

																1	2																	
																H	He																	
3	4															5	6	7	8	9	10													
Li	Be															B	C	N	O	F	Ne													
11	12															13	14	15	16	17	18													
Na	Mg															Al	Si	P	S	Cl	Ar													
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Cu	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																	
55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72																	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																	
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104																	
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub																							
																		89	90	91	92	93	94	95	96	97	98	99	100	101	102	103		
																		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
																		94	95	96	97	98	99	100	101	102	103	104	105	106	107			
																		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			

# 24

## Manganese, Technetium and Rhenium

### 24.1 Introduction

In terms of history, abundance and availability, it is difficult to imagine a greater contrast than exists in this group between manganese and its congeners, technetium and rhenium. Millions of tonnes of manganese are used annually, and its most common mineral, pyrolusite, has been used in glassmaking since the time of the Pharaohs. On the other hand, technetium and rhenium are exceedingly rare and were only discovered comparatively recently, the former being the first new element to have been produced artificially and the latter being the last naturally occurring element to be discovered.

Metallic manganese was first isolated in 1774 when C. W. Scheele recognized that pyrolusite contained a new element, and his fellow Swede, J. G. Gahn, heated the  $\text{MnO}_2$  with a mixture of charcoal and oil. The purity of this sample of the metal was low, and high-purity (99.9%) manganese was only produced in the 1930s when electrolysis of  $\text{Mn}^{\text{II}}$  solutions was used.

In Mendeleev's table, this group was completed by the then undiscovered eka-manganese ( $Z = 43$ ) and dvi-manganese ( $Z = 75$ ). Confirmation of the existence of these missing elements was not obtained until H. G. J. Moseley had introduced the method of X-ray spectroscopic analysis. Then in 1925 W. Noddack, I. Tacke (later Frau Noddack) and O. Berg discovered element 75 in a sample of gadolinite (a basic silicate of beryllium, iron and lanthanides) and named it rhenium after the river Rhine. The element was also discovered, independently by F. H. Loring and J. F. G. Druce, in manganese compounds, but is now most usually recovered from the flue dusts produced in the roasting of  $\text{CuMo}$  ores.

The Noddacks also claimed to have detected element 43 and named it masurium after Masuren in Prussia. This claim proved to be incorrect, however, and the element was actually detected in 1937 in Italy by C. Perrier and E. Segré in a sample of molybdenum which had been bombarded with deuterons in the cyclotron of E. O. Lawrence in California. It was present in the form of the  $\beta^-$  emitters  $^{95\text{m}}\text{Tc}$  and  $^{97\text{m}}\text{Tc}$

with half-lives of 61 and 90 days respectively. The name technetium (from Greek *τεχνητός*, artificial) is clearly appropriate even though minute traces of the more stable  $^{99}\text{Tc}$  (half-life =  $2.11 \times 10^5$  y) do occur naturally as a result of spontaneous fission of uranium.

## 24.2 The Elements

### 24.2.1 Terrestrial abundance and distribution

The natural abundance of technetium is, as just indicated, negligibly small. The concentration of rhenium in the earth's crust is extremely low (of the order of  $7 \times 10^{-8}\%$ , i.e. 0.0007 ppm) and it is also very diffuse. Being chemically akin to molybdenum it is in molybdenites that its highest concentrations (0.2%) are found. By contrast, manganese (0.106%, i.e. 1060 ppm of the earth's crustal rocks) is the twelfth most abundant element and the third most abundant transition element (exceeded only by iron and titanium). It is found in over 300 different and widely distributed minerals of which about twelve are commercially important. As a class-a metal it occurs in primary deposits as the silicate. Of more commercial importance are the secondary deposits of oxides and carbonates such as pyrolusite ( $\text{MnO}_2$ ), which is the most common, hausmannite ( $\text{Mn}_3\text{O}_4$ ), and rhodochrosite ( $\text{MnCO}_3$ ). These have been formed by weathering of the primary silicate deposits and are found in the former USSR, Gabon, South Africa, Brazil, Australia, India and China.

A further consequence of this weathering is that colloidal particles of the oxides of manganese, iron and other metals are continuously being washed into the sea where they agglomerate and are eventually compacted into the "manganese nodules" (so called because Mn is the chief constituent), first noted during the voyage of HMS *Challenger* (1872–6). Following a search in the Pacific organized by the University of California during the International Geophysical Year (1957), the magnitude and potential value of manganese nodules became

apparent. More than  $10^{12}$  tonnes are estimated to cover vast areas of the ocean beds and a further  $10^7$  tonnes are deposited annually. The composition varies but the dried nodules generally contain between 15 and 30% of Mn. This is less than the 35% normally regarded as the lower limit required for present-day commercial exploitation but, since the Mn is accompanied not only by Fe but more importantly by smaller amounts of Ni, Cu and Co, the combined recovery of Ni, Cu and Co, with Mn effectively as a byproduct could well be economical if performed on a sufficient scale. The technical, legal, and political problems involved are enormous, but perhaps even more importantly, overcapacity in conventional means of production has so far inhibited the exploitation of these reserves.

### 24.2.2 Preparation and uses of the metals

Over ninety per cent of all the manganese ores produced are used in steel manufacture, mostly in the form of ferromanganese.<sup>(1)</sup> This contains about 80% Mn and is made by reducing appropriate amounts of  $\text{MnO}_2$  and  $\text{Fe}_2\text{O}_3$  with coke in a blast furnace or, if cheap electricity is available, in an electric-arc furnace. Dolomite or limestone is also added to remove silica as a slag. Where the Mn content is lower (because of the particular ores used) the product is known as silicomanganese (65–70% Mn, 15–20% Si) or spiegeleisen (5–20% Mn). Where pure manganese metal is required it is prepared by the electrolysis of aqueous manganous(II) sulfate. Ore with an Mn content of over 8 million tonnes was produced in 1995, the most important sources being the former Soviet Union, the Republic of South Africa, Gabon and Australia.

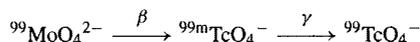
All steels contain some Mn, and its addition in 1856 by R. Mushet ensured the success of the Bessemer process. It serves two main purposes. As a "scavenger" it combines with sulfur to form

<sup>1</sup> Kirk-Othmer Encyclopedia of Chemical Technology, 4th edn., Vol. 15, pp. 963–91, Interscience, New York, 1995.

## Technetium in Diagnostic Nuclear Medicine<sup>(2)</sup>

<sup>99m</sup>Tc is one of the most widely used isotopes in nuclear medicine. It is injected into the patient in the form of a saline solution of a compound, chosen because it will be absorbed by the organ under investigation, which can then be "imaged" by an X-ray camera or scanner. Its properties are ideal for this purpose: it decays into <sup>99</sup>Tc by internal transition and  $\gamma$ -emission of sufficient energy to allow the use of physiologically insignificant quantities (nmol or even pmol — a permissible dose of 1 mCi corresponds to 1.92 pmol of <sup>99m</sup>Tc) and a half-life (6.01 h) short enough to preclude radiological damage due to prolonged exposure. It is obtained from <sup>99</sup>Mo ( $t_{1/2} = 65.94$  h), which in turn is obtained from the fission products of natural or reactor uranium, or else by neutron irradiation of <sup>98</sup>Mo.

Although details vary considerably, the <sup>99</sup>Mo is typically incorporated in a "generator" in the form of  $\text{MoO}_4^{2-}$  absorbed on a substrate such as alumina where it decays according to the scheme:



These generators can be made available virtually anywhere and, when required,  $\text{TcO}_4^-$  is eluted from the substrate and reduced ( $\text{Sn}^{\text{II}}$  is a common, but not the sole, reductant) in the presence of an appropriate ligand, ready for immediate use. A wide range of *N*-, *P*- and *S*-donor ligands has been used to prepare complexes of Tc, mainly in oxidation states III, IV and V, which are absorbed preferentially by different organs. Though the circumstances of clinical usage mean that the precise formulation of the compound actually administered is frequently uncertain,<sup>†</sup> the imaging of brain, heart, lung, bone and tumours etc. is possible. It is the search for compounds of increased specificity which has stimulated most of the recent work on the coordination chemistry of Tc.

<sup>†</sup> Interconversion between different oxidation states occurs easily for Tc (see Section 24.2.4.), and its control often requires careful adjustment of pH and the relative excess of reductant used.

MnS which passes into the slag and prevents the formation of FeS which would induce brittleness, and it also combines with oxygen to form MnO, so preventing the formation of bubbles and pin-holes in the cold steel. Secondly, the presence of Mn as an alloying metal increases the hardness of the steel. The hard, non-magnetic Hadfield steel containing about 13% Mn and 1.25% C, is the best known, and is used when resistance to severe mechanical shock and wear is required, e.g. for excavators, dredgers, rail crossings, etc.

Important, but less extensive, uses are found in the production of non-ferrous alloys. It is a scavenger in several Al and Cu alloys, while "manganin" is a well-known alloy (84% Cu, 12% Mn, 4% Ni) which is used in electrical instruments because the temperature coefficient of its resistivity is almost zero. A variety of other major uses have been found for Mn in the form of

its compounds and these will be dealt with later under the appropriate headings.

Technetium is obtained from nuclear power stations where it makes up about 6% of uranium fission products and is recovered from these after storage for several years to allow the highly radioactive, short-lived fission products to decay. The original process used the precipitation of  $[\text{AsPh}_4]^+[\text{ClO}_4]^-$  to carry with it  $[\text{AsPh}_4]^+[\text{TcO}_4]^-$  and so separate the Tc from other fission products, but solvent extraction and ion-exchange techniques are now used. The metal itself can be obtained by the high-temperature reduction of either  $\text{NH}_4\text{TcO}_4$  or  $\text{Tc}_2\text{S}_7$  with hydrogen. <sup>99</sup>Tc is the isotope available in kg quantities and the one used for virtually all chemical studies. Because of its long half-life it is not a major radiation hazard and, with standard manipulative techniques, can be safely handled in mg quantities. However, the main interest in Tc is its role in nuclear medicine, and here it is the metastable  $\gamma$ -emitting isotope <sup>99m</sup>Tc which is used (see Panel).

<sup>2</sup> S. JURISSON, D. BERNING, W. JIA and D. MA, *Chem. Revs.*, **93**, 1137–56 (1993). K. SCHWOCHALL, *Angew. Chem. Int. Edn. Engl.* **33**, 2258–67 (1994).

In the roasting of molybdenum sulfide ores, any rhenium which might be present is oxidized to volatile  $\text{Re}_2\text{O}_7$  which collects in the flue dusts and is the usual source of the metal via conversion to  $(\text{NH}_4)\text{ReO}_4$  and reduction by  $\text{H}_2$  at elevated temperatures. Being highly refractory and corrosion-resistant, rhenium metal would no doubt find widespread use were it not for its scarcity and consequent high cost. As it is, uses are essentially small scale. These include bimetallic Pt/Re catalysts for the production of lead-free, high octane petroleum products, high temperature superalloys for jet engine components, mass spectrometer filaments, furnace heating elements and thermocouples. World production is about 35 tonnes annually.

### 24.2.3 Properties of the elements

Some of the important properties of Group 7 elements are summarized in Table 24.1. Technetium is an artificial element, so its atomic weight depends on which isotope has been produced. The atomic weights of Mn and Re, however, are known with considerable accuracy. In the case of

the former this is because it has only 1 naturally occurring isotope and, in the case of the latter, because it has only 2 and the relative proportions of these in terrestrial samples are essentially constant ( $^{185}\text{Re}$  37.40%,  $^{187}\text{Re}$  62.60%).

In the solid state all three elements have typically metallic structures. Technetium and Re are isostructural with hcp lattices, but there are 4 allotropes of Mn of which the  $\alpha$ -form is the one stable at room temperature. This has a bcc structure in which, for reasons which are not clear, there are 4 distinct types of Mn atom. It is hard and brittle, and noticeably less refractory than its predecessors in the first transition series.

In continuance of the trends already noticed, the most stable oxidation state of manganese is +2, and in the group oxidation state of +7 it is even more strongly oxidizing than Cr(VI). Evidently the 3d electrons are more tightly held by the Mn atomic nucleus and this reduced delocalization produces weaker metallic bonding than in Cr. The same trends are also starting in the second and third series with Tc and Re, but are less marked, and Re in particular is very refractory, having a mp which is second only to that of tungsten amongst transition elements.

Table 24.1 Some properties of Group 7 elements

Property	Mn	Tc	Re
Atomic number	25	43	75
Number of naturally occurring isotopes	1	—	2
Atomic weight	54.938049(9)	98.9063 <sup>(a)</sup>	186.207(1)
Electronic configuration	[Ar]3d <sup>5</sup> 4s <sup>2</sup>	[Kr]4d <sup>6</sup> 5s <sup>1</sup>	[Xe]4f <sup>14</sup> 5d <sup>5</sup> 6s <sup>2</sup>
Electronegativity	1.5	1.9	1.9
Metal radius (12-coordinate)/pm	127	136	137
Ionic radius/pm	46	56	53
(4-coordinate if marked*; otherwise 6-coordinate)	25.5*	—	55
	V	60	58
	IV	64.5	63
	III	—	—
	II	—	—
MP/°C	1244	2200	3180
BP/°C	2060	4567	(5650)
$\Delta H_{\text{fus}}/\text{kJ mol}^{-1}$	(13.4)	23.8	34(±4)
$\Delta H_{\text{vap}}/\text{kJ mol}^{-1}$	221(±8)	585	704
$\Delta H_{\text{f}}(\text{monatomic gas})/\text{kJ mol}^{-1}$	281(±6)	—	779(±8)
Density (25°C)/g cm <sup>-3</sup>	7.43	11.5	21.0
Electrical resistivity (20°C)/μohm cm	185.0	—	19.3

<sup>(a)</sup>This refers to  $^{99}\text{Tc}$  ( $t_{1/2} 2.11 \times 10^5$  y). For  $^{97}\text{Tc}$  ( $t_{1/2} 2.6 \times 10^6$  y) and  $^{98}\text{Tc}$  ( $t_{1/2} 4.2 \times 10^6$  y) the values are 96.9064 and 97.9072 respectively.

### 24.2.4 Chemical reactivity and trends

Manganese is more electropositive than any of its neighbours in the periodic table and the metal is more reactive, especially when somewhat impure. In the massive state it is superficially oxidized on exposure to air but will burn if finely divided. It liberates hydrogen from water and dissolves readily in dilute aqueous acids to form manganese(II) salts. With non-metals it is not very reactive at ambient temperatures but frequently reacts vigorously when heated. Thus it burns in oxygen, nitrogen, chlorine and fluorine giving  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_3\text{N}_2$ ,  $\text{MnCl}_2$  and  $\text{MnF}_2 + \text{MnF}_3$  respectively, and it combines directly with B, C, Si, P, As and S.

Technetium and rhenium metals are less reactive than manganese and, as is to be expected for the two heavier elements, they are closely similar to each other. In the massive form they resist oxidation and are only tarnished slowly in moist air. However, they are normally produced as sponges or powders in which case they are more reactive. Heated in oxygen they burn to give volatile heptaoxides ( $\text{M}_2\text{O}_7$ ), and with fluorine they give  $\text{TcF}_5 + \text{TcF}_6$  and  $\text{ReF}_6 + \text{ReF}_7$  respectively.  $\text{MS}_2$  can also be produced by direct action. Although insoluble in hydrofluoric and hydrochloric acids, the metals dissolve readily in oxidizing acids such as  $\text{HNO}_3$  and conc  $\text{H}_2\text{SO}_4$  and also in bromine water, when "pertechnetic" and "perrhenic" acids ( $\text{HMO}_4$ ) are formed.

Because of the differing focus of interest in these elements their chemistries have not developed in parallel and the data on which strict comparisons might be based are not always available. Nevertheless many of the similarities and contrasts expected in the chemistry of transition elements are evident in this triad. The relative stabilities of different oxidation states in aqueous, acidic solutions are summarized in Table 24.2 and Fig. 24.1.

The most obvious features of Fig. 24.1 are the relative positions of the +2 oxidation states. For manganese this state, represented by the high-spin  $\text{Mn}^{\text{II}}$  cation, is much the most stable. This may be taken as an indication of the stability of the symmetrical  $d^5$  electron configuration.

Table 24.2  $E^\circ$  for some manganese, technetium and rhenium couples in acid solution at 25°C

Couple	$E^\circ/\text{V}$
$\text{Mn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mn}(\text{s})$	-1.185
$\text{Mn}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Mn}(\text{s})$	-0.283
$\text{MnO}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Mn}(\text{s}) + 2\text{H}_2\text{O}$	0.024
$\text{MnO}_4^{2-} + 8\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}$	1.742
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}$	1.507
$\text{Tc}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Tc}(\text{s})$	0.400
$\text{TcO}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Tc}(\text{s}) + 2\text{H}_2\text{O}$	0.272
$\text{TcO}_3 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{TcO}_2 + \text{H}_2\text{O}$	0.757
$\text{TcO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Tc}^{2+}(\text{aq}) + 4\text{H}_2\text{O}$	0.500
$\text{Re}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Re}(\text{s})$	0.300
$\text{ReO}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Re}(\text{s}) + 2\text{H}_2\text{O}$	0.251
$\text{ReO}_3 + 6\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{Re}^{3+}(\text{aq}) + 3\text{H}_2\text{O}$	0.318
$\text{ReO}_4^{2-} + 8\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{Re}^{3+}(\text{aq}) + 4\text{H}_2\text{O}$	0.795
$\text{ReO}_4^- + 8\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Re}^{3+}(\text{aq}) + 4\text{H}_2\text{O}$	0.422

However, like the mp, bp and enthalpy of atomization, it also reflects the weaker cohesive forces in the metallic lattice since for Tc and Re, which have much stronger metallic bonding, the +2 state is of little importance and the occurrence of cluster compounds with M–M bonds is a dominant feature of rhenium(III) chemistry. The almost uniform slope of the plot for Tc presages the facile interconversion between oxidation states, observed for this element.

Another marked contrast is evident in the +7 oxidation state where the manganate(VII) (permanganate) ion is an extremely strong oxidizing agent but  $(\text{TcO}_4)^-$  and  $(\text{ReO}_4)^-$  show only mild oxidizing properties. Indeed, the greater stability of Tc and Re compared to Mn in any oxidation state higher than +2 is apparent, as will be seen more fully in the following account of individual compounds.

Table 24.3 lists representative examples of the compounds of these elements in their various oxidation states. The wide range of the oxidation states is particularly noteworthy. It arises from the fact that, in moving across the transition series, the number of d electrons has increased and, in this mid-region, the d orbitals have not yet sunk energetically into the inert electron core. The number of d electrons available for bonding is consequently maximized, and not