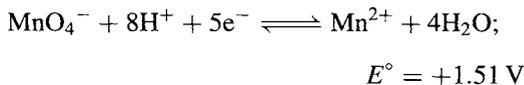$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$$
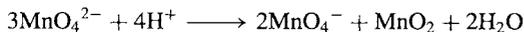
The deep-purple manganate(VII) salts (permanganates) may be prepared in aqueous solution by oxidation of manganese(II) salts with very strong oxidizing agents such as PbO_2 or $NaBiO_3$. They are manufactured commercially by alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate(VI):

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$
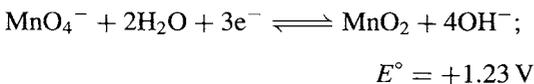
$$2K_2MnO_4 + 2H_2O \longrightarrow 2KMnO_4 + 2KOH + H_2$$
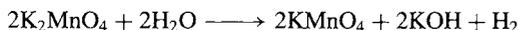
The most important manganate(VII) is $KMnO_4$ of which several tens of thousands of tonnes are produced annually. It is a well-known oxidizing agent, used analytically:

in acid solution:

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O;$$

$$E^\circ = +1.51\,V$$

in alkaline solution:

$$MnO_4^- + 2H_2O + 3e^- \rightleftharpoons MnO_2 + 4OH^-;$$

$$E^\circ = +1.23\,V$$

It is also important as an oxidizing agent in the industrial production of saccharin and benzoic acid, and medically as a disinfectant. It is increasingly being used also for purifying water, since it has the dual advantage over chlorine that it does not affect the taste, and the MnO_2 produced acts as a coagulant for colloidal impurities.

Reduction of $KMnO_4$ with aqueous Na_2SO_3 produces the bright-blue tetraoxomanganate(V) (hypomanganate), MnO_4^{3-}, which has also been postulated as a reaction intermediate in some organic oxidations; it is not stable, being prone to disproportionation.

All $[MnO_4]^{n-}$ ions are tetrahedral with Mn–O 162.9 pm in MnO_4^- and 165.9 pm in MnO_4^{2-}. K_2MnO_4 is isomorphous with K_2SO_4 and K_2CrO_4. By contrast, the only tetrahedral oxoanions of Tc and Re are the tetraoxotechnetate(VII) (pertechnetate) and tetraoxorhenate(VII) (perrhenate) ions. $HTcO_4$ and $HReO_4$ are strong acids like $HMnO_4$ and are formed when the heptoxides are dissolved in water. From such solutions dark-red crystals with the composition $HTcO_4$ in the case of technetium and, in the case of rhenium, yellowish crystals of $Re_2O_7.2H_2O$ or $HReO_4.H_2O$ (p. 1047) can be obtained.

$[TcO_4]^-$ and $[ReO_4]^-$ provide the starting point for virtually all the Tc and Re chemistry. They are produced whenever compounds of Tc and Re are treated with oxidizing agents such as nitric acid or hydrogen peroxide and, although reduced in aqueous solution by, for instance, Sn^{II}, Fe^{II}, Ti^{III} and I^-, they are much weaker oxidizing agents than $[MnO_4]^-$. In further contrast to $[MnO_4]^-$ they are also stable in alkaline solution and are colourless whereas $[MnO_4]^-$ is an intense purple. In fact, the absorption spectra of the 3 $[MO_4]^{-1}$ ions are very similar, arising in each case from charge transfer transitions between O^{2-} and M^{VII}, but the energies of these transitions reflect the relative oxidizing properties of M^{VII}. Thus the intense colour of $[MnO_4]^-$ arises because the absorption occurs in the visible region, whereas for $[ReO_4]^-$ it has shifted to the more energetic ultraviolet, and the ion is therefore colourless. $[TcO_4]^-$ is also normally colourless but the absorption starts on the very edge of the visible region and it may be that the red colour of crystalline $HTcO_4$, and other transient red colours which have been reported in some of its reactions, are due to slight distortions of the ion from tetrahedral symmetry causing the absorption to move sufficiently for it to "tail" into the blue end of the visible, thereby imparting a red coloration. $[MO_4]^-$ ions might be expected to act as Lewis bases (cf ClO_4^- p. 868) and, indeed, several mono- and bis- $[ReO_4]^-$ complexes with Co^{II}, Ni^{II} and Cu^{II} have been

Table 24.5 Halides of Group 7

Oxidation state	Fluorides	Chlorides	Bromides	Iodides
+7	ReF_7 yellow mp 48.3°, bp 73.7°			
+6	TcF_6 yellow mp 37.4°, bp 55.3° ReF_6 yellow mp 18.5°, bp 33.7°	$TcCl_6$ green mp 25° $ReCl_6$ red-green mp 29° (dichroic)		
+5	TcF_5 yellow mp 50°, bp (d) ReF_5 yellow-green mp 48°, bp(extrap) 221°	— $ReCl_5$ brown-black mp 220°	$ReBr_5$ dark brown (d 110°)	
+4	MnF_4 blue (d above rt) — ReF_4 blue (subl >300°)	$TcCl_4$ red (subl >300°) $ReCl_4$ purple-black (d 300°)	— (?$TcBr_4$) (red-brown) $ReBr_4$ dark red	— ReI_4 black (d above rt)
+3	MnF_3 red-purple —	— $[ReCl_3]_3$ dark red (subl 500°) (d)	— $[ReBr_3]_3$ red-brown	— $[ReI_3]_3$ lustrous black (d on warming)
+2	MnF_2 pale pink mp 920°	$MnCl_2$ pink mp 652°, bp ~1200°	$MnBr_2$ rose mp 695°	MnI_2 pink mp 613°

characterized, and both unidentate and bridging modes identified.[8]

Fusion of rhenates(VII) with a basic oxide yields so-called ortho- and meso-perrhenates (M_5ReO_6 and M_3ReO_5, M = Na, $\frac{1}{2}$Ca, etc.) while addition of rhenium metal to the fusion (and exclusion of oxygen) produces rhenate(VI) (e.g. Ca_3ReO_6). There is evidence suggesting the existence of $[ReO_6]^{5-}$ and $[ReO_6]^{6-}$ but it may be better to regard all these compounds as mixed oxides. In any case, it is clear that the coordination sphere of the metal has expanded compared to that of the smaller Mn in the tetrahedral $[MnO_4]^{n-}$ ions. Comparable technetium compounds have also been prepared.

24.3.3 Halides and oxohalides

The known halides and oxohalides of this group are listed in Tables 24.5 and 24.6 respectively.

The highest halide of each metal is of course a fluoride: ReF_7 (the only thermally stable heptahalide of a transition metal), TcF_6, and MnF_4. This again indicates the diminished ability of manganese to attain high oxidation states when compared not only to Tc and Re but also to

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[8] M. C. Chakravorty, *Coord. Chem. Revs.* **106**, 205–25 (1990).

Table 24.6 Oxohalides of Group 7

Oxidation state	Fluorides			Chlorides	Bromides
+7	—	—	MnO$_3$F dark green mp −78°, bp(extrap) 60°	MnO$_3$Cl vol green liq	—
	—	—	TcO$_3$F yellow mp 18.3°, bp ~100°	TcO$_3$Cl colourless	—
	ReOF$_5$ cream mp 43.8°, bp 73.0°	ReO$_2$F$_2$ yellow mp 90°, bp 185°	ReO$_3$F yellow mp 147°, bp 164°	ReO$_3$Cl colourless mp 4.5°, bp 130°	ReO$_3$Br colourless mp 39.5°
+6	—			MnO$_2$Cl$_2$ vol brown liq	—
	TcOF$_4$ blue mp 134° bp(extrap) 165°			TcOCl$_4$ blue	—
	ReOF$_4$ blue mp 108°, bp 171°			ReOCl$_4$ brown mp 30°, bp(extrap) 228°	ReOBr$_4$ blue
+5	—			MnOCl$_3$ vol liq	—
	—			TcOCl$_3$	TcOBr$_3$ black
	ReOF$_3$ black			—	—

chromium, which forms CrF$_5$ and CrF$_6$. The most interesting of the lower halides are the rhenium trihalides which exist as trimeric clusters which persist throughout much of the chemistry of Re^{III}.

Apart from ReF$_5$, which is produced when ReF$_6$ is reduced by tungsten wire at 600°C, all the known penta-, hexa- and hepta- halides of Re and Tc can be prepared directly from the elements by suitably adjusting the temperature and pressure, although various specific methods have been suggested. They are volatile solids varying in colour from pale yellow (ReF$_7$) to dark brown (ReBr$_5$), and are readily hydrolysed by water with accompanying disproportionation into the comparatively more stable [MO$_4$]$^-$ and MO$_2$, e.g.:

$$3ReCl_5 + 8H_2O \longrightarrow HReO_4 + 2ReO_2 + 15HCl$$

Because of the tendency to produce mixtures of the halides, and the facile formation of oxohalides if air and moisture are not rigorously excluded (or even, in some cases, also by attacking glass), not all of these halides have been characterized as well as might be desired. There is spectroscopic evidence that ReF$_7$ has a pentagonal bipyramidal structure, and ReX$_6$ are probably octahedral. ReCl$_5$ is actually a dimer, Cl$_4$Re(μ-Cl)$_2$ReCl$_4$, in which the rhenium is octahedrally coordinated.

The tetrahalides are made by a variety of methods. MnF$_4$, being the highest halide formed by Mn, can be prepared directly from the elements, as can TcCl$_4$, which is the only thermally stable chloride of Tc. TcCl$_4$ is a red sublimable solid consisting of infinite chains of edge-sharing TcCl$_6$ octahedra. By contrast the

black $ReCl_4$, which is prepared by heating $ReCl_3$ and $ReCl_5$ in a sealed tube at 300°C, is made up of pairs of $ReCl_6$ octahedra which share faces (as in $[W_2Cl_9]^{3-}$, p. 1021), these dimeric units then being linked in chains by corner-sharing. The closeness of the Re atoms in each pair (273 pm) is indicative of a metal–metal bond though not so pronounced as the more extensive metal–metal bonding found in Re^{III} chemistry.

MnF_3 is a red-purple, reactive, but thermally stable solid; it is prepared by fluorinating any of the Mn^{II} halides and its crystal lattice consists of MnF_6 octahedra which are distorted, presumably because of the Jahn–Teller effect expected for d^4 ions. The Re^{III} halides are obtained by thermal decomposition of $ReCl_5$, $ReBr_5$ and ReI_4. The dark-red chloride is composed of triangular clusters of chloride-bridged Re atoms with 1 of the 2 out-of-plane Cl on each Re bridging to adjacent trimeric clusters (Fig. 24.3). After allowing for the Re–Cl bonds, each Re^{III} has a d^4 configuration and the observed diamagnetism can be accounted for by assuming that these four d electrons on each Re are used in forming
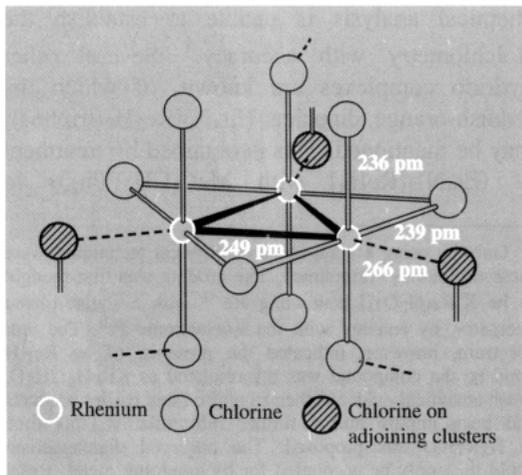

Figure 24.3   Idealized structure of Re_3Cl_9; in crystalline $ReCl_3$ the trimeric units are linked into planar hexagonal networks. The coordination sites occupied by Cl from adjoining clusters can readily be occupied by a variety of other ligands instead.

double bonds ($\sigma + \pi$) to its 2 Re neighbours. The Re–Re distance of 249 pm is consistent with this (cf. 275 pm in Re metal). Re_3Cl_9 can be sublimed under vacuum but the green colour of the vapour probably indicates breakdown of the cluster in the vapour phase. The compound dissolves in water to give a red solution which slowly hydrolyses to hydrated Re_2O_3, and in conc hydrochloric acid it gives a red solution which is stable to oxidation and from which can be precipitated hydrates of Re_3Cl_9 and a number of complex chlorides in which the trimeric clusters persist.[9]

Re_3Br_9 is similar to Re_3Cl_9 but the iodide, which is a black solid and is similarly trinuclear, differs in that it is thermally less stable and only 2 Re atoms in each cluster are linked to adjacent clusters, thereby forming infinite chains of trimeric units rather than planar networks.

Except for the possible existence of ReI_2, the only simple dihalides of this group that are known (so far) are those of manganese. They are pale-pink salts obtained by simply dissolving the metal or carbonate in aqueous HX. MnF_2 is insoluble in water and forms no hydrate, but the others form a variety of very water-soluble hydrates of which the tetrahydrates are the most common.

The oxohalides of manganese are green liquids (except MnO_2Cl_2 which is brown); they are notable for their explosive instability. MnO_3F can be prepared by treating $KMnO_4$ with fluorosulfuric acid, HSO_3F, whereas reaction of Mn_2O_7 with chlorosulfuric acid yields $MnO_3Cl + MnO_2Cl_2 + MnOCl_3$.

The oxohalides of technetium and rhenium are more numerous than those of manganese and are not so unstable, although all of them readily hydrolyse (with dis-proportionation to $[MO_4]^-$ and MO_2 in the case of oxidation states +5 and +6). In this respect they may be regarded as being intermediate between the halides and the oxides which, in the higher oxidation states, are the more stable. Treatment of the oxides with halogens, or the halides with oxygen are common preparative methods. The structures are not all

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[9] M. IRMLER and G. MEYER, *Z. anorg. allg. Chem.* **581**, 104–10 (1990); B. JUNG, G. MEYER and E. HERDTWECK, *ibid.* **604**, 27–33 (1991).