

																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			
K		Ca		Sc		Ti		V		Cr		Mn		Fe		Co		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		104		105			
Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu									
105		106		107		108		109		110		111		112		113		114		115		116		117		118		119		120					
Th		Pa		U		Np		Pu		Am		Cm		Bk		Cf		Es		Fm		Md		No		Lr									

# 23

## Chromium, Molybdenum and Tungsten

### 23.1 Introduction

The discoveries of these elements span a period of about 20 y at the end of the eighteenth century. In 1778 the famous Swedish chemist C. W. Scheele produced from the mineral molybdenite ( $\text{MoS}_2$ ) the oxide of a new element, thereby distinguishing the mineral from graphite with which it had hitherto been thought to be identical. Molybdenum metal was isolated 3 or 4 y later by P. J. Hjelm by heating the oxide with charcoal. The name is derived from the Greek word for lead ( $\mu\acute{o}\lambda\upsilon\beta\delta\omicron\varsigma$ , *molybdos*), owing to the ancient confusion between any soft black minerals which could be used for writing (this is further illustrated by the use of the names “plumbago” and “black lead” for graphite).

In 1781 Scheele, and also T. Bergman, isolated another new oxide, this time from the mineral now known as scheelite ( $\text{CaWO}_4$ ) but then called “tungsten” (Swedish *tung sten*, heavy stone). Two years later the Spanish brothers J. J.

and F. d’Elhuyar showed that the same oxide was a constituent of the mineral wolframite and reduced it to the metal by heating with charcoal. The name “wolfram”, from which the symbol of the element is derived, is still widely used in the German literature and is recommended by IUPAC, but the allowed alternative “tungsten” is used in the English-speaking world.

Finally, in 1797, the Frenchman L. N. Vauquelin discovered the oxide of a new element in a Siberian mineral, now known as crocoite ( $\text{PbCrO}_4$ ), and in the following year isolated the metal itself by charcoal reduction. This was subsequently named chromium (Greek  $\chi\rho\omega\mu\iota\alpha$ , *chroma*, colour) because of the variety of colours found in its compounds. Since their discoveries the metals and their compounds have become vitally important in many industries and, as one of the biologically active transition elements, molybdenum has been the subject of a great deal of attention in recent years, especially in the field of nitrogen fixation (p. 1035).

## 23.2 The Elements

### 23.2.1 Terrestrial abundance and distribution

Chromium, 122 ppm of the earth's crustal rocks, is comparable in abundance with vanadium (136 ppm) and chlorine (126 ppm), but molybdenum and tungsten (both ~1.2 ppm) are much rarer (cf. Ho 1.4 ppm, Tb 1.2 ppm), and the concentration in their ores is low. The only ore of chromium of any commercial importance is chromite,  $\text{FeCr}_2\text{O}_4$ , which is produced principally in southern Africa (where 96% of the known reserves are located), the former Soviet Union and the Philippines. Other less plentiful sources are crocoite,  $\text{PbCrO}_4$ , and chrome ochre,  $\text{Cr}_2\text{O}_3$ , while the gemstones emerald and ruby owe their colours to traces of chromium (pp. 107, 242).

The most important ore of molybdenum is the sulphide molybdenite,  $\text{MoS}_2$ , of which the largest known deposit is in Colorado, USA, but it is also found in Canada and Chile. Less important ores are wulfenite,  $\text{PbMoO}_4$ , and powellite,  $\text{Ca}(\text{Mo},\text{W})\text{O}_4$ .

Tungsten occurs in the form of the tungstates scheelite,  $\text{CaWO}_4$ , and wolframite,  $(\text{Fe},\text{Mn})\text{WO}_4$ , which are found in China (thought to have perhaps 75% of the world's reserves), the former Soviet Union, Korea, Austria and Portugal.

### 23.2.2 Preparation and uses of the metals

Chromium is produced in two forms:<sup>(1)</sup>

- (a) Ferrochrome by the reduction of chromite with coke in an electric arc furnace. A low-carbon ferrochrome can be produced by using ferrosilicon (p. 330) instead of coke as the reductant. This iron/chromium alloy is used directly as an additive

to produce chromium-steels which are "stainless" and hard.

- (b) Chromium metal by the reduction of  $\text{Cr}_2\text{O}_3$ . This is obtained by aerial oxidation of chromite in molten alkali to give sodium chromate,  $\text{Na}_2\text{CrO}_4$ , which is leached out with water, precipitated and then reduced to the Cr(III) oxide by carbon. The oxide can be reduced by aluminium (aluminothermic process) or silicon:



The main use of the chromium metal so produced is in the production of non-ferrous alloys, the use of pure chromium being limited because of its low ductility at ordinary temperatures. Alternatively, the  $\text{Cr}_2\text{O}_3$  can be dissolved in sulphuric acid to give the electrolyte used to produce the ubiquitous chromium-plating which is at once both protective and decorative.

The sodium chromate produced in the isolation of chromium is itself the basis for the manufacture of all industrially important chromium chemicals. World production of chromite ores approached 12 million tonnes in 1995.

Molybdenum is obtained as a primary product but mainly as a byproduct in the production of copper. In either case  $\text{MoS}_2$  is separated by flotation and then roasted to  $\text{MoO}_3$ . In the manufacture of stainless steel and high-speed tools, which account for about 85% of molybdenum consumption, the  $\text{MoO}_3$  may be used directly or after conversion to ferromolybdenum by the aluminothermic process. Otherwise, further purification is possible by dissolution in aqueous ammonia and crystallization of ammonium molybdate (sometimes as the dimolybdate,  $[\text{NH}_4]_2[\text{Mo}_2\text{O}_7]$ , sometimes as the paramolybdate,  $[\text{NH}_4]_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ , depending on conditions), which is the starting material for the manufacture of molybdenum chemicals. Pure molybdenum, which finds important applications as a catalyst in a variety of petrochemical processes and as an electrode material, can be

<sup>1</sup> Kirk-Othmer, *Encyclopedia of Chemical Technology*, 4th edn., Vol. 6, pp. 228-63, Interscience, New York, 1993.

obtained by hydrogen reduction of ammonium molybdate. In 1995 world production of molybdenum ores was equivalent to 130 000 tonnes of contained Mo.

The isolation of tungsten is effected by the formation of "tungstic acid" (hydrous  $\text{WO}_3$ ), but the chemical route chosen depends on the ore being used. After pulverization and concentration of the ore:

- (a) Wolframite is converted to soluble alkali tungstate either by fusing with NaOH and leaching the cooled product with water, or by protracted boiling with aqueous alkali. Acidification with hydrochloric acid then precipitates the tungstic acid.
- (b) Scheelite is converted to insoluble tungstic acid by direct treatment with hydrochloric acid and separated from the soluble salts of other metals.

Tungstic acid is then roasted to  $\text{WO}_3$  which is reduced to the metal by heating with hydrogen at  $850^\circ\text{C}$ . Half of the tungsten produced is used as the carbide, WC, which is extremely hard and wear-resistant and so ideal as a tool-tip. Other

major uses are in the production of numerous heat-resistant alloys, but the most important use of the *pure* metal is still as a filament in electric light bulbs, in which role it has never been bettered since it was first used in 1908. In 1995, world production of tungsten ores contained 31 000 tonnes of tungsten.

Both molybdenum and tungsten are obtained initially in the form of powders and, since fusion is impracticable because of their high mps, they are converted to the massive state by compression and sintering under  $\text{H}_2$  at high temperatures.

### 23.2.3 Properties of the elements

As can be seen from Table 23.1, which summarizes some of the important properties of Group 6, each of these elements has several naturally occurring isotopes which imposes limits on the precision with which their atomic weights have been determined, especially for Mo and W.

The elements all have typically metallic bcc structures and in the massive state are lustrous, silvery, and (when pure) fairly soft. However, the most obvious characteristic at least of

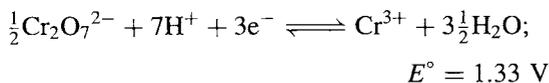
**Table 23.1** Some properties of Group 6 elements

Property	Cr	Mo	W
Atomic number	24	42	74
Number of naturally occurring isotopes	4	7	5
Atomic weight	51.9961(6)	95.94(1)	183.84(1)
Electronic configuration	$[\text{Ar}]3d^54s^1$	$[\text{Kr}]4d^55s^1$	$[\text{Xe}]4f^{14}5d^46s^2$
Electronegativity	1.6	1.8	1.7
Metal radius (12-coordinate)/pm	128	139	139
Ionic radius (6-coordinate)/pm	VI V IV III II <sup>(a)</sup>	44 49 55 61.5	59 61 65 69
	73 (ls), 80 (hs)	—	—
MP/ $^\circ\text{C}$	1900	1620	3422
BP/ $^\circ\text{C}$	2690	4650	(5500)
$\Delta H_{\text{fus}}/\text{kJ mol}^{-1}$	21( $\pm$ 2)	28( $\pm$ 3)	(35)
$\Delta H_{\text{vap}}/\text{kJ mol}^{-1}$	342( $\pm$ 6)	590( $\pm$ 21)	824( $\pm$ 21)
$\Delta H_{\text{f}}$ (monatomic gas)/ $\text{kJ mol}^{-1}$	397( $\pm$ 3)	664( $\pm$ 13)	849( $\pm$ 13)
Density ( $20^\circ\text{C}$ )/ $\text{g cm}^{-3}$	7.14	10.28	19.3
Electrical resistivity ( $20^\circ\text{C}$ )/ $\mu\text{ohm cm}$	13	$\sim$ 5	$\sim$ 5

<sup>(a)</sup>Radius depends on whether Cr(II) is low-spin (ls) or high-spin (hs).

molybdenum and tungsten, is their refractive nature, and tungsten has the highest mp of all metals — indeed, of all elements except carbon. For this reason, metallic Mo and W are fabricated by the techniques of powder metallurgy and, in consequence, many of their bulk physical properties depend critically on the nature of their mechanical history.

As in the preceding transition-metal groups, the refractory behaviour and the relative stabilities of the different oxidation states can be explained by the role of the  $(n - 1)d$  electrons. Compared to vanadium, chromium has a lower mp, bp and enthalpy of atomization which implies that the 3d electrons are now just beginning to enter the inert electron core of the atom, and so are less readily delocalized by the formation of metal bonds. This is reflected too in the fact that the most stable oxidation state has dropped to +3, while chromium(VI) is strongly oxidizing:



For the heavier congeners, tungsten in the group oxidation state is much more stable to reduction, and it is apparently the last element in the third transition series in which all the 5d electrons participate in metal bonding.

### 23.2.4 Chemical reactivity and trends

At ambient temperatures all three elements resist atmospheric attack, which is why chromium is so widely used to protect other more reactive metals. They become more susceptible to attack at high temperatures, when they react with many non-metals giving frequently interstitial and non-stoichiometric products. Chromium reacts more readily with acids than does either molybdenum or tungsten though its reactivity depends on its purity and it can easily be rendered passive. Thus, it dissolves readily in dil HCl but, if very pure, will often resist dil  $\text{H}_2\text{SO}_4$ ; again,  $\text{HNO}_3$ , whether

dilute or concentrated, and aqua regia will render it passive for reasons which are by no means clear. In the presence of oxidizing agents such as  $\text{KNO}_3$  or  $\text{KClO}_3$ , alkali melts rapidly attack the metals producing  $\text{MO}_4^{2-}$ .

Once again the two heavier elements are closely similar to each other and show marked differences from the lightest element. This is reflected particularly in the relative stabilities of the oxidation states, all of which are known from +6 down to -2.

The stability of the group oxidation state +6 was referred to above and it may be further noted that, while chromium(VI) tends to form poly oxoanions, the diversity of these is but a pale shadow of that of the polymolybdates and polytungstates (p. 1009). Oxidation states +5 and +4 are represented by chromium largely as unstable intermediates, and +3 is much its most stable oxidation state, the symmetrical  $t_{2g}^3$  configuration leading to a coordination chemistry, the fecundity of which is exceeded only by that of cobalt(III). Chromium(II) is strongly reducing ( $\text{Cr}^{3+}/\text{Cr}^{2+}$ ,  $E^\circ - 0.41 \text{ V}$ ) but it still has an extensive cationic chemistry. By contrast, the chemistry of molybdenum and tungsten in oxidation states +5 to +2 is dominated by clusters and multiple-bonded species which, particularly in the case of molybdenum, has produced an effusion of publications in recent years. This is due not only to the intrinsically interesting chemistry involved but also because of molybdenum's role in biological processes and, catalytically, in the hydrodesulfurization (HDS) process for removing S-compounds from petroleum feedstocks. In the still lower oxidation states, found in compounds with  $\pi$ -acceptor ligands, the metals are quite similar.

Table 23.2 lists the oxidation states of the elements along with representative examples of their compounds. Coordination numbers as high as 12 can be attained, but those over 7 in the case of Cr and 9 in the cases of Mo and W involve the presence of the peroxo ligand or  $\pi$ -bonded aromatic rings systems such as  $\eta^5\text{-C}_5\text{H}_5^-$  or  $\eta^6\text{-C}_6\text{H}_6$ .

**Table 23.2** Oxidation states and stereochemistries of compounds of chromium, molybdenum and tungsten

Oxidation state	Coordination number	Stereochemistry	Cr	Mo/W
-4	4	Tetrahedral	$[\text{Cr}(\text{CO})_4]^{4-}$	$[\text{M}(\text{CO})_4]^{4-}$
-2 ( $d^8$ )	5	Trigonal bipyramidal(?)	$[\text{Cr}(\text{CO})_5]^{2-}$	$[\text{M}(\text{CO})_5]^{2-}$
-1 ( $d^7$ )	6	Octahedral	$[\text{Cr}_2(\text{CO})_{10}]^{2-}$	$[\text{M}_2(\text{CO})_{10}]^{2-}$
0 ( $d^6$ )	6	Octahedral	$[\text{Cr}(\text{bipy})_3]$	$[\text{M}(\text{CO})_6]$
	9	—	$[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3]$	—
	12	—	$[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$	—
1 ( $d^5$ )	6	Octahedral	$[\text{Cr}(\text{CNR})_6]^+$	$[\text{MoCl}(\text{N}_2)(\text{diphos})_2]$
	8	—	—	$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$
	11	—	—	$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{H}_6)]$
	12	—	—	$[\text{Mo}(\eta^6\text{-C}_6\text{H}_6)_2]^+$
2 ( $d^4$ )	4	Tetrahedral	$[\text{CrI}_2(\text{OPPh}_3)_2]$	—
	4	Square Planar	$\{\text{Cr}(\text{acac})_2\}$	—
	5	Trigonal bipyramidal	$[\text{CrBr}\{\text{N}(\text{C}_2\text{H}_4\text{NMe}_2)_3\}]^+$	—
		Square pyramidal	—	$[\text{Mo}_2\text{Cl}_8]^{4-}$ , $[\text{W}_2\text{Me}_8]^{4-}$
	6	Octahedral	$[\text{Cr}(\text{en}_3)]^{2+}$	$[\text{M}(\text{diars})_2\text{I}_2]$
	7	Capped trigonal prismatic	$[\text{Cr}(\text{CO})_2(\text{diars})_2\text{X}]^+$	$[\text{Mo}(\text{CNR})_7]^{2+ \dagger}$
		Pentagonal bipyramidal	—	$[\text{MoH}(\eta^2\text{-O}_2\text{CCF}_3)\{\text{P}(\text{OMe})_3\}_4]$
	8	—	$[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{NO})_2]$	—
	9	—	—	$[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$ , $\text{M}_6\text{Cl}_{12}$ clusters
	10	—	$[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)_2]$	—
3 ( $d^3$ )	3	Planar	$[\text{Cr}(\text{NPr}_2)_3]$	—
	4	Tetrahedral	$[\text{CrCl}_4]^-$	$[(\text{RO})_3\text{Mo}\equiv\text{Mo}(\text{OR})_3]$ , $[(\text{R}_2\text{N})_3\text{W}\equiv\text{W}(\text{NR}_2)_3]$
	5	Trigonal bipyramidal	$[\text{CrCl}_3(\text{NMe}_3)_2]$	—
	6	Octahedral	$[\text{Cr}(\text{NH}_3)_6]^{3+}$	$[\text{M}_2\text{Cl}_9]^{3-}$
	7	?	—	$[\text{WBr}_2(\text{CO})_3(\text{diars})]^+$
	8	Dodecahedral(?)	—	$[\text{Mo}(\text{CN})_7(\text{H}_2\text{O})]^{4-}$
	8 or 12	—	—	$[\text{Mo}(\eta^1\text{-C}_5\text{H}_5)(\eta^x\text{-C}_5\text{H}_5)_2(\text{NO})]$ , $x = 3 \text{ or } 5$
4 ( $d^2$ )	4	Tetrahedral	$[\text{Cr}(\text{OBU}^t)_4]$	$[\text{Mo}(\text{NMe}_2)_4]$
	6	Octahedral	$[\text{CrF}_6]^{2-}$	$[\text{MCl}_6]^{2-}$
		Trigonal prismatic	—	$\text{MS}_2$
	8	Dodecahedral	$[\text{CrH}_4(\text{dmpe})_2]^{(a)}$	$[\text{M}(\text{CN})_8]^{4-}$
		Square antiprismatic(?)	—	$\text{Mo}(\text{S}_2\text{CNMe}_2)_4$ , $[\text{M}(\text{picolate})_4]$
	12	—	—	$[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2\text{X}_2]$
5 ( $d^1$ )	4	Tetrahedral	$[\text{CrO}_4]^{3-}$	—
	5	Square pyramidal	$[\text{CrOCl}_4]^-$	—
		Trigonal bipyramidal	$\text{CrF}_5(\text{g})$	$\text{MoCl}_5(\text{g})$
	6	Octahedral	$[\text{CrOCl}_5]^{2-}$	$[\text{MF}_6]^-$
	8	Dodecahedral	$[\text{Cr}(\text{O}_2)_4]^{3-}$	$[\text{M}(\text{CN})_8]^{3-}$
	13	—	—	$[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}_3]$
6 ( $d^0$ )	4	Tetrahedral	$[\text{CrO}_4]^{2-}$	$[\text{MO}_4]^{2-}$
	5	?	—	$[\text{MOX}_4]$
		Square pyramidal	—	$[\text{W}(\equiv\text{CCMe}_3)(\leftarrow\text{CHCMe}_3)\text{-}(\text{CH}_2\text{CMe}_3)\{\text{PMe}_2\text{CH}_2\text{-}\}_2]$
	6	Octahedral	$\text{CrF}_6$	$\{\text{MO}_6\}$ in polymetallates
		Trigonal prismatic	—	$[\text{M}(\text{S}_2\text{C}_2\text{H}_2)_3]$
		Pentagonal bipyramidal	—	$[\text{WOCl}_4(\text{diars})]$
	8	?	—	$[\text{MF}_8]^{2-}$
	9	Tricapped trigonal prismatic ( $C_{2v}$ )	—	$[\text{WH}_6(\text{PPhPr}_2)_3]$

<sup>†</sup>The structure of these complexes is not regular and has been described as "4:3 ( $C_s$ ) piano stool", which is obtained by slight distortion of a capped trigonal prism ( $C_{2v}$ ).

<sup>(a)</sup>dmpe, 1,2-bis(dimethylphosphino)ethane,  $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ .