2 SECOND AND THIRD TRANSITION SERIES

In general, the elements of second and third transition series of a given group have similar chemical properties but both show pronounced differences from their light congeners. For example, a number of cobalt (+2) complexes having tetrahedral and octahedral geometry are known and also a characteristic state in ordinary aqueous solution. But few complexes of Rh(+2) is known and Ir(+2) is unknown. Similarly Mn(+2) ion is very stable whereas few compounds of Tc and Re in +2 oxidation state are known. Cr(+3) is the most stable oxidation states and forms number of complexes. Cr(+6) is quite unstable Mo(III) and W(III) compounds are not stable as Cr(+3) compounds. Mo(VI) and W(+6) are quite stable oxidation states.

This is not to say that there is no valid analogy between the chemistry of three series of transition elements. For example, the chemistry of Rh (III) complexes is general similar to that of Co (III) complexes, and here as elsewhere, the ligand field bonds in the spectra of the complexes in corresponding to oxidation states are similar. However, there are some differences between the 1st row, second and third row transion elements. General characteristic of $4d$ and $5d$ elements are discussed below.

ELECTRONIC CONFIGURATION

The elements Y_{39} to Cd_{48} (10 elements) constitute the second transition series whereas La_{157}, Hf_{72}—Hg constitute third transition series. The filling of $4d$ and $5d$ orbitals continues as we move from left to right in the periods. The electronic configurations of $4d$ and $5d$ transition series are given in Table 2.1. The electronic configuration of first raw transition elements is regular with only exception of Cr ($3d^5 4s^1$) and Cu($3d^{10} 4s^1$) electronic configuration. However, for second and third row transition elements the electronic configuration is not regular. There are evidently some pronounced irregularities in the configuration of these elements. Like Cr and Cu the electronic configuration of Mo($4d^5 5s^1$), Ag($4d^{10} 5s^1$) Re ($5d^5 6s^2$) and Au ($5d^{10} 6s^1$) can be easily understood on the basis of higher stability of exactly half filled and fully filled d orbital. However, this concept cannot explain the anomalous configuration of Nb, Ru, Rh, Pd, W, Pt. As a matter of fact, no simple explanation for such anomalies can be offered. There are two factors which play a significant role in determining these configurations.

(1) Electron-Nuclear attraction

(2) Electron-Electron repulsion.

Table 2.1 Electronic configuration of second and third row transition series

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
[Kr]	$4d^1 5s^2$	$4d^2 5s^2$	$4d^4 5s^1$	$4d^5 5s^1$	$4d^5 5s^2$	$4d^7 5s^1$	$4d^8 5s^1$	$4d^{10} 5s^0$	$4d^{10} 5s^1$	$4d^{10} 5s^2$
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
[Xe]	$5d^1 6s^2$	$5d^2 4s^2$	$5d^3 4s^2$	$5d^4 4s^2$	$5d^5 4s^2$	$5d^6 4s^2$	$5d^7 6s^2$	$5d^{10} 6s^0$	$5d^{10} 6s^1$	$5d^{10} 6s^2$

Physical Properties: These are given in Table 2.2 and 2.3

Size of atoms and ions

The atomic and ionic radii decreases as we move from left to right. However, there is a slight increase in radii at the end of series. It is due to increase in repulsion due to almost completely filled *d*-orbital (Table 2.1).

On descending one of the main groups of elements, the size of atoms increases because extra shells of electron present. The elements of the first group in the d-block show the expected increase in size Sc→Y→La. However, in the subsequent groups there is an increase in the radius 1—2pm between the first and second number, but hardly any increase between the second and third elements. This trend is shown in both in the covalent and ionic radii (Table 2.2). There are 14 elements called lathanides between La and Hf. In these elements penultimate $4f$ shell of electrons is filled. There is a gradual decrease in size of the 14 lanthanides elements from Ce to Lu. This is called lanthanide contraction. The lanthanide contraction cancels almost exactly the normal size increase on descending a group of transition elements. The covalent radii of Hf and the ionic radii of Hf^{4+} are actually smaller than the corresponding value of Zr.
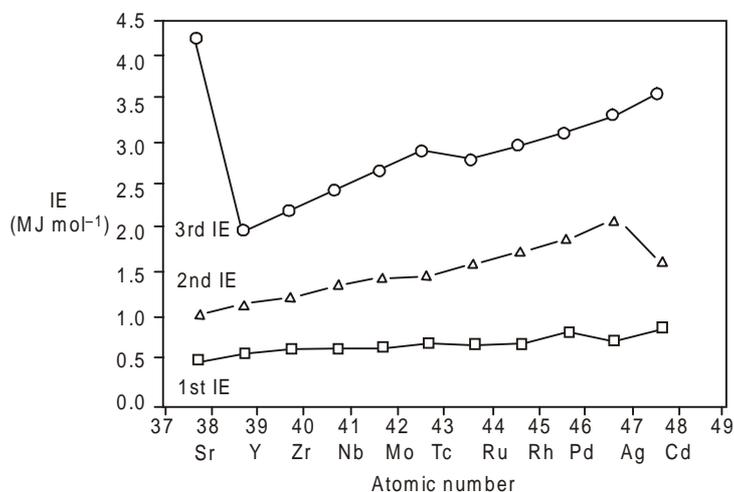

Fig. 2.1 The variation in ionization energies (E) with atomic number for the second row of the d-block.

Ionization Energy

Due to almost same size of second and third row transition series, they show almost same value of ionization energy (Fig. 2.1). A particular feature of third IE against atomic number is discontinuity between Tc and Ru in second row and Re and Os in third row. This reflects the additional energy is required to break into half filled subshells.

Table 2.2 Some important physical properties of the second transition series

Property	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Atomic number	39	40	41	42	43	44	45	46	47	48
Outer electronic configuration	$4d^1 5s^2$	$4d^2 5s^2$	$4d^4 5s^1$	$4d^5 5s^1$	$4d^5 5s^2$	$4d^7 5s^1$	$4d^8 5s^1$	$4d^{10} 5s^0$	$4d^{10} 5s^1$	$4d^{10} 5s^2$

(Cont.)

Atomic size (pm)	180	157	141	136	130	133	134	138	144	149
Ionic radius (pm)	090	080	070	—	—	081	069	050	126	097
	(Y^{3+})	(Zr^{4+})	(Nb^{5+})	—	—	(Ru^{3+})	(Rh^{3+})	(Pd^{2+})	(Ag^{+})	(Cd^{2+})
Crystal structure	hcp	hcp, bcc	bcc	bcc	hcp	hcp	fcc	fcc	fcc	hcp
Density (g/ml)	5.5	6.5	8.6	10.2	11.5	12.4	12.4	12.0	10.5	8.7
Melting point (°C)	1490	1860	1950	2620	≃ 2100	2450	1970	1550	960	320
Boiling point (°C)	2900	≃ 2900	3300	≃ 4800	—	> 2700	> 2500	2200	1950	760
Stable oxidation states	+3	+4	+5	+6	+4	+3	+3	+2	+1	+2
First ionisation energy (kJ mol^{-1})	636	669	652	694	698	724	745	803	732	866
Electronegativity	1.2	1.4	1.6	1.8	2.9	2.9	2.2	2.2	1.9	1.9
Heat of fusion (kJ mol^{-1})	11.28	16.7	26.7	27.6	23	25.5	21.7	16.7	11.3	6.1
Heat of vaporization (kJ mol^{-1})	389	502	—	535	502	603	577	381	286	180

Table 2.3 Some important physical properties of the third transition series

Property	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Atomic number	57	72	73	74	75	76	77	78	79	80
Outer electronic configuration	$5d^1 6s^2$	$5d^2 6s^2$	$5d^3 6s^2$	$5d^4 6s^2$	$5d^5 6s^2$	$5d^6 6s^2$	$5d^7 6s^2$	$5d^9 6s^1$	$5d^{10} 6s^1$	$5d^{10} 6s^2$
Atomic size (pm)	188	157	143	137	136	134	135	138	144	155
Ionic radius (pm)	106	080	073	068	068	078	066	052	137	110
	(La^{3+})	(Hf^{4+})	(Ta^{5+})	(W^{6+})	(Re^{7+})	(Os^{4+})	—	—	(Au^{+})	(Hg^{2+})
Crystal structure	hcp, fcc	hcp	bcc	bcc	hcp	hcp	fcc	fcc	fcc	rhombic
Density (g/ml)	6.2	13.3	16.6	19.3	20.5	22.7	22.6	21.5	19.3	13.6
Melting point (°C)	890	2200	3030	3370	3200	2700	2450	1774	1060	– 39
Boiling point (°C)	3450	5100	5425	5930	5900	7530	4190	4130	2600	357
Stable oxidation states	+3	+4	+5	+6	+2 to+7	+4, +6	+3, +4	+2, +4	+1, +3	+2
First ionisation energy (kJ mol^{-1})	541.3	531	577	770	761	841	887	866	891	1008
Electronegativity	1.1	1.3	1.7	1.7	1.9	2.2	2.01	2.2	2.4	1.9
Heat of fusion (kJ mol^{-1})	10	21.7	28.4	33.7	33.0	26.8	27.6	21.7	12.7	2.37
Heat of vaporization (kJ mol^{-1})	339	648	753	774	636	690	648	565	363	58

OXIDATION STATES

The elements of second and third row do not show identical pyramid of oxidation states as the first row. In a iron family Os and Ru show oxidation states upto (VIII) for example OsO_4 and RuO_4 Table 2.4.

The highest oxidation state available to an element is usually found among its compounds with two most electronegative elements, fluorine and oxygen, so that an examination of the binary fluorides and oxides of the transition elements should reveal their maximum chemically attainable oxidation states. The stoichiometric oxides and fluorides of the second and third row elements are given in Tables 2.5 and 2.6. Binary compounds with less electronegative element chlorine might be expected to show a slightly different range of oxidation states. The elements second and third rows they show maximum oxidation state for example MO_4 (M = Os or Ru) with oxygen and Re(+VII) in ReF_7 with fluorine Tables 2.5 and 2.6.

MAGNETIC PROPERTIES

One important characteristic of the heavier elements is that they tend to give low-spin compounds, which means that in oxidation states where there is an odd number of d-electrons there is frequently only one unpaired electron, and ions with an even number of d-electrons are often diamagnetic. There are two reasons for this intrinsically greater tendency to spin pairing. First, the $4d$ and $5d$ orbitals are spatially larger than $3d$ orbitals so that double occupation of an orbital produces significantly less inter electronic repulsion. Second a given set of light atoms produces longer splittings of $5d$ than $4d$ orbitals and in both larger splitting than for $3d$ orbitals.

Table 2.4 Oxidation states of $4d$ and $5d$ elements.
Second transition series

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
								+1	
					+2		+2	+2	+2
+3		+3	+3		+3	+3	(+3)	(+3)	
	+4		+4	+4	+4	+4	+4		
		+5	+5		+5				
			+6	(+6)	+6	+6	+6		
				(+7)	(+7)				
					(+8)				

Third transition series

La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
								+1	+1
			(+2)		(+2)	(+2)	+2		+2
+3			(+3)	(+3)	(+3)	+3	(+3)	+3	
	+4	(+4)	+4	+4	+4	+4	+4		
		+5	+5	+5	+5				
			+6	+6	+6	+6			
				+7					
				+8					

* The values in the parentheses are for the less common states.

Table 2.5 Oxides and halides of the second row

		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
+II	O			NbO				RhO	PdO	AgO^x	CdO
	F								PdF$_2$	AgF$_2$	CdF$_2$
	Cl		ZrCl$_2$		[Mo$_6$Cl$_8$]Cl$_4^c$				PdCl$_2$		CdCl$_2$
	Br		ZrBr$_2$?		[Mo$_6$Br$_8$]Br$_4^c$				PdBr$_2$		CdBr$_2$
	I		ZrI$_2$?		[Mo$_6$I$_8$]I$_4^c$				PdI$_2$		CdI$_2$
+III	O	Y$_2$O$_3$					Ru$_2$O$_3^b$	Rh$_2$O$_3$	(Pd$_2$O$_3$)^h?	(Ag$_2$O$_3$)	
	F	YF$_3$		(NbF$_3$)^c	MoF$_3$		RuF$_3$	RhF$_3$	Pd[PdF$_6$]		
	Cl	YCl$_3$	ZrCl$_3$	NbCl$_3^c$	MoCl$_3^m$		RuCl$_3$	RhCl$_3$			
	Br	YBr$_3$	ZrBr$_3$	NbBr$_3^c$	MoBr$_3$		RuBr$_3$	RhBr$_3$			
	I	YI$_3$	ZrI$_3$	NbI$_3^c$	MoI$_3$		RuI$_3$	RhI$_3$			
+IV	O		ZrO$_2$	NbO$_2$	MoO$_2^m$	TcO$_{2m}$	RuO$_2$	RhO$_2$	(PdO$_2$)^h		
	F		ZrF$_4$	NbF$_4$	MoF$_4$		RuF$_4$	RhF$_4$	PdF$_4$		
	Cl		ZrCl$_4$	NbCl$_4^m$	MoCl$_4^m$	TcCl$_4$	RuCl$_4$				
	Br		ZrBr$_4$	NbBr$_4^m$	MoBr$_4$						
	I		ZrI$_4$	NbI$_4^m$	MoI$_4$?						
+V	O			Nb$_2$O$_5$	Mo$_2$O$_5$						
	F			NbF$_5$	MoF$_5$	TcF$_5$	RuF$_5$	(RhF$_5$)			
	Cl			NbCl$_5$	MoCl$_5$						
	Br			NbBr$_5$							
	I			NbI$_5$							
+VI	O				MoO3	TcO$_3$	(RuO$_3$)^h				
	F				MoF$_6$	TcF$_6$	RuF$_6$	RhF$_6$			
	Cl				(MoCl$_6$)	(TcCl$_6$)?					
	Br										
	I										
+VII	O					Tc$_2$O$_7$					
	F										
	Cl										
	Br										
	I										
Other compounds				Nb$_6$F$_{14}^c$ Nb$_6$I$_{14}^c$			RuO$_4$			Ag$_2$O AgF AgCl AgBr AgI	

Table 2.6 Oxides and halides of the third row

		La	Hf	Ta	W	Rc	Os	Ir	Pt	Au	Hg
+II	O			(TaO)					(PtO)^h		HgO
	F										HgF$_2$
	Cl		HfCl$_2$?		W$_6$Cl$_{12}^c$	[ReCl$_2$]		(IrCl$_2$)?	PtCl$_2$		HgCl$_2$

(Contd.)

		La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
	Br		$HfBr_2$?		$W_6Br_{12}{}^c$	$(ReBr_2)$			$PrBr_2$		$HgBr_2$
	I				$W_6I_{12}{}^c$	(ReI_2)			PtI_2		HgI_2
+III	O	La_2O_3				$Re_2O_3{}^h$		$Ir_2O_3{}^h$	$(Pt_2O_3)^h$?	Au_2O_3	
	F	LaF_3		$(TaF_3)^c$				IrF_3		AuF_3	
	Cl	$LaCl_3$	$HfCl_3$	$TaCl_3{}^c$	$W_6Cl_{18}{}^c$	$Re_3Cl_9{}^c$		$IrCl_3$	$PtCl_3$?	$AuCl_3$	
	Br	$LaBr_3$	$HfBr_3$	$TaBr_3{}^c$	$W_6Br_{18}{}^c$	$Re_3Br_9{}^c$		$IrBr_3$	$PtBr_3$?	$AuBr_3$	
	I	LaI_3	HfI_3		$W_6I_{18}{}^c$	$Re_3I_9{}^c$		IrI_3	PtI_3?		
+IV	O		HfO_2	TaO_2	$WO_2{}^m$	$ReO_2{}^m$	OsO_2	IrO_2	PtO_2		
	F		HfF_2		WF_4	ReF_4	OsF_4	IrF_4	PtF_4		
	Cl		$HfCl_2$	$TaCl_4{}^m$	WCl_4	$ReCl_4{}^m$	$OsCl_4$	$(IrCl_4)$	$PtCl_4$		
	Br		$HfBr_2$	$TaBr_4{}^m$	WBr_4	$ReBr_4$	$OsBr_4$		$PtBr_4$		
	I		HfI_2	$TaI_4{}^m$	WI_4?	ReI_4	OsI_4		PtI_4		
+V	O			Ta_2O_5	(W_2O_5)	(Re_2O_5)					
	F			TaF_5	$WF_5{}^d$	ReF_5	OsF_5	(IrF_5)	$(PtF_5)_4$		
	Cl			$TaCl_5$	WCl_5	$ReCl_5$	$OsCl_5$				
	Br			$TaBr_5$	WBr_5	$ReBr_5$					
	I			TaI_5							
+VI	O				WO_3	ReO_3	$(OsO_3)^h$	(IrO_3)	$(PtO_3)^h$		
	F				WF_6	ReF_6	OsF_6	IrF_6	PtF_6		
	Cl				WCl_6	$(ReCl_6)$?					
	Br				WBr_6						
	I										
+VII	O										
	F										
	Cl					Re_2O_7					
	Br					ReF_7	(OsF_7)				
	I										
Other compounds							OsO_4 $OsCl_{3.5}$		Pt_3O_4	Au_2O $AuCl$ AuI	$Hg_2F_2{}^m$ $Hg_2Cl_2{}^m$ $Hg_2Br_2{}^m$ $Hg_2I_2{}^m$

ZIRCONIUM AND HAFNIUM

Zirconium occurs widely over the earth's crust but not in very concentrated deposits. The major minerals are baddeleyite, ZrO_2 and Zircon, $ZrSiO_4$. Hafnium is found in Nature in all zirconium minerals in the range of a percent of the Zirconium content extraction methods. Zr is made by Kroll process. Hf always occurs with Zr. There chemical properties are almost same. Separation of two elements is difficult. But now they can be separated effectively by ion exchange or solvent extraction. Zr and Hf are separated by solvent extraction of their nitrates into tri-n butyl phosphate or thiocyanates into methylisobutyl ketone. Alternatively the elements can be separated by ion exchange of an alcoholic solution of tetrachlorides on silica gel columns. On eluting the column with an alcohol/HCl mixture, the Zr comes off first.

Properties and Uses

Like titanium both Zr and Hf are metal, hard and corrosion resistant and their melting point 1855°C and 2222°C respectively. They are resistant to acids and they are best dissolved in HF where the formation of anionic fluoro complexes is important in the stabilization of solutions. Zr reacts with air at high temperature to give a mixture of nitride, oxide and oxide-nitride Zr_2ON_2.

Zr is used for cladding. Zr is also used to make alloys with steel and Zr/Nb alloy is an important superconductor. The very high absorption of thermal neutrons by Hf is turned to good use. Hf is used to make control rods for regulating the free neutron levels in the nuclear reactors used in submarines.

Compounds of Zr and Hf

Zr and Hf show oxidation states (+II), (+III) and (+IV). (+IV) is the stable oxidation for both the metals. So most of compounds are known in (+IV) oxidation states.

Oxides

On addition of hydroxide to Zirconium (IV) solutions a gelatinous precipitate $ZrO_2.nH_2O$ is formed. Where n is variable. ZrO_2 and HfO_2 are stable white solids, non-volatile and rendered refractory by strong ignition. On strong heating ZrO_2 becomes very hard and its high melting point of 2700°C and its resistance to chemical attack make it useful for making high temperature crucibles and furnace lining. If the solids have been prepared dry or have been heated, they do react with acids.

ZrO_2 and HfO_2 are basic. Like TIO^{2+}, ZrO^{2+} exists in solution and form polymeric species in solution. $ZrO(NO_3)_2$ forms an oxygen bridged chain structure and soluble in water. If the ZrO_2 and HfO_2 are fused with the appropriate quantities of other metal oxides at 1000°C–2500°C. Zinconates and hafnates are formed. These are mixed oxides.

Halides

All the halides of the type MX_4 (where M = Zr or Hf and X = F, Cl, Br, I) are known.

$ZrCl_4$. It can be prepared by the chlorination of heated Zirconium, Zirconium carbide and a mixture of ZrO_2 and charcoal. It is white solid, subliming at 331°C.

It fumes in moist air and hydrolyzed vigorously by water. Hydrolysis proceeds only part way at room temperature, affording the stable oxide chloride.

$$ZrCl_4 + 9H_2O \longrightarrow ZrOCl_2.8H_2O + 2HCl$$
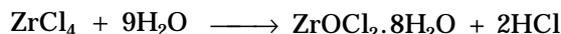
$ZrCl_4$ and $HfCl_4$ also combine with donors such as ethers, $POCl_3$ and CH_3CN and with Cl^- ions to form six-co-ordinate species.

$$ZrCl_4 + 2Cl^- \longrightarrow \left[ZrCl_6\right]^{2-}$$

$ZrCl_4$ and $HfCl_4$ also combine with diarsines to form $ZrCl_4$ $(dias)_2$ which has the dodecahedral type eight-coordinate structure. $ZrCl_4$ reacts with carboxylic acid at 100°C to give $Zr(RCO_2)_4$. The compounds $ZrBr_4$, ZrI_4, $HfBr_4$ are similar to $ZrCl_4$. ZrF_4 is a white solid subliming at 903° which unlike other halides, is insoluble in donor solvents. Hydrated $ZrF_4.1$ or $3H_2O$ can be obtained from HF-HNO_3 solution.

Zr^{4+} is relatively large, highly charged and spherical with no partly filled shell to give it stereochemical preferences. Therefore, Zr(iv) compounds exhibit high coordination number for example, Li_2ZrF_6, $CuZrF_6.4H_2O$, ZrF_7^{3-}. ZrF_7^{3-} has two different structures (1) pentagonal bipyramid Na_3ZrF_7 (2) capped trigonal prism $(NH_4)_3 ZrF_7$. $[Zr_2F_{12}]^{4-}$, $Cu_2ZrF_8.12H_2O$ and $Cu_3Zr_2F_{14}$ are also known. With oxygen ligands high coordination number and varied stereochemistry are also prevalent. Thus $M_6^I [Zr(OH)_2(CO_3)_6].nH_2O$ contain OH bridged binuclear units in which each Zr atom is in dodecahedral 8-coordination and ZrO_7 pentagonal bipiramids are found in $ZrO_2 (OH) OMO_2O_4(OH)_5$.

AQUEOUS CHEMISTRY AND COMPLEXES

ZrO_2 is more basic as compared to TiO_2, therefore it is virtually insoluble in an excess base. The aqueous chemistry of Zr^{4+} is well known since it is doubtful that hydrolysis of Zr^{4+} takes place. The hydrolyzed ion is often known as Zirconyl ion and written ZrO^{2+}. The most important Zirconyl salt is $ZrOCl_2.8H_2O$ which crystallizes from dil. HCl and contain $[Zr_4(OH)_8|H_2O_{16}]^{8+}$.

In acid solutions except concentration. HF, where ZrF_6^{2-} and HfF_6^{2-} are present. $[Zr_3(OH)_4]^{8+}$ and $[Zr_4(OH)_8]^{8+}$ are exist in 1–2M perchloric acid.

Chelating agent such as EDTA and NTA form complexes with Zr^{IV}, the $[Zr(N(CH_2COO)_3)_2]^{2-}$ ion has been shown to be dodecahedral.

$M(acac)_2X_2$ and $M(acac)_3X$ type of complexes were known with acetylacetonate. The former have cis octahedral whereas the latter one 7-coordinate. Zr^{IV} forms complexes or with carboxylate, $Zr(OCOR)_4$, the tetratries (acetylacetonate), the oxalate. It also forms covalent compounds with NO_3^-.

$$ZrCl_4 + 4 N_2O_5 \xrightarrow{30°} Zr(NO_3)_4.XN_2O_5.YN_2O_4 + 4NO_2Cl$$

LOWER OXIDATION STATES

The chemistry of lower oxidation states is so far limited to non-aqueous chemistry of lower halides and some complexes thereof.

The halides of Zr in trivalent states such as $ZrCl_3$, $ZrBr_3$ and ZrI_3 are well known. These can be prepared, by reduction of tetrahalides with H_2, $2ZrCl_4 + H_2 \rightarrow 2Zr Cl_3 + 2HCl$. HfI_3 is isotypic. ZrX_3 compounds react readily at room temperature with bases such as Pyridine, bipyridine, phenanthroline and $CH_3 CN$ to form $ZrX_3.2Py$, $2ZrX_3.5CH_3CN$. The trihalides of Hf are nonstoichiometric $HfI_{3.0}$ to $HfI_{3.5}$.

The lower chlorides of Zr and Hf have recently been carefully studied. $ZrBr_2$ and ZrI_2 are well known.

Organometallic Compounds

Most of the Organometallic compounds of Zr and Hf are similar to their Ti analogs. The general formula is $(\eta^4-C_5H_5)_2ZrX_2$.

NIOBIUM AND TANTALUM

Niobium and tantalum occur together. Niobium is 10–12 times more abundant in the earth crust than tantalum. The main commercial source of both are the columbity–tantalite] $(FeMnNb_2O_6)$ $Fe,MnTa_2O_6)$ series of minerals. The most important mineral is Pyrochlorite $CaNaNb_2O_6F$. However 60% of Ta is recovered from the slag from extracting Sn. The ores

are dissolved either fusion with alkali or in acid. Formally the separation of Nb and Ta was achieved by treatment with a solution of HFNb forms a soluble K_2 [NbOF$_5$] and Ta forms insoluble K_2[TaF$_7$]. Separation is now performed by solvent extraction from dil. HF to methyl isobutyl ketone. The metals are obtained either by reducing pentaoxide with Na, or by electrolysis of molten fluoro complexes such as K_2[NbF$_7$].

Properties and Uses

Nb and Ta are silvery coloured metals with high melting points. The pure Nb and Ta are moderately soft and ductile, but traces of impurities make them harder and brittle. They are extremely resistant to corrosion due to the formation of oxide film on the surface. At room temperature they are not affected by air, water or acids other than HF with which they form complexes. Nb and Ta both dissolve in fused alkali. Nb and Ta do not form positive ion. Thus though Nb and Ta are metals, their compounds in the (+V) state are mostly, volatile and readily hydrolyzed. Nb_2O_5 and Ta_2O_5 are amphoteric. They have only weak acidic properties. Niobates and tantalates are only formed by fusing with NaOH.

Nb is used in various stainless steels, and Nb/steel is used to encapsulate the fuel elements for some nuclear reactors. A Nb/Zr alloy is a superconductor at low temperatures, and is used to make wire for very powerful electromagnets. Ta is used to make capacitors for the electronics industry. Because it is not rejected by the human body it is valuable for making metal plates screws and wire for repairing badly fractured bones. TaC is one of the highest melting solids known (is 3800°C).

Compounds

Nb and Ta react with all of the halogens on heating to give pentahalides MX_5. The range of halides is given in Table 2.7. All the halides are volatile, covalent and hydrolyzed by water.

Table 2.7 Halides of Niobium

+III	+IV	+V
NbF$_3$	NbF$_4$	NbF$_5$
NbCl$_3$	NbCl$_4$	NbCl$_5$
NbBr$_3$	NbBr$_4$	NbBr$_5$
NbI$_3$	NbI$_4$	NbI$_5$
	--	TaF$_5$
TaF$_3$	TaCl$_4$	TaCl$_5$
TaCl$_3$	TaBr$_4$	TaBr$_5$
TaBr$_3$	TaI$_4$	TaI$_5$

+V Halides

Nb and Ta form penta halides. These may be formed by direct reaction of the elements or by the reaction oxides.

$$M_2O_5 + F_2 \longrightarrow MF_5,$$

$$NbCl_5 \text{ or } TaCl_5 + F_2 \longrightarrow MF_5$$

$$\text{NbCl}_5 \text{ or TaCl}_5 + \text{HF} \longrightarrow \text{MF}_5$$
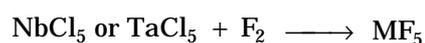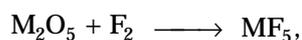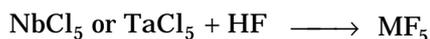
NbF_5 and TaF_5 form cyclic tetramers with four octahedra joined in this way (Fig. 2.2). Solid NbCl_5 and TaCl_5 are dimeric with two octahedra joined by sharing two corners (Fig. 2.2b). All the pentahalides can be sublimed under an atmosphere of the appropriate halogen. Pentafluorides react with F^- to give MF_6^-.

$$\text{MF}_5 + \text{F}^- \longrightarrow \left[\text{MF}_6\right]^-$$
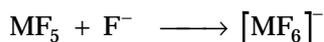
If the conc. of F^- is higher than the complexes $[\text{NbOF}_5]^{2-}$ $[\text{NbF}_7]^{2-}$ and $[\text{TaF}_7]^{2-}$ are formed. The structure of seven-coordinate species are capped trigonal prism. Ta forms $[\text{TaF}_8]^{3-}$ with a square antiprism whereas, Nb forms $[\text{NbOF}_6]^{3-}$. This inability of Ta to form oxohalides has been used to separate Nb and Ta. Fluoride are white but other halides are coloured due to change transfer.
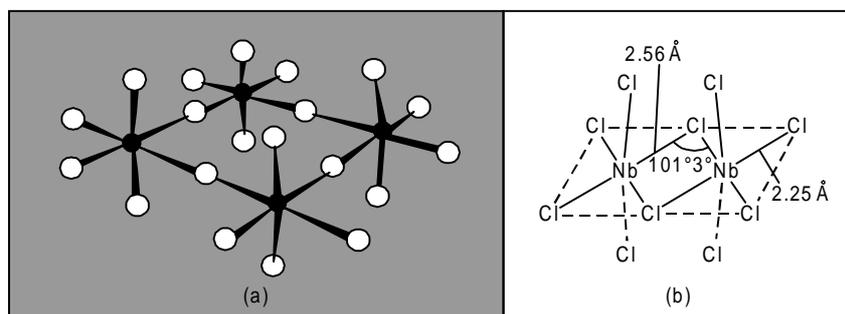
Fig. 2.2 The tetrameric structures of NbF_5 and TaF_5. The dinuclear structure
of crystalline $\text{Nb}_2\text{Cl}_{10}$. The octahedra are distorted.

(+IV) Halides

The tetrahalides are formed by the reduction of pentahalides with H_2, Al, Nb or Ta.

$$\text{NbX}_5 \text{ or TaX}_5 \xrightarrow[\text{H}_2, \text{ Al, Nb or Ta}]{\text{reduce with}} \text{MX}_4$$
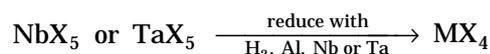
NbF_4 is black paramagnetic nonvolatile solid made up of regular octahedra joined in chain by their edges. Other tetrahalides are brown-black solids and are diamagnetic. This suggests extensive metal-metal interaction. NbI_4 the structure is a chain of octahedra joined by their edges. NbCl_4 is similar. Tetrahalides tend to disproportionate.

$$2\text{TaCl}_4 \xrightarrow{400°C} \text{TaCl}_3 + \text{TaCl}_5$$

They hydrolyze by water

$$4\text{TaCl}_4 + 5\text{H}_2\text{O} \longrightarrow \text{Ta}_2\text{O}_5 + \text{TaCl}_3 + 10\text{HCl}$$
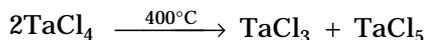
(+III) Halides

All the trihalides are known except TaI_3. They are reducing, have a d^1 configuration. They are brown or black in colour. The trihalides of Nb and Ta are typically nonstoichiometric. In NbCl_3 the Nb ions occupy octahedral holes in a distorted hexagonal close packed array of Cl^- ions in such a way that niobium atoms in three adjacent octahedral are close enough to bonded together into metal cluster.

Lower Halides

High temperature reduction of the pentahalides. NbX_5 and TaX_5 with Na or Al give a series of lower halides such as M_6Cl_{14}, M_6I_{14}, Nb_6F_{15}, Ta_6Cl_{15}, Ta_6Br_{15} and Ta_6Br_{17}. These are all based on the $[M_6X_{12}]^{n+}$ unit. For example

$$Nb_6Cl_{14} \xrightarrow[\text{water}]{AgNO_3} 2AgCl + [Nb_6Cl_{12}]^{2+}$$
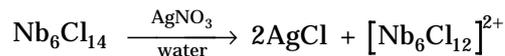
These are known as cluster. The cluster can be oxidized:

$$[M_6X_{12}]^{2+} \longrightarrow [M_6Cl_{12}]^{3+} \longrightarrow [M_6Cl_{12}]^{4+}$$
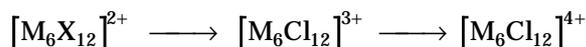
Oxides

The metals all react with O_2 at elevated temperatures and give pentaoxide M_2O_5. The main oxides formed are shown in Table 2.8.

Table 2.8 Oxides

(+II)	(+III)	(+IV)	(+V)
NbO	–	NbO_2	Nb_2O_5
TaO	–	TaO_2	Ta_2O_5

Pentaoxides of Nb_2O_5 and Ta_2O_5 are commonly made by ignition of other Nb or Ta compounds in air. Nb_2O_5 and Ta_2O_5 are colourless (d°). Nb_2O_5 and Ta_2O_5 react with HF. They form niobates and tetalates when fused NaOH. These precipitate the hydrated oxide at PH 7 and 10 respectively and the only isopoly ion found in solution in $[M_6O_{19}]^{8-}$.

Organometallic Compounds

Nb and Ta form cyclopentadienyl compounds such as $[Nb(\eta^5-C_5H_5)_2 \ (\eta^1-C_5H_5)_2]$. $[Nb(\eta^5-C_5H_5)_2 \ (\eta^1.C_5Hd_5)_2 \ Cl_3]$ and $[Nb(\eta^5-C_5H_5)_2 \ (\eta^1-C_5Hd_5)_2Cl_3]$.

MOLYBDENUM AND TUNGSTEN

Mo and W are quite rare. Abundance of Mo and W in the earth's crust by weight is 1.2 ppm.

Molybdenum occurs chiefly as molybdenite MoS_2, but also as molybdates such as Wulfenite ($PbMoO_4$) or $MgMoO_4$. Tungsten is found almost exclusively in the form of tungstate, the chief ore being Wolframite ($FeWO_4$ and $MnPO_4$), scheelite ($CaWO_4$) and stolzite ($PbWO_4$).

The small amounts of MoS_2 in ores are concentrated by the foam flotation process. This is converted into MoO_3. It is reduced to metal with hydrogen. Reduction with carbon should be avoided because it form carbides instead of metal.

Tungsten ores are concentrated by mechanical and magnetic processes and the concentrate attacked by fusion with NaOH. The cooled melts are leached with water, giving solutions of sodium tungstate from which hydrous WO_3 is precipitated on acidification. The hydrous oxide is dried and reduced to metal by hydrogen.

Properties and Uses

The metals are hard and have very high melting and low volatility (Tables 2.2 and 2.3). The melting point of W is next to carbon. In the powder form in which they are first

obtained both metals are dull grey, but when converted into the massive state by fusion are lustrous silver white substances of typically metallic appearance in properties. They have electrical conductance 30% that of Ag. They are extremely refractory. The melting points of Mo and W are 2610°C and 3418°C respectively.

These metals do not react with air at room temperature. However, on strong heating both form oxide of the type MO_3 (M = Mo or W).

$$2Mo + 3O_2 \longrightarrow 2MoO_3$$
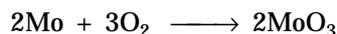
They also combine with Cl_2 to give MCl_6. They react with F_2 at room temperature to form MF_6.

$$Mo + 3Cl_2 \longrightarrow MoCl_6$$

Neither metal is readily attacked by acids. Con. HNO_3 initially attacks Mo but metal surface is soon passivated. Both metals can be dissolved in a mixture of con. HNO_3 and HF. W dissolves slowly. Aqueous alkali does not react with the metals however, oxidizing alkaline such as fused KNO_3–NaOH or Na_2O_2 attack them rapidly.

As a result of lanthanide contraction, there is a close similarity in the size and properties. The difference in properties is greater as compared to Zr and Hf. Thus Mo and W can be easily separated by using conventional scheme *i.e.,* qualitative analysis. $WO_3(H_2O)_n$ is precipitated in the 1st group and molybdates are reduced by H_2S in IInd-group where MoS is precipitated out.

The chief uses of both the metals are in the production of alloy steel, even small amounts cause tremendous increases in hardness and strength. High speed steels which are used to make cutting tools and remain hard even at red heat. Tungsten is also used for lamp filaments. The element give hard, refractory and chemically inert industrial compounds with B, C, N or Si on direct reaction at high temperatures. Tungsten carbide is also used for tipping cutting tools.

Compounds +VI oxidation State

A number of the stable compounds of Mo and W are known in (+VI) oxidation state.

Oxides

Oxides of MoO_3 and WO_3 are known in (+VI) oxidation state. They are formed by heating the metal in air.

$$Mo + Air \longrightarrow MoO_3$$

They are acidic in nature therefore, except HF they are not attacked by acids. They dissolve in NaOH by forming MoO_4^{2-} and WO_4^{2-} ions. MoO_3 is a white solid at room temperature but becomes yellow when hot and melting at 795°C to a deep yellow liquid. It is anhydride of molybdic acid, but it does not form hydrates directly. MoO_3 has a rare type of layer structure in which each molybdenum atom is surrounded by a distorted octahedron of oxygen atoms. WO_3 is lemon yellow solid. M.P. 1473°C.

MoO_3 and WO_3 differ from CrO_3 in several ways:

1. MoO_3 and Wo_3 are stable and having no oxidizing properties.

2. They are insoluble in water.

3. They have high melting points.

    CrO_3 (197°C) MoO_3 (795°C) and WO_3 (1473°C)

4. Their colour and structures are different.

Mixed Oxides

Several mixed oxides can be made by fusing MoO_3 or WO_3 with group I or II oxides. These contain chains or rings of MoO_6 or WO_6 octahedra. moist WO_3 turns slightly blue on exposure to U.V. light. Mild reduction of aqueous suspensions of MoO_3 and WO_3 or acidic solutions of molybdates $K_2Mo_4O_{13}$ or tungstate $K_2W_4O_{13}$ also gives a blue colour. The blue oxide so produced are thought to have Mo or W in oxidation states of (+VI) and (+V) and contain some OH^- instead of O^{2-} to balance the charge.

Halides and Oxyhalides

The MF_6 type compounds are volatile colourless and diamagnetic. MoF_6 and WF_6 are quite stable. They show low melting points (MoF_6, 17.4°C and WF_6 1.9°C) and easily hydrolyzed. MoF_6 is reduced easily and attack organic matter while WF_6 is less active. $MoCl_6$ was claimed in 1967 as a black powder very sensitive to water and prepared by the action of $SOCl_2$ on MoO_3. WCl_6 is formed by the direct chlorination of metal. It is moderatly volatile, monomeric in vapour and soluble in organic solvents such as CS_2, CCl_4 Alcohol etc. It reacts slowly with cold water but rapidly with hot water to give tungstic acid. It is used as catalyst for alkylation of benzene. W Br_6 can also be obtained by direct halogenation of metal. It is dark blue solid.

Molybdenyl chlorides are covalent and readily decomposed by water. Tungstenyl chloride hydrolyze less readily.

(+V) Oxidation State
Oxides

MO_2O_5, a violet solid soluble in warm acids. It is prepared by heating the required quantity of finely divided molybdenum with MoO_3 at 750°C. On addition of NH_3 a brown precipitated $MnO(OH)_3$ is formed. On heating it gives Mo_2O_5.

Halides

Treatment of molybdenum carbonyl with fluorine diluted in nitrogen at –75°C gives a product of composition Mo_2F_9. On heating Mo_2F_9 at 150°C gave the nonvolatile MoF_4 as a residue and volatile MoF_5 which condenses in a cooler regions of the apparatus. MoF_5 is also obtained by the reactions.

$$5MoF_6 + Mo(CO)_6 \xrightarrow{25°C} 6MoF_5 + 6CO$$

$$Mo + 5MoF_6 \longrightarrow 6MoF_5$$

$$Mo + F_2(dil) \xrightarrow{400°C} MoF_5$$
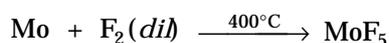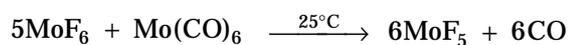
WF_5 is obtained by quenching the products of reaction of W with WF_6 at 800–1000°C. It disproportionates above 320°C into WF_4 and WF_6. Crystalline MoF_5 and WF_5 have the

tetrameric structure common to many pentaflourides. Heating of Mo with Cl_2 gives Mo_2Cl_{10}. This is soluble in benzene and other organic solvents. It exists as monomeric $MoCl_5$ in solution, but dimerize to Mo_2Cl_{10} in the solid. Mo_2Cl_{10} is used as the starting point for making other Mo compounds (scheme 1 Fig. 2.3). It is rapidly hydrolyzed by water, and removes O from oxygenated solvents, forming oxychlorides. Mo_2Cl_{10} is paramagnetic (M = 1.6 B.M.), indicating that there is one unpaired electron and thus no metal-metal bonding.
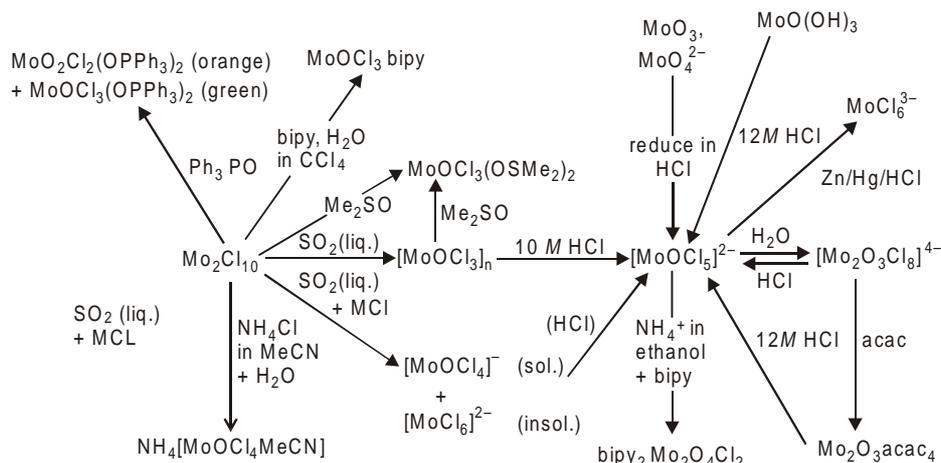
Fig. 2.3 Some preparations and reactions of molybdenum pentachloride and of oxomolybdenum compounds.

Green WCl_5 and black WBr_5 are prepared by direct halogenation, the condition being critical, especially the temperature.

(+IV) Oxidation State

Oxide

Molybdenum (IV) oxide MoO_2 is obtained by reducing MoO_3 with hydrogen or NH_3 below 470°C (above the temperature reduction proceed to metal) and by reaction of Mo with steam at 800°C. It is a brown violet solid with a coppery luster, in soluble in nonoxidizing mineral acids but soluble in con. HNO_3 with oxidation of the Mo(IV) – Mo(VI). The structure is similar to that of Rutile but so distorted that strong Mo–Mo bonds are formed. WO_2 is similar.

Halides

The tetrahalides include MoF_4 and WF_4. The MoF_4 is obtained on disproportionation of Mo_2O_9. Both can be prepared by the reduction of hexahalides with hydrocarbon *i.e.,* C_6H_6 at is 110°C. Both are nonvolatile. $MoCl_4$ which is very sensitive to oxidation and hydrolysis exists in two forms.

$$MoCl_5 \xrightarrow{\text{Hydrocarbons}} \alpha\ MoCl_4$$
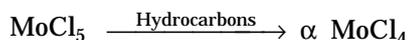
On heating α-$MoCl_4$ at 250°C in the presence of $MoCl_5$, it is changes to β-form. α-$MoCl_4$ has partial spin pairing through Mo–Mo interactions whereas the β-form has an hcp away of Cl atoms with Mo atoms so distributed in octahedral interstices. That no Mo–Mo bond is formed. WCl_4 is best obtained by reducing WCl_6 with Al in a thermal gradient. It disproportionate at 500°C to $WCl_2 + 2WCl_5$. $MoBr_4$, WBr_4 and WI_4 all exist but are not well known.

+III Oxidation State

Mo(III) and W(III) do not form oxides, but all the halides are known except WF_3 (Table 2.9a). These compounds do not contain simple ions. Mo(III) compounds are fairly stable. However, they oxidize in air and hydrolyse in water. They react with halide ion to form octahedral complexes.

$$MoCl_3 + 3Cl^- \longrightarrow [MoCl_6]^{3-}$$
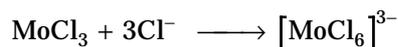
Two forms of $MoCl_3$ are known.

Reaction of $MoCl_3$ are given Fig. 2.5. One with cubic close packing of chlorate atom, the other based on hexagonal close packing.

W(III) compounds are unstable. WCl_3 is really W_6Cl_{18} and forms a cluster compound $[W_6Cl_{12}]^{6+}$. W_6Br_{18} also forms a cluster compound $[W_6Br_8]^{6+}$.

+II Oxidation State

Mo and W do not form difluorides, but other six (+II) halides Fig. 2.4 are known. They are usually made by reduction or thermal decomposition of higher halides. They do not exist as simple ion but form cluster compounds instead. $MoBr_2$ is really $[Mo_6Br_8]Br_4.2H_2O$. All Six dihalides have same structure based on cluster $[M_6X_8]^{4+}$ unit ion an octahedral cluster of six metal atomes (Fig. 2.5). There is a strong M-M bonding. These compounds are diamagnetic. Mo_6Cl_{12} is not reducing whereas W_6Cl_{12} is reducing in solution. $Mo_2(CH_3COO)_4$ is a compounds which is also diamagnetic due to quadrupole interaction.
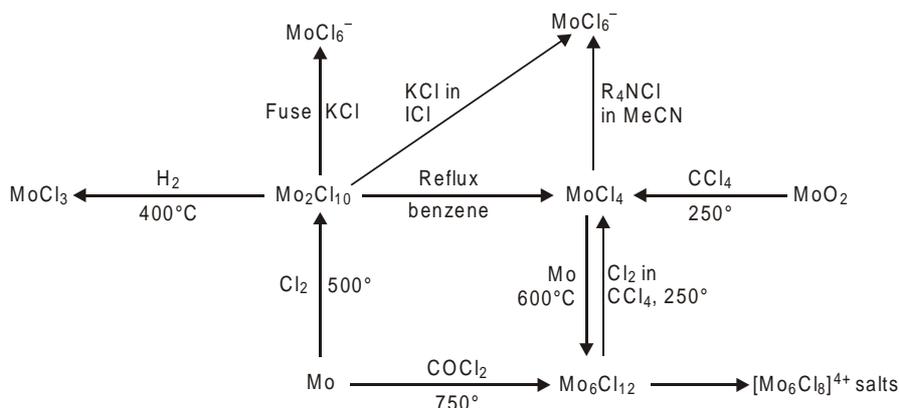
Fig. 2.4 Preparation of molybdenum chlorides and chloro complexes.
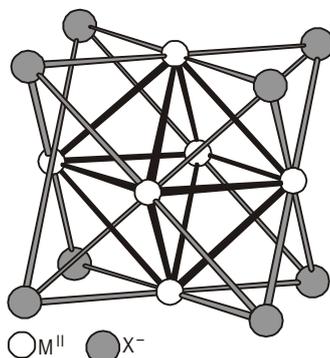
Fig. 2.5 $[M_6X_8]^{4+}$ clusters with X bridges over each face of the octahedron of metal ions.

Table 2.9 Halides of Group VI (mp°C)

State	Fluorides	Chlorides	Bromides	Iodides
+6	MoF_6 colourless (17.4°) bp 34°	($MoCl_6$) black		
	WF_6 colourless (1.9°) bp 17.1°	WCl_6 dark blue (275°) bp 346°	WBr_6 dark blue (309°)	
+5	MoF_5 yellow (67°) bp 213°	$MoCl_5$ black (194°) bp 268°		
	WF_5 yellow	WCl_5 dark green (242°) bp 286°	WBr_5 Black	
+4	MoF_4 pale green	$MoCl_4$ black	$MoBr_4$ black	MoI_4?
	WF_4 red-brown	WCl_4 black	WBr_4 black	WI_4?
+3	MoF_3 brown (>600°)	$MoCl_3$ very dark red (1027°)	$MoBr_3$ green (977°)	MoI_3 black (927°)
		WCl_3 red	WBr_3 black ($d > 80°$)	WI_3
+2		$MoCl_2$ yellow ($d > 530°$)	$MoBr_2$ yellow-red ($d > 900°$)	MoI_2
		WCl_2 yellow	WBr_2 yellow	WI_2 brown

MOLYBDATES AND TUNGSTATES

On acidification the solution of molybdates or tungstate, they condensed and give a range of various polymolybdates or polytungstate. Below pH 1 a hydrated oxide $MoO_3.2H_2O$ yellow or $WO_3.2H_2$ (White) are precipitated out. The formation of polyacids is a prominent feature of the chemistry of Mo and W. The polyanions contain MoO_6 or WO_6 octahedra. When one joined together in a variety of ways by sharing of edges but not faces. The poly acids of Mo and W are classified into two main groups.

1. Isopolyacids, where the anions which condense together are all of the same type for example all MoO_6 groups or all WO_6 groups.

2. Heteropolyacids, where two or more different types of anion condense together for example molybdates or tungstate groups with phosphate, solicate or borate groups.

The isopolyacids Fig. 2.6a of Mo and W are not completely understood. It is quite difficult to study them because extent or hydration and protonation of various species in solution are not known. The relationship between the stable species so far known is.

$$[MoO_4]^{4-} \xrightarrow{\text{pH 6}} [Mo_7O_{24}]^{6-} \xrightarrow{\text{ph 1.5–2.9}} [Mo_8O_{26}]^{4-} \xrightarrow{\text{pH < 1}} MoO_3 2H_2O$$

Normal molybdate   Polymolybdates   Polymolybdates   hydrated oxide

The structures of polymolybdates are confirmed by X-ray crystallography.

Tungstate

$$[WO_4]^{2-} \underset{\text{Biol OH}^-}{\overset{\text{pH 6.7}}{\rightleftharpoons}} [HW_6O_{21}]^{5-} \overset{\text{Slow}}{\rightleftharpoons} [W_{12}O_{41}]^{10}$$

or

$$[W_{12}O_{36}(OH)_{10}]^{10-}$$

$$\downarrow \text{pH = 3.3}$$

$$[H_3W_6O_{21}]^{3-}$$

$$\downarrow \text{H}^+$$

$$\downarrow \text{pH < 1}$$

$$[H_2W_{12}O_{40}]^{6-}$$

$$WO_3.2H_2O$$
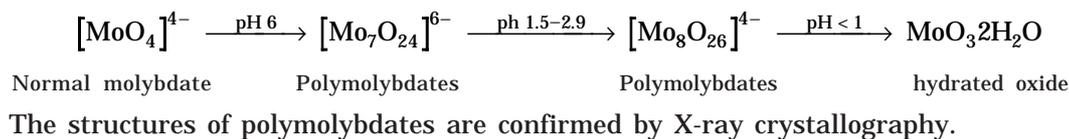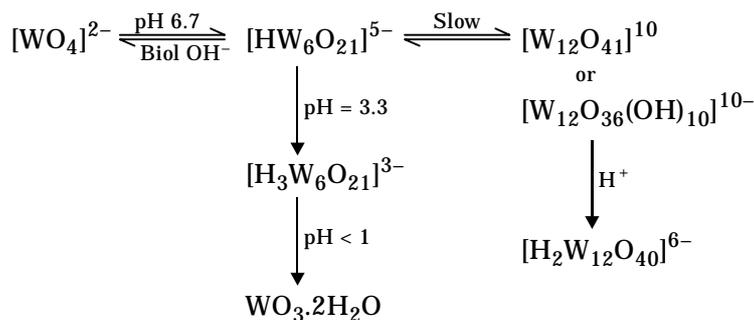
Heteropolyacids are formed if a molybdate or tungstate solution is acidified in the presence of phosphate, silicate or metal ion. The second anion provides a centre round which the MoO_6 or WO_6 octahedra condense, by sharing oxygen atom with other octahedra and with the central group. The central groups are oxoanions such as PO_4^{3-}, SiO_4^{4-} and BO_4^{3-} but other elements including Al, Ge, Sn, As, Sb, Sc, Te I and many of the transition elements will serve as the second group. The ratio of MoO_6 or WO_6 octahedra to P, Si, B or other central atom is usually 12:1, 9:1 and 6 : 1. A well known example of heterpolymolydate as $(NH_4)_3 [Mo_{12}O_{36}.PO_4]$. The structure of several heteropolyacids are known (Fig. 2.6).
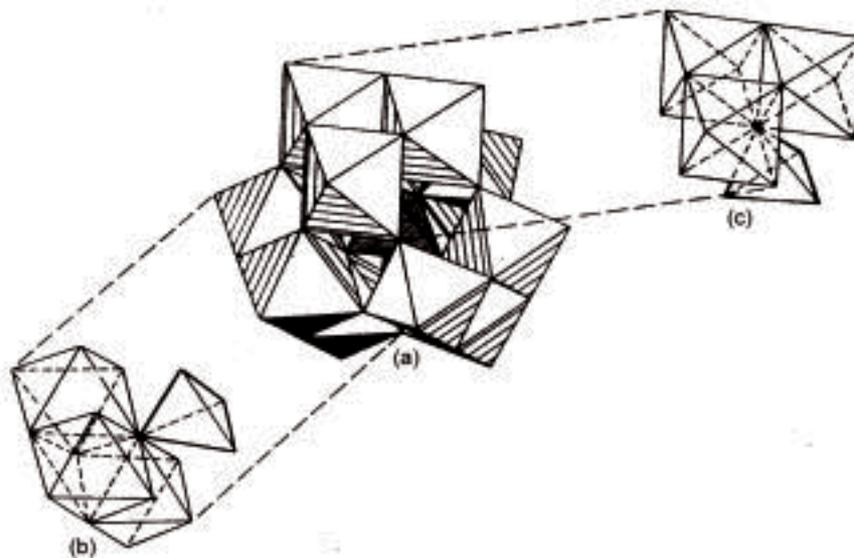
Fig. 2.6 The structues of two heteropoly anions: (a) 12-molybdophosphate or 12-tungstophosphate; (b) and (c) details of coordiantion of three MO_6 octahedra with one corner of the heteroatom tetrahedron.

Tungsten Bronze

The reduction of sodium tungstate with hydrogen at red heat gives a chemically inert substance with a bronze like appearance. Similar compounds are obtained by vapour phase reaction of alkali metals with WO_3. They are now made up by heating Na_2WO_4 with W metal.

Tungsten bronze are nonstochiometric substances of general formula $M^I_nWO_3$ (O < n ≤ 1). The colours vary greatly with composition from golden n is 0.7 yellow for $n ≈ 0.9$ to blue-violet n ≈ 0.3. Tungsten bronze with $n > 0.3$ are extremely inert and have semimetallic properties, especially metallic in cluster and good electrical conductivity which the charge carriers are electrons. Those with $n < 0.3$ are semiconductors. They are insoluble in water and resistant to all acid except HF. They can be oxidized to tungstate (VI) by oxygen in the presence of base.

$$4NaWO_3 + 4NaOH + O_2 \longrightarrow 4Na_2WO_4 + 2H_2O$$
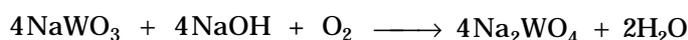
Structurally, the sodium tungsten bronzes may be regarded as defective. M^1WO_3 phases having the perovskite structure. In a defective phase $M^I_nWO_3$, there are $(1 – n)W^{VI}$ atoms and $(1 – n)$ of Na sites of the pure $NaWO_3$ phase are unoccupied. It appears that completely pure $NaWO_3$ has not been prepared, although phase with sodium enrichment upto perhaps n = ~0.95 are known. The cubic structure changes to rhombic and then triclinic for $n < ~$ 0.3. In the limit of $n = 0$ we have of course WO_3, Thus the actual range of composition of the tungsten bronze is approximately NaO_3WO_3 to $Na_{0.95}WO_3$.

The semimetallic properties of the tungsten bronzes are associated with the fact that no distinction can be made between W^V and W^{VI} atoms in the lattice, all W atoms appearing equivalent. Thus the n "extra" electrons per mole the distributed throughout the lattice, delocalized in energy bonds some what similar to those of metals.

Mo also forms bronze similar to W, but a high pressure is required to form them and the Mo compounds are less stable.

Preparation of some carbonyl containing molybdenum arsine and phosphine is given in Fig. 2.6(a).
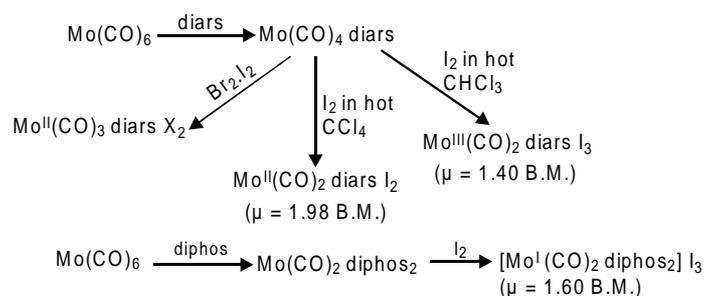
Fig. 2.6(a) Preparation of some carbonyl-containing molybdenum arsine and phosphine complexes.

TECHNETIUM AND RHENIUM

Technetium does not occur in nature and was the first manmade element. All the isotopes are radioactive. ^{99}Tc is one of the fission products of uranium. It is a β emitter with half-life of 2.1×10^5 years. It is obtained in kilogram quantities from spent fuel rods from reactors at nuclear power station. The rods may contain 6% Tc. These rods must be stored for several years to allow the short lived radioactive species to decay. Tc can be extracted by oxidation to Tc_2O_7

which is volatile. Alternatively solutions can be separated by in exchange and solvent extraction. It can be dissolved in water, forming TcO_4^- ion and crystallize as NH_4TcO_4 or $KTcO_4$. They can be reduced with H_2 to give metal. Tc has no commercial use ^{97}Tc and ^{98}Tc can be made by neutron bombardment of Mo, small amounts of Tc compounds are sometimes injected into patients to allow radiographic scanning of the liver and other organs.

Rhenium is a very rare element, and occurs in small amounts in molybdenum sulphide ores. Re is recovered as Re_2O_7 from the flue dust from roasting these ores. This is dissolved in NaOH, giving a solution containing ReO_4^- ion. The solution is concentrated and then KCl added to precipitate $KReO_4$. The metal is obtained by reducing $KReO_4$ or NH_4ReO_4 with H_2. It is used to make Pt-Re alloy which one used as catalyst for making low lead or lead free petrol. It is also used as catalyst for hydrogenation and dehydrogenation reactions. Due to its high m.p. (3180°C) it is used in thermocouple, electric furnace windings and mass spectrometer filaments.

Properties

Tc and Re are less reactive. They do not react with H_2O or non-oxidizing acids. They do not dissolve in HCl and HF, but they react with oxidizing acids, such as conc. HNO_3 and H_2SO_4 forming pertechnic acid $HTeO_4$ and perhenic acid $HReO_4$. Tc and Re undergoes similar reaction with H_2O_2 and bromine water. They get tarnish slowly in moist air, but powder metal is more reactive. Heating with O_2 gives Tc_2O_7 and Re_2O_7 which are low melting point (119.5°C) and 300°C respectively) and volatile. On heating with F_2 gives MF_6 and MF_7 (M = Tc or Re).

Compounds

Tc and Re form compounds in +VIII, +VI, V, VI, III, II oxidation states. Some compounds are also known in lower oxidation states.

+VII oxidation states

Many compounds such as M_2O_7, M_2S_7 MO_3^- ion oxhalides hydrides and ReF_7 are known in (+VII) oxidation states. The oxides Tc_2O_7 and Re_2O_7 are formed when metals are heated in air or oxygen. Both are yellow solids. Tc_2O_7 and Re_2O_7 have melting point 120°C and 220°C respectively. Tc_2O_7 is more oxidizing than Re_2O_7.

Both oxides are soluble in water and form $HTeO_4$ and $HReO_4$ ions which are colourless. Another form purhenic and known as TcO_4^- and ReO_4^- are tetrahederal. TcO_4^- and ReO_4^- react with H_2S to form Tc_2S_7 and Re_2S_7 respectively. TcO_4^- and ReO_4^- are stable in acidic metals.

$$KTcO_4 + K \xrightarrow{en} K_2[TcH_9]$$
$$KReO_4 + K \xrightarrow{en} K_2[ReH_9]$$
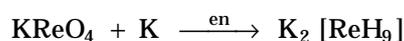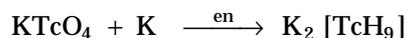
TcO_4^- and ReO_4^- are colourless because the charge transfer band occur at higher energy in the UV region. However solution $HTcO_4$ (Red solid) and $HReO_4$ yellow-green. These colours arise because the tetrahaderal ReO_4^- ion becomes less symmetrical when undissociated $HO-ReO_3$ is formed. Raman spectrum shows lines due to acid.

Halides

On heating Re with fluroine to form ReF_7. Tc forms only TcF_6. Several oxohalides are formed such as $ReOF_5$, ReO_2F_3, ReO_3F, TeO_3F and TcO_3Cl. These are pale yellow or colourless compounds. They exist either as low melting solid or liquid.

(+VI) State

Re(+VI) is known as the red coloured oxide ReO_3, but the existance of TcO_3 uncertain. The structure of ReO_3 is shown in Fig. 2.7a. Each metal is octahedrally surrounded by oxygen atoms. The halides TcF_6, ReF_6 and $ReCl_6$ are known. The fluorides are prepared by direct reaction of elements with fluorine, chlorides are prepared by treating fluorine with BCl_3. Fluoride and chlorides are yellow and green-black in colour. These compounds have low melting points ranging from 18°C to 33°C. They show magnetic moment lower than spin only value due to strong spin-orbit coupling.
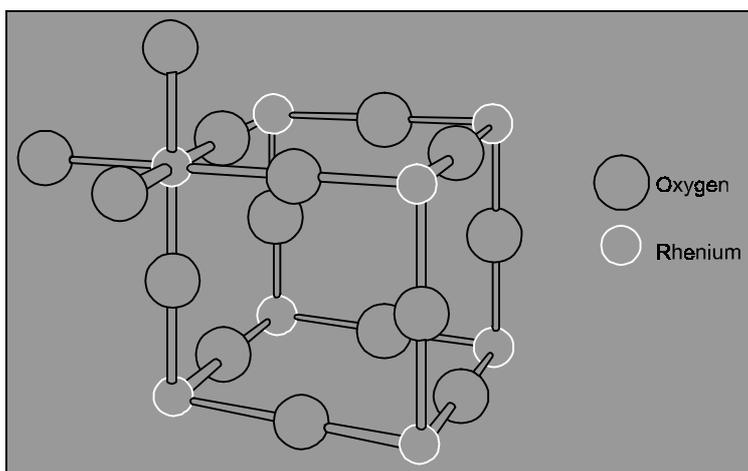
Fig. 2.7(a) The structure of ReO_3.

They are sensitive to water

$$ReFe_6 + H_2O \longrightarrow HRe^{(VII)}O_4 + Re^{(IV)}O_2 + HF$$

(V) Oxidation State

Tc is reluctant to form the (+V) state and Re(+V) compounds readily hydrolysed by water and at the same time they disproportionate.

$$3Re^{(V)}Cl_5 + 8H_2O \longrightarrow HReO_4 + ReO_2(H_2O)_n$$
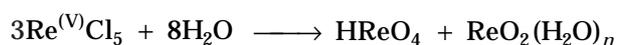
$ReCl_5$ is dimeric. The oxide Re_2O_5 is also known.

(+IV) state

It is second most stable state for Tc and Re.

The oxides TcO_2 and ReO_2 can be prepared by using the following methods.

(1) By burning the metal in a limited supply of oxygen.

$$M + O_2 \longrightarrow MO_2$$

(2) By heating M_2O_7 with M.

$$M_2O_7 + M \longrightarrow MO_2$$
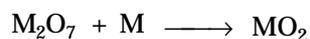
(3) Thermal decomposition of NH_4MO_4

(4) By reducing TcO_4^- and ReO_4^- with Zn/HCl. The hydrated oxides so form can be dehydrated by heating.

TcO_2 and ReO_2 are black and brown respectively. TcO_2 is insoluble in alkali but ReO_2 reacts with fused alkali, forming ReO_3^{2-}. Both the oxides have distorted rutile structure.

The sulphides TcS_2 and ReS_2 are known. These are obtained by heating heptasulphides with sulphur in vacuum. They have the advantage over heterogenous platinum metal catlysts ion that they are poisoned by sulphur compounds.

Halides

The known halides of the elements are shown in Table 2.9(b). $TcCl_4$ has a solid structure. It is permagnetic and there is metal-metal bonds. All four ReX_4 halides are known. $ReCl_4$ can be prepared by the action of $SOCl_2$ on $ReO_2.XH_2O$. However, the other methods are more important.

$$2ReCl_4 + SbCl_3 \longrightarrow 2ReCl_4 + SbCl_5$$

$$3ReCl_5 + Re_3Cl_9 \longrightarrow 6ReCl_4$$

$$2ReCl_5 + Cl_2C = CCl_2 \longrightarrow 2ReCl_4 + C_2Cl_6$$
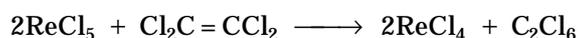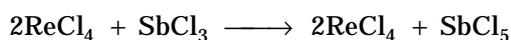
Table 2.9 Halides of Group 7

State	Fluorides	Chlorides	Bromides	Iodides
+7	ReF$_2$ 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 100°)	
+4	– 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	–	– [ReCl$_3$]$_3$ dark red (subl 500°) (d)	– [ReBr$_3$]$_3$ red-brown	– [ReI$_3$]$_3$ lustrous black (d on warming)

It is metastable and reactive and has a structure based on cubic close packed chlorine atoms. The adjacent octahdera have a common face and the Re-Re distance is only 237 pm, indicative of a bond.

Many complexes are known $[ReCl_6]^{2-}$ $(TcCl_6)^{2-}$ are octahedral and obtained by reduction of KMO_4^-.

$$MO_4^- \xrightarrow[+KI]{Con.\ HCl} [MCl_6]^{2-}$$
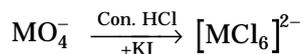
$ReCl_6$ is hydrolysed by water

$$[ReCl_6]^{2-} + H_2O \longrightarrow ReO_2.(H_2O)_n$$
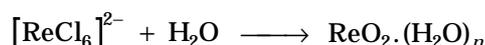
A number of other halo-complexes are known of these metals ion. For example $[MF_6]^{2-}$ $[MBr_6]^{2-}$ and $[MI_6]^{2-}$. They can be prepared by the reaction of hexachlroide with appropriate halogen acid. ReF_6 is stable in water. On treatment of $[MI_6]^{2-}$ with KCN. Cyano complexes *i.e.,* $[Tc(CN)_6]^{2-}$ and $[Re(CN)_6]^{2-}$ are formed. However Re is oxidized by CN^- and forms $[Re^V(CN)_8]^{3-}$.

+(III) States

Tc(III) is unstable but $Re_2O_3.(H_2O)_n$ and the heavier halides are known. The chloride, bromide, and iodide have been structurally characterized and their true molecular formulas are Re_3X_9. They are not isomorphous but all consist of Re_3X_9 units connected by sharing of X atoms as shown in Fig. 2.7b. Re_3X_9 units are metal-atom cluster compounds. The Re-Re distances are 248 pm and the M-M bonds are order 2. The simplest explanation of the double bonds between Re atoms is that each Re has nine atomic orbitals available for bonding (five d, one s and three p). The metal is surrounded by five ligands, leaving four unused orbitals. Assuming the unused orbitals are pure *d* or mainly *d* in character, there are 12 atomic orbitals for Re-Re bonding. If these are delocalized over the three atoms there will be six bonding MO's, corresponding to double bonds between each of the three Re atoms. Since all the electrons are paired, the clusters should be diamagnetic and this has been proved experimently.
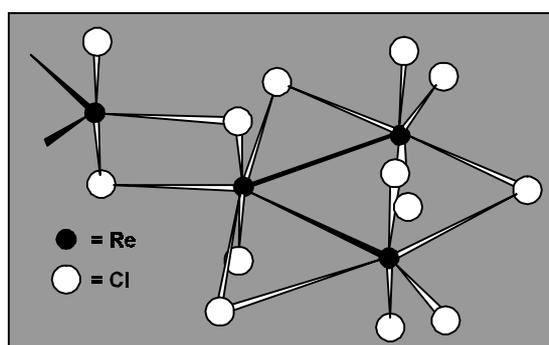

Fig. 2.7(b) The cluster structure of Re_3Cl_9.

When Re_3Cl_9 or Re_3Br_9 are dissolve in con. HCl or HBr, one, two or three halides ions may be attached to the isolated Re_3X_9 unit. For example $K^+[Re_3Br_{10}]$, $K_2[Re_3Br_{11}]$ and $K_3[Re_3Br_{12}]$.

Re(II) is not ionic and is formed only few complexes such as [Re (pyridine)$_2$Cl$_2$], ReCl$_2$ (dians) and ReCl(N$_2$) (diphos)$_2$]$^+$.

RUTHENIUM AND OSMIUM

Ru and Os are very rare. They are found in metallic state together with the platinum metals and the coinage metals (Cu, Ag and Au). The main sources are traces found in NiS/ CuS ores mined in South Africa, Canada and USSR. The largest sources are South Africa 45%, the USSR 44%, Canada 4%, the USA 2% and Japan 0.8%.

Abundance of the elements in the earth's crust by weight is Ru (.0001 ppm) and OS (0.005 ppm).

Ru and Os are obtained from the anode slime which accumulates in the electrolytic refining of Ni. This contains a mixture of platinum metals together with Ag and Au. The elements Pd, Pt, Ag and Au are dissolved in aquaregia and the residue contains Ru, Os, Rh and Ir. After a complex separaion Ru and Os are obtained as powders and powder forming techniques are used to give the massive metal.

Properties and Uses

Ru and Os are unaffected by mineral acids below ~ 100°C and are best dissolved by alkaline oxidizing fusion for example NaOH + Na$_2$O$_2$, KClO$_3$ etc.

Os is oxidized to OsO$_4$ by aqua-regia. The effect of lanthanide contraction is less pronounced in this part of the periodic table. Therefore, the similarities between the second and third row elements are not so close as one found in the earlier transition groups. Density of Os 22.57 g cm^{-3} and Ir is 22.61 g cm^{-3}. These elements are both scarce and expensive. Ru is used to alloy with Pd and Pt, and Os is also used to make hard alloys. All these metals have specific catalyst properties.

Compounds

Ru and Os form RuO$_4$ andOsO$_4$ which are in the (+VIII) state. Ru(III) and Os(+IV) are the most stable states. Ru(+V), Os(VI) and Os(VIII) are also reasonably stable.

Thus the usual trend is observed that on descending a group, the higher oxidation states become more stable.

(+VIII) state

OsO$_4$ is prepared either by burning finely divided metal in O$_2$, or by treating it with concentrated HNO$_3$. RuO$_4$ is prepared by oxidation with permagnet or bromate in H$_2$SO$_4$. It is less stable. Both are yellow coloured volatile solids with melting points of 25°C and 40°C respectively. Both the oxides are toxic, smell like ozone and are strongly oxidizing. They are slightly soluble in water but are soluble in CCl$_4$. Aqueous solution of OsO$_4$ are used as a biological stain because the organic matter reduces it to black OsO$_2$ or Os. OsO$_4$ vapour is harmful to the eyes for this reason. OsO$_4$ is also used in organic chemistry to add double bonds and give us glycols. The tetraoxides do not show basic properties and HCl reduces to trans [OsO$_2$Cl$_4$]$^{2-}$, [OsCl$_6$]$^{2-}$ and [Os$_2$OCl$_{10}$]$^{2-}$. RuO$_4$ dissolves in NaOH solution and liberats O$_2$. Ru (VIII) reduced to peruthenate (+VII) ion and ruthenate (+V) ion.

$$4RuO_4 + 4OH^- \longrightarrow 4RuO_4^- + 2H_2O + O_2$$

$$4RuO_4 + 4OH \longrightarrow 4RuO_4^{2-} + 2H_2O + O_2$$
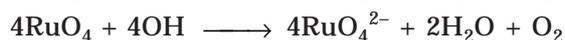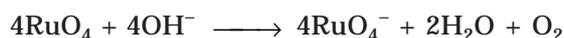
When RuO_4 is heated with HCl (g) and Cl_2 hygroscopic crystals of $(H_3O)_2 [RuO_2Cl_4]$ is produced. The ion is hydrolysed by water.

$$2Cs_2RuO_3Cl_4 + 2H_2O \longrightarrow RuO_4 + RuO_2 + 4CsCl + 4HCl$$

If RuO_4 in dil. H_2SO_4 reduced with Na_2SO_3 green solution $[RuO_2(SO_4)_2]^{2-}$ are obtained. It can also be formed by mixing Ru^{IV} solution with RuO_4 in dil H_2SO_4.

$$Ru^{IV} + Ru^{VIII} \longrightarrow Ru^{VI}$$

However, OsO_4 is more stable and is not reduced by NaOH, but form trans Osmetic ion.

$$OsO_4 + 2OH^- \longrightarrow [OsO_4(OH)_2]^{2-}$$

This reacts with NH_3 to give unusual nitride complex $[OsO_3N]^-$ and reduced trans $[OsO_2(OH_4]^{2-}$ by E + OH (+VI and +VII) state.

As discussed above the fusion of Ru and its compounds with alkali give $Ru^{VII}O_4^-$ or $Ru^{VI}O_4^{2-}$ ion. The tetrahedral RuO_4^{2-} ion is moderately stable in alkali solutions. It is paramagnetic with two unpaired electrons. Some reactions are given in Fig. 2.8a, RuF_6 is the highest halide of Ru. It is prepared by heating the elements and quenching. RuF_6 is unstable, but in contrast OsF_6 is stable.
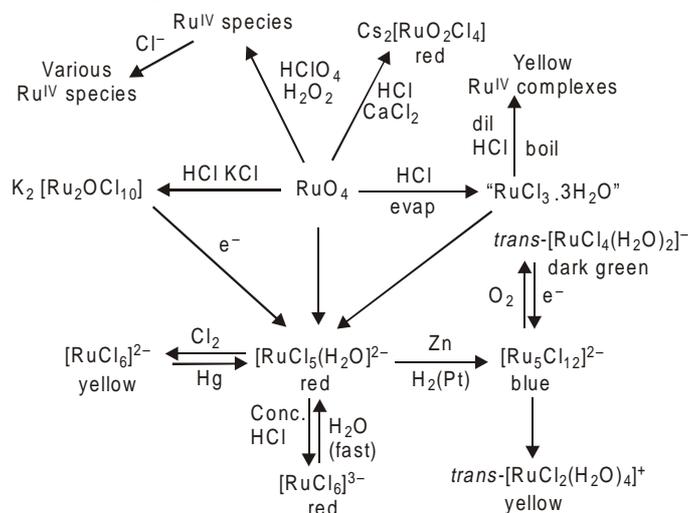
Fig. 2.8(a) Some reactions of ruthenium chloro complexes.

(+IV) States

By burning Ru or Os metals in air to give RuO_2 as a blue-black solid and OsO_2 as a coppery coloured solid. Os also forms a stable tetrafluoride and tetrachloride.

(+III) State

A number of Ru(III) compluxes are known as compared to Os (III) complexes. Both elements form $[M^{III}(NH_3)_6]^{3+}$ and Ru forms a range of mixed halogen-ammonia complexes. If RuO_4 is added to con. HCl and evaporated a dark red material formulated $RuCl_3.3H_2O$ is formed. Reactions of $RuCl_3.3H_2O$ are given in Fig. 2.8b. This is readily soluble in water. It contain not only Ru^{III} species but also some polynuclear Ru^{IV} species. Ru (III) forms basic acetate $[Ru_3O(CH_3COO)_6L_3]^+$. The chloro species of Ru (III) catalyse the hydration of alkynes.

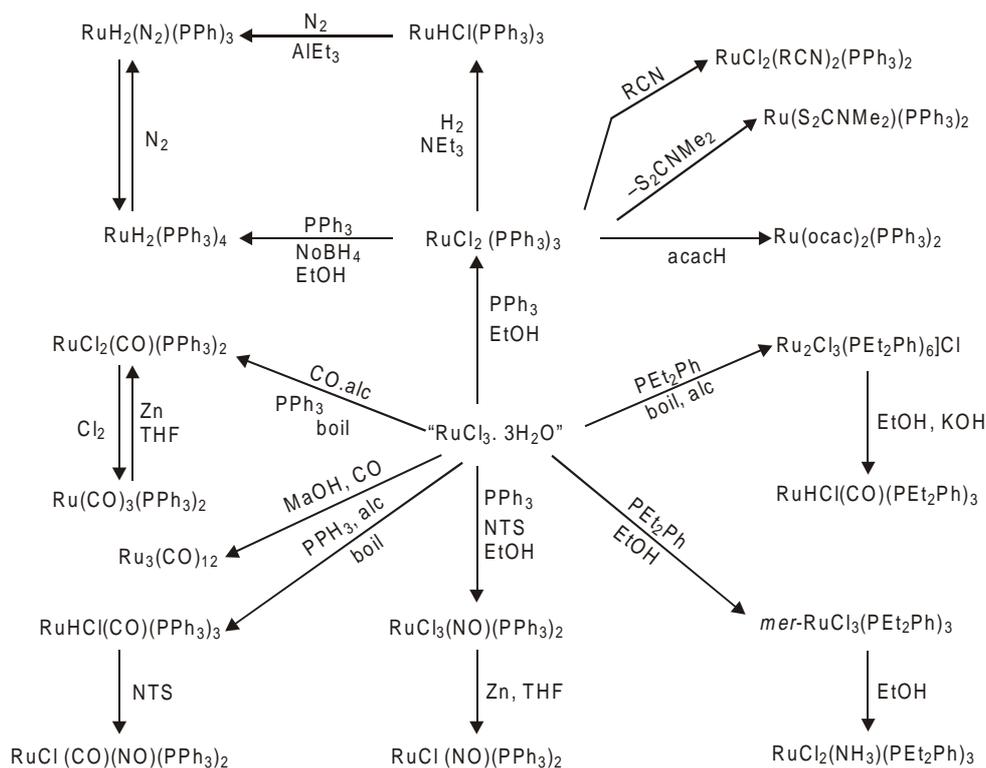RuH$_2$(N$_2$)(PPh)$_3$ $\xleftarrow{\text{N}_2 \atop \text{AlEt}_3}$ RuHCl(PPh$_3$)$_3$

$\xrightarrow{\text{RCN}}$ RuCl$_2$(RCN)$_2$(PPh$_3$)$_2$

$\xrightarrow{-\text{S}_2\text{CNMe}_2}$ Ru(S$_2$CNMe$_2$)(PPh$_3$)$_2$

$\updownarrow$ N$_2$

H$_2$ NEt$_3$

RuH$_2$(PPh$_3$)$_4$ $\xleftarrow{\text{PPh}_3 \atop \text{NoBH}_4 \atop \text{EtOH}}$ RuCl$_2$ (PPh$_3$)$_3$ $\xrightarrow{\text{acacH}}$ Ru(ocac)$_2$(PPh$_3$)$_2$

PPh$_3$ EtOH

RuCl$_2$(CO)(PPh$_3$)$_2$ $\xleftarrow{\text{CO.alc} \atop \text{PPh}_3 \atop \text{boil}}$

$\xrightarrow{\text{PEt}_2\text{Ph} \atop \text{boil, alc}}$ Ru$_2$Cl$_3$(PEt$_2$Ph)$_6$]Cl

Cl$_2$ $\updownarrow$ Zn THF

EtOH, KOH

Ru(CO)$_3$(PPh$_3$)$_2$ "RuCl$_3$. 3H$_2$O" $\xrightarrow{\text{MaOH, CO} \atop \text{PPH}_3, \text{alc} \atop \text{boil}}$ RuHCl(CO)(PEt$_2$Ph)$_3$

Ru$_3$(CO)$_{12}$

PPh$_3$ NTS EtOH

$\xrightarrow{\text{PEt}_2\text{Ph} \atop \text{EtOH}}$

RuHCl(CO)(PPh$_3$)$_3$ RuCl$_3$(NO)(PPh$_3$)$_2$ mer-RuCl$_3$(PEt$_2$Ph)$_3$

NTS Zn, THF EtOH

RuCl (CO)(NO)(PPh$_3$)$_2$ RuCl (NO)(PPh$_3$)$_2$ RuCl$_2$(NH$_3$)(PEt$_2$Ph)$_3$

Fig. 2.8(b) Some reactions of RuCl$_3$.3H.

Tertiary Phosphine Complexes

Both elements have an extenisve chemistry with these π-acid ligands. Some representative reactions are shown for Ru in Fig. 2.8(c). The complexes RuHCl (PPh$_3$)$_3$ and RuH$_2$(PPh$_3$)$_3$ are of interest in that they are highly active catalysts for the selective homogeneous hydrogenation of alkenes.

RuH$_2$(N$_2$)(PPh$_3$)$_3$ $\xleftarrow{\text{N}_2 \atop \text{AlEt}_3}$ RuClH(PPh$_3$)$_3$ $\xrightarrow{\text{CO}}$ RuClH(CO)(PPh$_3$)$_3$

$\updownarrow$ N$_2$

H$_2$. Net$_3$ benzene

RuH$_2$(PPh$_3$)$_4$ $\xleftarrow{\text{PPh}_3 \atop \text{NaBH}_4 \atop \text{benzene}}$ RuHCl$_2$(PPh$_3$)$_3$ $\xrightarrow{\text{acacH}}$ Ru(acac)$_2$(PPh$_3$)$_3$

PPh$_3$ EtOH

mer-RuCl$_2$(PPhEt$_2$)$_3$ $\xleftarrow{\text{PPhEt}_2 \atop \text{EtOH}}$ "RuCl$_3$. (3H$_2$O)"

MeOCH$_2$CH$_2$OH boil $\downarrow$ PPhEt$_2$

[Ru$_2$Cl$_3$(PPhEt$_2$)$_6$]Cl
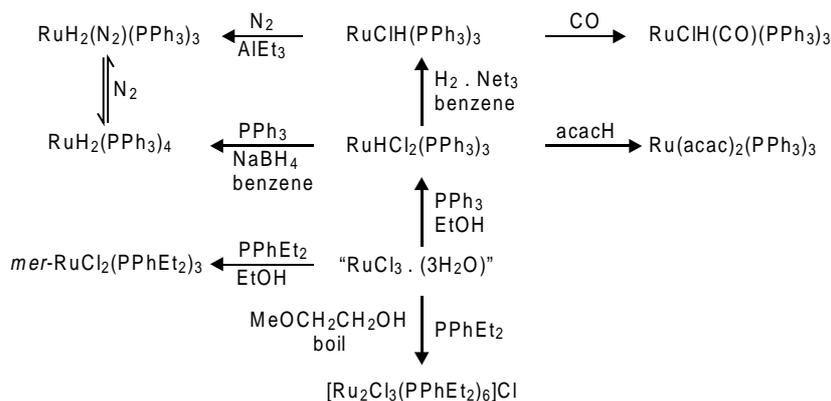
Fig. 2.8(c) Some reactions of tertiary phosphine complexes of ruthenium. Note that the use of different phosphines may give different products.

A characteristic of ruthenium complex ammine chemistry is the formation of highly red or brown coloured species usually known as ruthenium reds. If commercial ruthenium

chloride is treated with NH_3 in air for several days, a red solution is obtained. It can also be prepared by reducing Ru^{III} chloro complexes by ethanol and then treated with ammonia at 90°C.

The structure of red species appears to be that of linear trinuclear ion with oxygen bridges between the metal atoms.

$$[(NH_3)_5 Ru^{III}—O—Ru^{III} (NH_3)_4—O—Ru (NH_3)_5]^{6+}$$

Reaction of ammine complexes of Ru are given in Fig. 2.9.

Fig. 2.9 Some reactions of ruthenium ammines in aqueous solutions.

Low oxidation states

The (–II) state is rare but found in carbonyl $Ru(CO)_4{}^{2-}$. Zero valent state occurs in carbonyls $Ru(CO)_5$ $Os(CO)_5$ $Os_2(CO)_9$, $Ru_3(CO)_2$, $OS_3(CO)_2$. (Fig. 2.10)

Fig. 2.10(a) Structures of carbonyls.

RHODIUM AND IRIDIUM

The elements have odd atomic numbers and have low abundance in the earth's crust. Rh (0.0001 ppm) and Ir (0.001 ppm) are rarely found in earth crust. Trace amounts of Rh and Ir are found in the metallic state together with the platinum metals and the coinage metals in the NiS/CuS ores mixed in the South Africa, Canada and USSR. The largest source were South Africa 45% the USSR 44% Canada 4% the USA 2% and Japan 0.8%. Rh and Ir

are obtained from the anode slime which accumulates in electrolytic refining of Ni. This contains a mixture of the platinum metals together with Ag and Au. The element Pd, Pt, Ag and Au are dissolved in aqua-regia and the residue contains Ru, Os, Rh and Ir. After a complex separation Rh and Ir are obtained as powders. (Extraction scheme of Rhodium and Iridium is given in Fig. 2.10(b)).
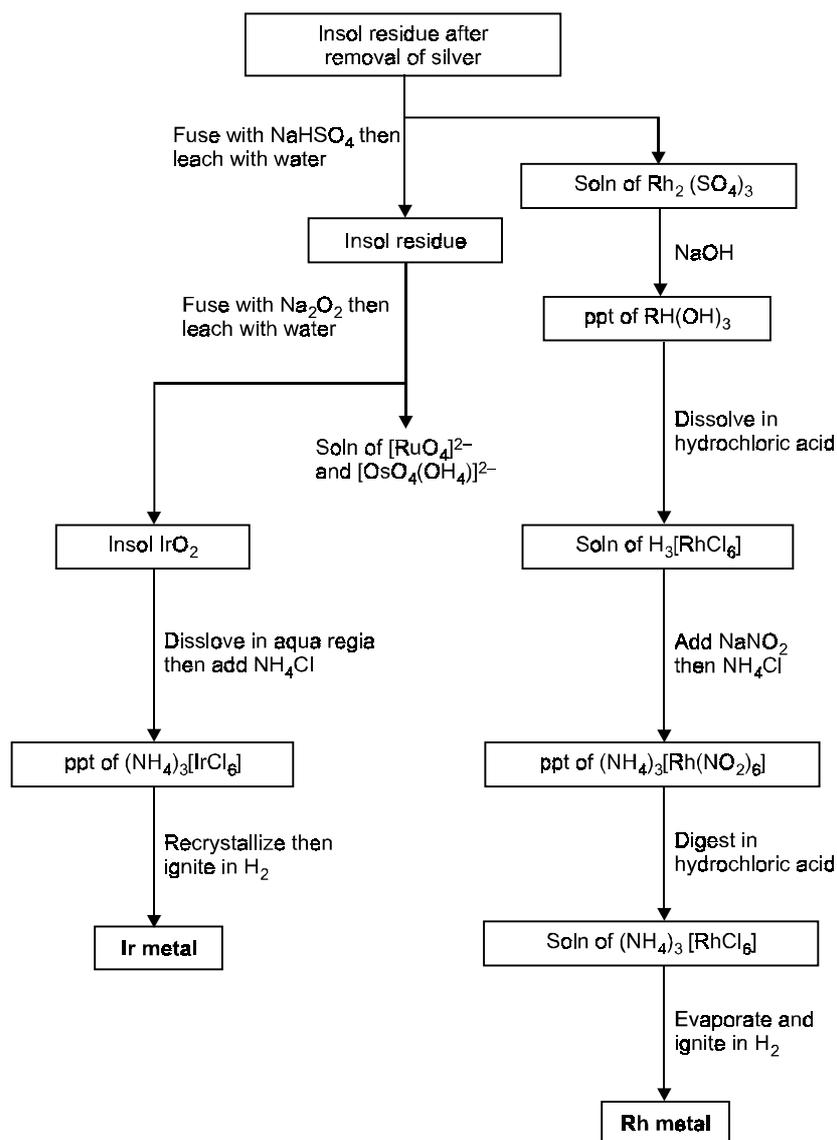
Fig. 2.10(b) Flow diagram for the extraction of rhodium and iridium.

Properties and uses

Rh and Ir are hard metals. They are noble and unreactive. Ir has highest density, 22.61 gcm^{-3}. Rh and Ir are resistant to acids, but react with O_2 and halogens at high temperature. Both the elements form a large number of coordination compounds.

Compounds

The trend for the elements in the second half of the *d*-block not to use all their outer electrons for bonding in the maximum oxidation state is continued. The most stable state for these elements are Rh (+III), Ir (+III) and Ir (+IV). Simple ionic compounds of these elements are uncommon. The halides formed are shown in Table 2.10.

Table 2.10 Halides of rhodium and iridum (mp°C)

Oxidation state	Fluorides	Chlorides	Bromides	Iodides
+6	RhF_6 black (70) IrF_6 yellow (44) bp 53			
+5	$[RhF_5]_4$ dark red $[IrF_5]_4$ yellow (104)			
+4	RhF_4 purple-red IrF_4 dark brown	$IrCl_4$?	$IrBr_4$?	IrI_4 ?
+3	RhF_3 red IrF_3 black	$RHCl_3$ red $IrCl_3$ red	$RhBr_3$ red-brown $IrBr_3$ red-brown	RhI_3 black IrI_3 dark brown

(+V) and (+VI) states

Rh (+V) and Ir (+V) exist as pentafluorides $(RhF_5)_4$ and $(IrF_5)_4$. These are very reactive and are readily hydrolysed. The only complexes known are $Cs[RhF_6]$ and $Cr[IrF_6]$.

RhF_6 and IrF_6 are the only compounds known in (+VI) oxidation states. They can be prepared by direct reaction. These compounds are not stable. However, IrF_6 is more stable than RhF_6.

(+IV) State

Ir (IV) is one of the most stable states but Rh (+IV) is unstable and forms few compounds. Both metals form tetrafluorides. RhF_4 can be prepared from $RhCl_3$ and BrF_3. $IrCl_4$ is not very stable. IrO_2 is formed by burning the metal in air, but RhO_2 is only formed by strongly oxidizing Rh (+III) in alkaline solution, for example $NaBiO_3$. Rhodium forms only few complexes for example $K_2[RhF_6]$ and $K_2[RhCl_6]$. The complexes react with water to form RhO_2 and liberate O_2. However, a number of complexes of iridium are known. For example $K_2[IrCl_6]$, $[IrCl_3(H_2O_3)Cl]$, $[IrCl_4(H_2O)_2]$ and $K [IrCl_5.H_2O]$. The oxalate complex $[Ir (ox)_3]^{2-}$ can be resolved in *d* and *l* optical isomes.

(+III) state

Almost all halides of Rh and Ir are known in trivalent state. RhF_3 is prepared by fluorinating $RhCl_3$ and IrF_3 by reducing IrF_6 with Ir. Other halides are prepared by direct reaction. All the halides are insoluble in water and also unreactive. Probably they have layer lattice. Rh_2O_3 is prepared by burning the metal in air however, hydrated Ir_2O_3 is prepared with difficulty. It is prepared by adding alkali to Ir (III) solution under an inert atmosphere because it oxidizes to IrO_2.

A adequate number of the complexes of Rh (III) and Ir (III) are knwon. For example $[RhCl_6]^{3-}$, $[Rh(H_2O)_6]^{3+}$ and $[Rh(NH_3)_6]^{3+}$. The chloro complexes are prepared by heating finely divided Rh or Ir with alkali metal chloride and chlorine.

$$2Rh + 6NaCl + 3Cl_2 \longrightarrow 2Na_3[RhCl_6]$$

Hydrated complexes $[Rh(Cl_6)]^{5-} . 12H_2O$ is of Red colour. (Red)

On boiling with water it gives $[Rh(H_2O)_6]^{3+}$. On addition of NaOH it gives $Rh_2O_3.H_2O$. If a limited amount of HCl in added to $[Rh(H_2O)_6]^{3+}$ then $RhCl_3.3H_2O$ is obtained however, if excess HCl is added then $[RhCl_6]^{2-}$ is regenerated. The complexes are diamagnetic end of octahedral geometry. $RhCl_3.3H_2O$ exists in two fac and mer isomers. Reactions of $RhCl_3.3H_2O$ are given in Fig. 2.11(a) Few complexes of these elements are known which are not octahedral for example $[RhBr_5]^{2-}$ and $[RhBr_7]^{4-}$. Few complexes are also known having M-M bond.

$$[(R_3As)_3 Rh(HgCl)]^+ Cl^- \text{ (Rh-Hg) and } [Ir_2Cl_6(SnCl_3)_4]^{4-}$$
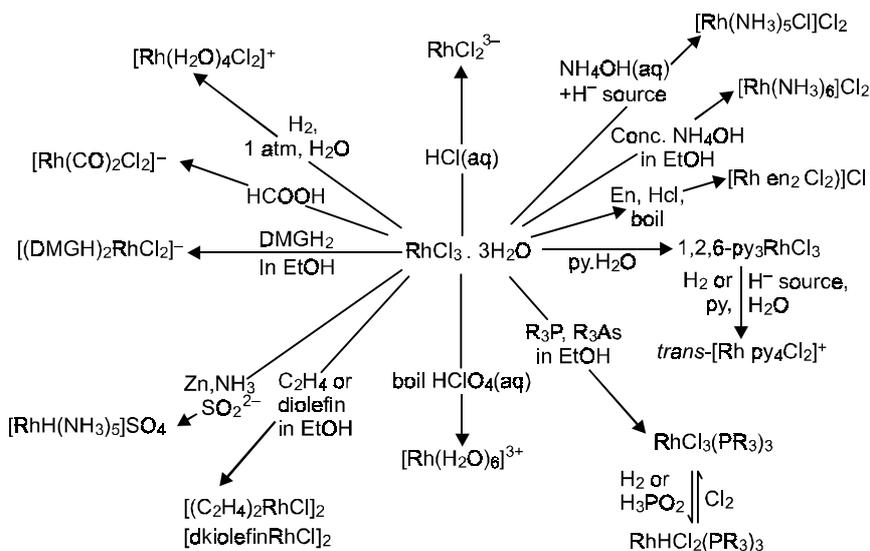
Fig. 2.11(a) Some reactions of rhodium trichloride.

Rh (III) and Ir (III) form basic acetates $[Rh_3O(CH_3COO)_6L_3]^+$ which have unusual structure. Rh atoms form a triangle with an O atom at the centre. The six acetate groups act as bridges between the Rh atoms–two acetate groups across each edge of the triangle. Thus each Rh atom linked to four acetate groups and the central O and the sixth position of octahedron is occupied by water or another ligand. The magnetic moment is reduced due to partial pairing of d-electrons on the three metal atoms by means of $d\pi$-$p\pi$ bonding through O. A

number of hydride complexes $[Rh(R_3P)_3.HCl_2]^{2+}$ and $[Ir(R_3P)_3.H.Cl_2]^{2+}$, $[Ir(R_3P)_3.H_2Cl]^{4+}$ and $[Ir(R_3P)_3H_3]^{6+}$ are also known.

(+II) State

Few compounds are known of Rh(II) and Ir(II) because on reduction of Rh (III) and Ir(III) gives metal instead of Rh(II) or Ir(II). The existance of RhO is uncertain and $IrCl_2$ exists as a polymer. On warming the solution of $R-HCl_3.3H_2O$ of sodium acetate in methanol a dimeric diacetate is formed $HOH_3C.Rh.(R.COO)_4.Rh.CH_3OH$. The four carboxylate groups bridge the two Rh atoms. This has a M-M bond of 239 pm. Some complexes of phosphine are also known. Rhodocene $[Rh^{II}(n^5-C_5H_5)_2]$ is a less stable compound. It tends to dimerize.

(+I) State

There is a fairly extensive chemistry of Rh (+I) and Ir (+I) complexes with π-bonding ligands such as CO, PH_3, PR_3 and alkene. Two are the important compounds of Rh (I) and Ir(I) *i.e.* $[Rh(Cl) (PPh_3)_3]$ Wilkinson catalyst and trans $[IrClCO(PPh_3)_2]$.

1. Wilkinson Catalyst. This red-violet compound which is readily obtained by refluxing ethanolic $RhCl_3.3H_2O$. Fig. 2.11 (b) with an excess PPh_3 was discovered in 1965. It undergoes a variety of reactions, most of which involve either replacement of a phosphine ligand with CO, CS, C_2H_4 or O_2 giving trans products or oxidative addition with H_2 or MeI to form Rh^{III}. However, its importance arises from its effectiveness as a catalyst for highly selective hydrogenations of complicated organic molecules which are of great importance in the pharmaceutical industries.

2.11(b) Some preparations and reactions of rhodium (I) compounds.

$$>C=C< \; + \; H_2 \; \xrightarrow{\text{Catalyst}} \; -\underset{H}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}-$$
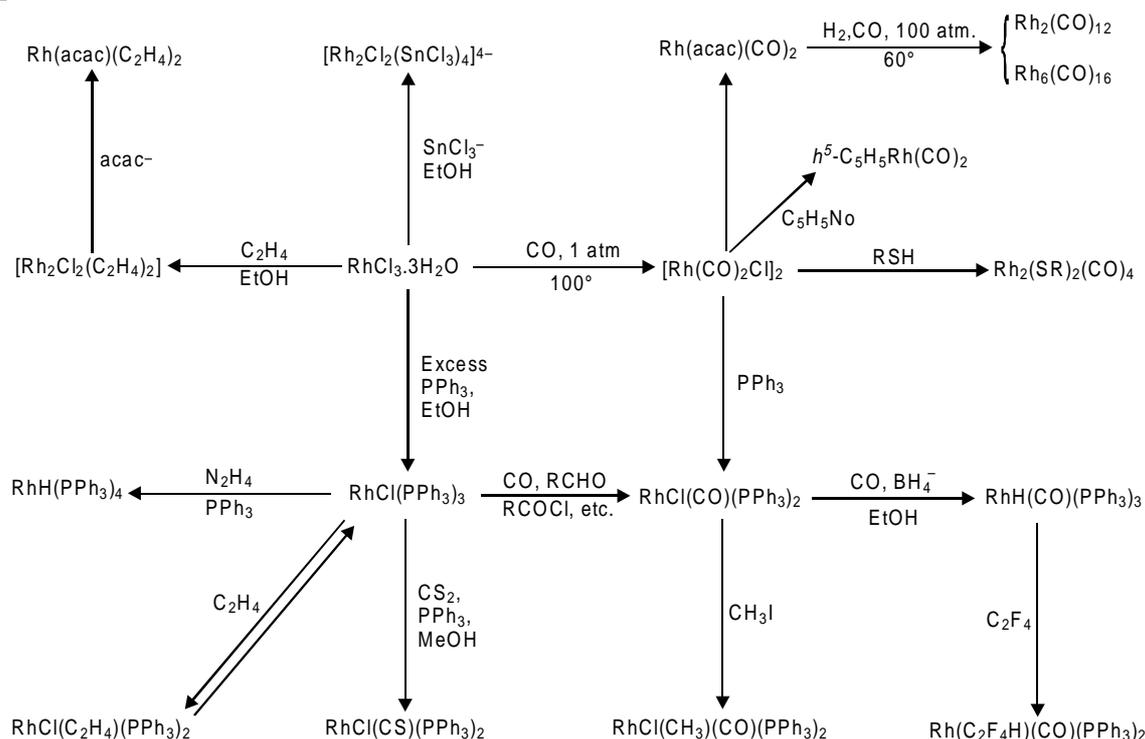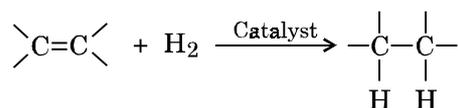
The simplified mechanism is given in Fig. 2.12.
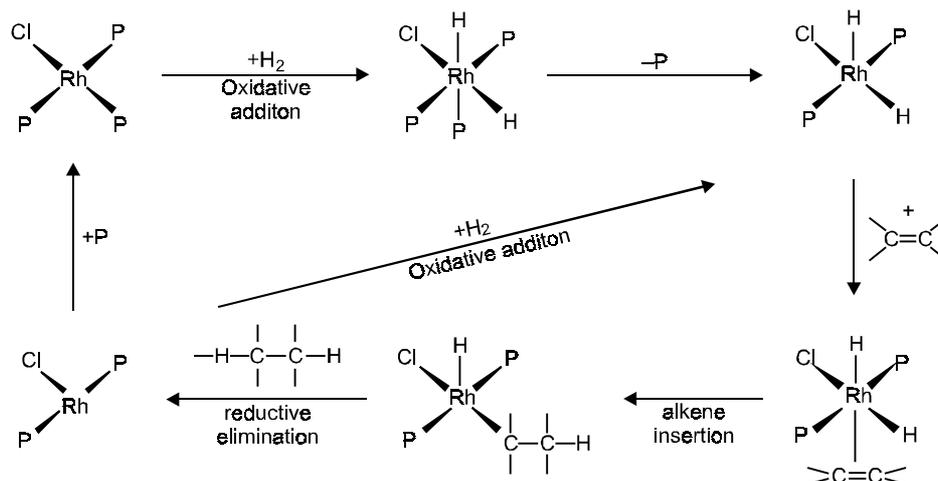
Fig. 2.12 The catalytic cycle for the hydrogenation of an alkene, catalysed by [RhCI(PPh₃)₃] in benzene : possible coordination of solvent molecules has been ignored and the ligand PPh₃ has been represented as P throughout, for clarity.

The complex trans [Rh(CO) (H) (PPh₃)₃] has also been used in-oxo process and is an important catalyst in the hydrogenation of alkenes (Fig. 2.13).
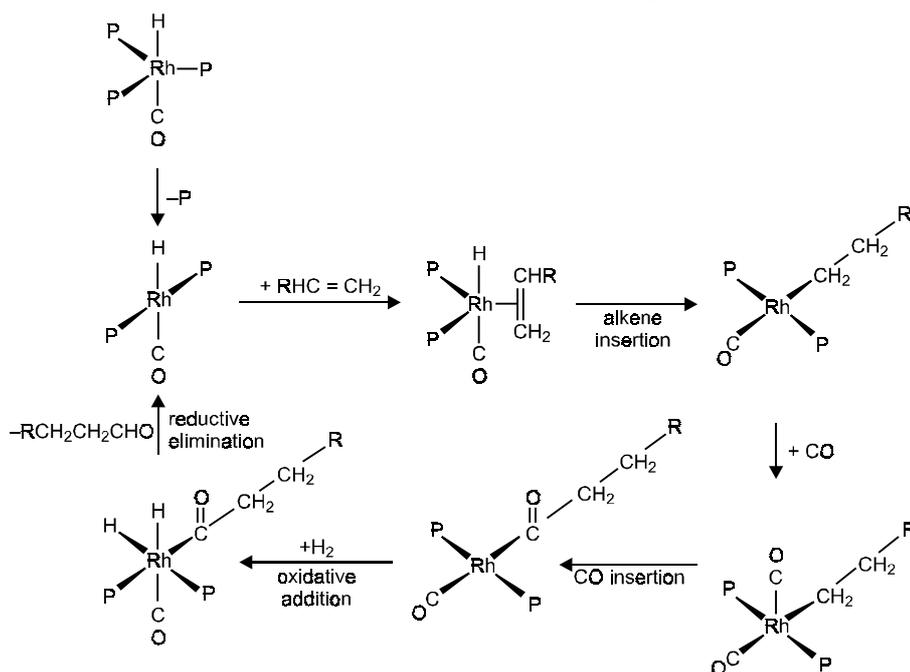
Fig. 2.13 The catalytic cycle for the hydroformylation of an alkene catalysed by *trans*-[RhH(CO)(PPh₃)₃]. The tertiary phosphine ligand has been represented as P throughout.

Vaska's compound

This yellow compound can be prepared $[IrCl(CO)(PPh_3)_2]$ by the reaction of triphenyl phosphine and $IrCl_3$ in solvent such as 2-methoxy ethanol which acts both as reducing agent and supplier of CO. It was discovered in 1961 by L. Vaska and J.W. di Luzio and recognized as ideal material for the study of oxidative addition reactions, since it products ore generally stable and readily characterized. It is containly the most throughly investigated compound of Ir^I. It forms octahedral Ir^{III} complexes in oxidative addition reactions with H_2, Cl_2, HX, MeI and RCO_3H. Spectral studies indicate that in all cases the phosphine ligands are trans to each other. The 4 remaining ligands (Cl, CO and two components of the reactant,) therefore lie in plane and 3 isomers are possible.
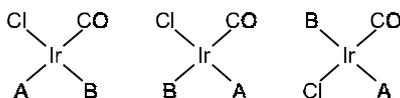
It readily absorbs O_2 and becomes orange coloured. The O_2 may be removed by flusing with N_2. This reversible oxygenation has been studied as a model for oxygen carrying ability of haemoglobin.

Lower oxidation states

Numerous compounds of Rh and Ir are known in which the formal oxidation state of metal is Zero, –1 or even lower. Many these compounds contain CO, CN or RNC as ligands. The (–1) state is found in the tetrahedral complexes $[Rh(CO)_4^-$ and $K[Ir(PF_3)_4]$. The zero oxidation state occurs as carbonyls such as $Rh_4(CO)_{12}$ and Ir_4 $(CO)_{12}$. All have M-M bonds and contain a cluster of four metal atoms Fig. 2.14. $Rh_6(CO)_{11}$ is also known and has usual structure.

(a)   (b)   (c)

○ Metal

⊘ C of CO (O omitted for clarity)
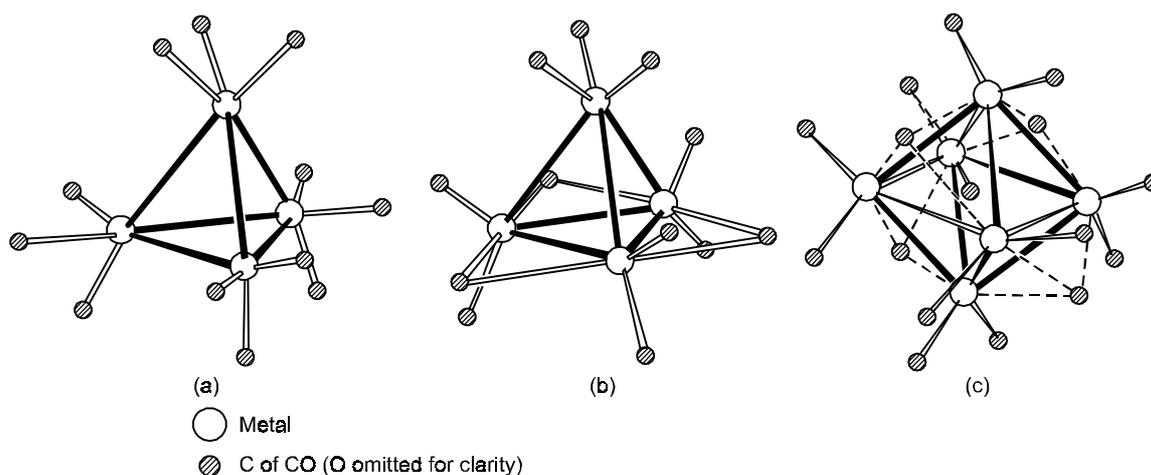
Fig. 2.14 Molecular structures of some binary carbonyls of Rh and Ir. (a) $Ir_4(CO)_{12}$. (b) $M_4(CO)_{12}$, M = CO, Rh (c) Rh_6 $(CO)_{16}$.

PALLADIUM AND PLATINUM

Pd and Pt are rare elements, but they are appreciably more abundant than the other platinum group metals. Even through Pd is slightly more abundant than Pt, but production of Pt is greater than that of Pd.

The platinum group metals occur as traces in the sulphide ores of Cu and Ni. They are obtained as concentrates as anode sludge from electrolyte process for the major metals. The platinum group metals are also obtained from the Cu/Ni alloy produced in the separation of the sulphide matte of Cu_2S/Ni_2S_3. The sulphide matte is cooled slowly giving an upper slivery layer of Cu_2S and a lower black layer of Ni_2S_3 which can be separated mechanically. A small amount of metallic Cu/Ni alloy is also formed. This dissolve any of the paltinum group metals present, and is used as a source of these rare and expensive elements.

Separation of the platinium metals is complex, but in the last stages $(NH_4)_2[PtCl_6]$ and $[Pd(NH_3)_2Cl_2]$ are ignited to given the respective metals. The metals are obtained as powders or sponges and are fabricated into solids objects by sintering. Extraction scheme for Pd and Pt is given in Fig. 2.15.
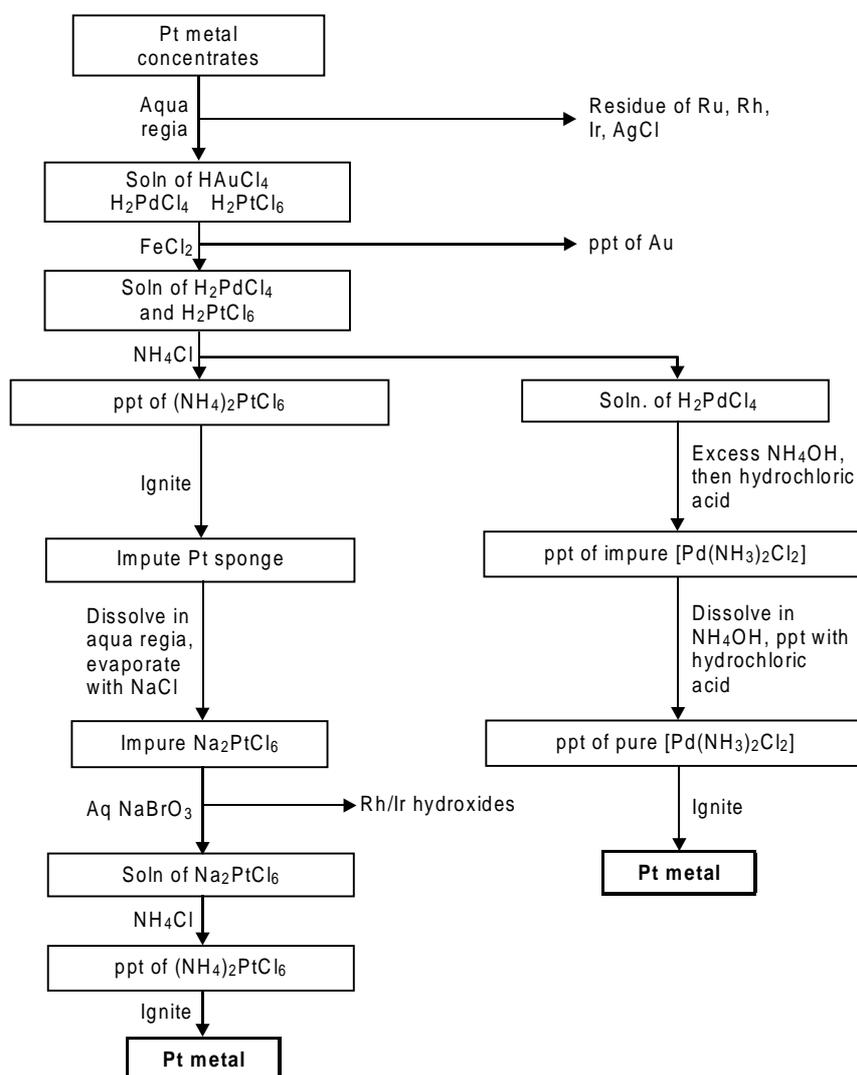
Fig. 2.15 Flow diagram for the extraction of palladium and platinum.

Properties and uses

Palladium and platinum are both rare and expensive. They are noble and not very reactive, but are slightly more reactive than the other platinum group metals. Both are used as catalyst. The most common oxidation state as Pd(II) and Pt(II) and Pt(IV). These are not ionic. Pd dissolve slowly in concentrated HCl in the presence of O_2 or Cl_2, and fairly readily in con^n. HNO_3 giving $[Pd^{IV} (NO_3)_2 (OH)_2]$. Pt is the most resistant to acids, but dissolve in aqua-regia, giving chloroplatinic acid $H_2[PtCl_6]$. Both Pd and Pt are rapidly attacked by fused alkali metal oxides and peroxides for example Na_2O and Na_2O_2. Red heat Pd reacts with F_2, Cl_2 and O_2. Pt is less reactive but at red heat it reacts with F_2, and at a high temperature and pressure it reacts with O_2. Both absorb hydrogen. The amount absorbed depend on the physical state of gaseus H_2. Pt (II) and Pt (IV) form an extremely large number of complexes.

Pd and Pt find extensive chemical uses as catalyst.

A new increasing use of Pt is three way catalytic convertors. $PdCl_2$ is used in Waker process for converting C_2H_4 to CH_3CHO. Pd is used for hydrogenations such as phenol to cyclohexanone and also for dehydrogenations. Pt is very important as a catalyst in the oil industry in the reforming of hydrocarbon. Pt/PtO is used as Adam's catalyst for reductions. Pt was used as catalyst for manufacture of H_2SO_4 (Contact Process) and HNO_3 (Ostwald's) Pt is also used to make apparatus to handle HF and to seal into soda glass to allow electrical connections to pass through the glass. This is important in making electrodes, thermionic valves etc.

(+V) and (+VI) States

These are only found for Pt, and are rare. The (+V) state is represented by PtF_5, which is tetrameric and has the same structure as many transition metal fluorides. The $[Pt F_6]^-$ ion also contains Pt (+V) and was first formed by reacting Pt F_6 with O_2 to give compound $O_2^+ [Pt F_6]^-$. The only examples of the (+VI) state which are known for certain are PtO_3 and PtF_6.

(+IV) State

Pd oxide (PdO_2) is known only in hydrated form. However, Pt forms stable oxides in both anhydrous and hydrated forms. The anhydrous oxide is insoluble but the hydrated form dissolves in acids and alkalies. Only tetrafluoride of palladium (PdF_4) is known whereas all the halides of Pt (Pt X_4) are known. Direct reaction of Pd and F_2 gives PdF_3 $[Pd^{II}(Pd^{IV} F_6)]$ and Pd F_4 whereas Pt gives PtF_4, Pt F_5 and Pt F_6. $PtCl_4$ is formed either direct reaction or by heating $H_2[PtCl_6]$.

$$Pt \xrightarrow{\text{aqua-regia}} H_2 [PtCl_6] \xrightarrow{\text{Heat}} PtCl_4 + 2HCl$$
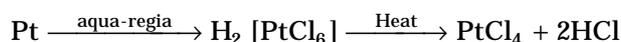
Pd (+IV) forms a few octahedral complexes $[Pd X_6]^{2-}$ where X = F, Cl or Br and $[Pd X_4 (NH_3)_2]$. They are reactive. $[PdF_6]^{2-}$ hydrolyses rapidly in water whereas the other halides complexes are decomposed by hot water, giving $[Pd^{II} X_4]^{2-}$ and halogen.

However, Pt (+IV) forms a large number of octahedral compexes for example $[Pt(NH_3)_6]^{4+}$, $[Pt(NH_3)_5Cl]^{3+}$, $[Pt(NH_3)_4Cl_2]^{2+}$ and $[PtCl_6]^{2-}$. Similar series of complexes exist with a wide range of ligands such as F^-, Cl^-, Br^-, I^-, OH, acetylacetone, CN^- etc. Chloroplatinic acid is commercially the most common Pt compound. It is prepared either by dissolving Pt in aqua-regia or con^n-HCl with Cl_2. It forms red crystals of $H_2[PtCl_6].2H_2O$. Sodium or potassium

salts are common starting material for making other platinum (IV) compounds. Platinum is unusual in that it forms alkyl derivatives by a Grignard reaction.

$$4Pt\ Cl_4 + 12CH_3MgI \longrightarrow [(CH_3)_3\ Pt\ I]_4 + 8MgCl_2 + 4MgI_2$$

But actual compound is $[(CH_3)_3\ Pt(OH)]_4$.

(+III) State

The compounds of Pd (III) are rare and it is doubtful that the Pt (III) exists. The complexes $Na[PdF_4]$ and $NaK_2\ [PdF_6]$ have been repeated. Some compounds of mixed oxidation states are known for example $Pd^{2+}\ [Pd\ F_6]$ etc.

(+II) State

Pd (II) and Pt (II) exist as oxides, halides, nitrates and sulphates. Generally anhydrous solids are not ionic. PdO is found in ahydrous form whereas PtO is only known as an unstable hydrated form. Except PtF_2, all the halides are known. PdF_2 is ionic. All the complexes for example $[Pd\ (OH)_4]^{2-}$ are diamagnetic. It is due to large crystal field splitting energy. All the dihalides are molecular and are diamagnetic. The chloride of Pd (II) and Pt are prepard from the elements. They exist in two different forms depending upon the conditions used.

$$Pd + Cl_2 \xrightarrow[<50°C]{>550°C} \begin{array}{l} \alpha\ (PdCl_2)_n \\ \beta\ (PdCl_2) \end{array}$$
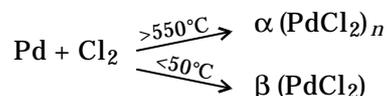
α-forms of $PdCl_2$ and $PtCl_2$ are dark-red and olive green in colour respectively. α-$PdCl_2$ is hygroscopic and soluble in water and has a polymeric chain type structure. α-$PtCl_2$ is insoluble in water and dissolve in HCl due to formation of $[PtCl_4]^{2-}$. Its structure is not known. β forms of $PdCl_2$ of $PtCl_2$ have an unusual molecular structure. This is based on Pd_6Cl_{12} or Pt_6Cl_{12} unit. The structure is best described as metal surrounded by four Cl atoms in a square planar environment, with six units linked by halogen bridged (Fig. 2.15 a & b). β-$PdCl_2$ is soluble in benzene.
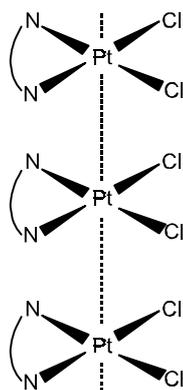

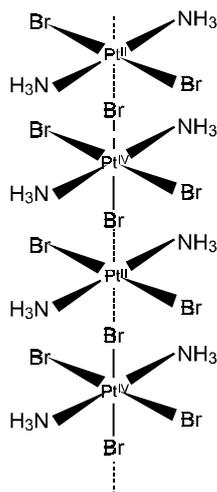**Fig. 2.15(a)** Stacks of square planar [Pt(ethylenediamine)Cl$_2$] molecules.

Fig. 2.15(b) Structure of [Pt(NH$_3$)$_2$Br$_3$].

An imporant reaction occurs between $PdCl_2$ and alkenes. With ethene complexes such $[Pd(C_2H_4)Cl_3]^-$, $[Pd(C_2H_4)Cl_2]_2$ and $[Pd(C_2H_4)_2Cl_2]$ are formed. Similar compounds are known for Pt. For example Zeise's salt $K[Pt(C_2H_4)Cl_3]$. H_2O yellow coloured compound. It is known since 1825. It is of square planar geometry with 3Cl at the corners and $H_2C = CH_2$ at the other corner. Bonding in such type of complexes will be discussed latter.

The very importnat medical use of Pt (II) compounds is the use of cis-isomer of $[Pt(NH_3)_2Cl_2]$ as an anticancer drug for treating several types of malignant tumours. The trans-isomer is ineffective. The cis isomer is called cis-platin and is highly toxic.

The complexes between $PdCl_2$ and alkenes are decomposed by water, giving ethanal

$$C_2H_4 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd + 2HCl$$
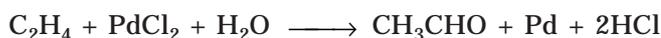
This reaction forms the basic of the Waker Proces for the production of CH_3CHO. The Pd is converted back into $PdCl_2$ in situ by $CuCl_2$.

$$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$$

$PdCl_2$ catalyse the reaction between ethene, CO and H_2O.

$$CH_2 = CH_2 + CO + H_2 \longrightarrow CH_3CH_2COOH$$

Magnus green salt has the formula $[Pd(NH_3)_4]^{2+}$, $(PtCl_4)^{2+}$ and the square planar anion and cations are stacked on top of each other. Similar structure is reported for $K_2[Pt(CN)_4].3H_2O$.

Lower Oxidation State

Pd and Pt do not form complexes with phosphines such as $[Pd(PPh_3)_3]$, $[Pt(PPh_3)_3]$, $[Pd(PPh_3)_4]$ and $[Pt(PPh_3)_4]$. However $[Pd(CO)(PPh_3)_3]$ and $[Pt(CO)(PPh_3)_2]$ are known. A series of cluster compounds such as $[Pt_3(CO)_6]_n^{2-}$ are formed by reducing $[PdCl_6]^{2-}$ in alkaline solution under an atmosphere of CO. Similar complexes of Pd are not known.

SILVER AND GOLD

Silver is found as sulphide ores Ag_2S (argentite), as the chloride AgCl (horn silver) and as the native metal. There are three process of extraction.

1. It is obtained mostly as a biproduct from the extraction of Cu, Pb or Zn. It may be extracted from the anode slime formed in the electrolytic refining of Cu and Zn.

2. Zinc is used to extract silver by solvent extraction from molten lead in Parke's process.

3. Silver and gold are extracted by making soluble cyanide complexes.

$$2Ag_2S + 8CN^- + O_2 + 2H_2O \longrightarrow 4Ag(CN)_2^- + 2S + 4OH$$
$$2Ag(CN)_2^- + Zn \longrightarrow 2Ag + [Zn(CN)_4]^{2-}$$
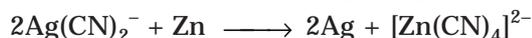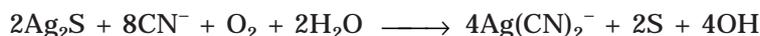
Historically gold has been found as lumps of metal in the ground called nuggets. Gold occurs mainly as grains of metal disseminated in quartz veins. Many of these rocks have weathered with time. The gold and powdered rock are washed away in streams and accumulate as sediments in river beds. The grains of gold can be separated from silica by panning *i.e.* swirling them both with water. Gold is very dense and settles to the bottom.

Now a days rocks containing traces of gold are crushed and extracted either with mercury or with sodium cyanide. Gold dissolve in murcury forming an amalgam. By distillation gold is recovered.
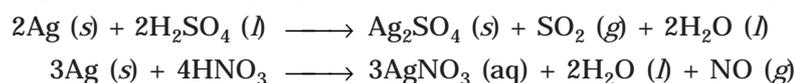
It can also be extracted by cyanide process

$$4Au + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Au(CN)_2] + 4NaOH$$
$$\text{Complex}$$
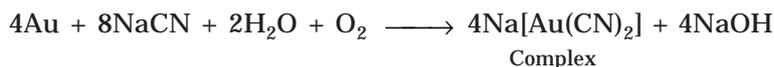
This complex is soluble and separated from the rest of the rock. The gold can be obtained by adding Zn powder.

$$[Au(CN)_2]^- + Zn \longrightarrow Zn(CN)_4 + 2Au\ (s)$$
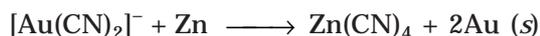
The main use of Ag are as AgCl and AgBr in photographic emulsions, for jewellery and silver ornaments, for batteries and silvering mirrors. Gold is used in jewellery. It is alloyed with a mixture of Cu and Ag. These alloy retain the golden colour but are harder. The proportion of gold in the alloy is expressed in carats. Pure gold is 24 carats and contain 9/24, 18/24, 22/24 carats gold respectively.

Small amounts of gold are used to make corrosion-free electrical contacts. For example on computer boards, thin film of this metal reflects unwanted heat from sun in the summer. The liquid gold is used to decorate picture frames, glass and ceramic ornaments.

The metals in the group have the highest electrical and thermal conductivities known. They are the most melleable and ductile. The higher enthalpy of sublimation and higher ionization energy are the reason why Ag and Au tend to be unreactive *i.e.* show noble character. The metals have positive E° values and are thus below hydrogen in the electrochemical series. Thus they do not react with water or liberate H_2 with acids. Ag dissolve in dil. HNO_3 and hot Con. H_2SO_4 whereas Au is inert to all acids except aqua-regia.

$$2Ag\ (s) + 2H_2SO_4\ (l) \longrightarrow Ag_2SO_4\ (s) + SO_2\ (g) + 2H_2O\ (l)$$
$$3Ag\ (s) + 4HNO_3 \longrightarrow 3AgNO_3\ (aq) + 2H_2O\ (l) + NO\ (g)$$

The HNO_3 acts as an oxidizing agent and the chloride ions as complexing agent. Ag and Au both are inert toward O_2. Ag reacts with H_2S to give sulphide but Au does not react with H_2S.

$$2Ag + H_2S \longrightarrow Ag_2S + H_2$$

Compounds. The most common oxidation states are Ag (+1) and Au (+III) and the two elements differ widely in their Chemistries. The univalent Au disproportionate in the water.

(+III) State

A black oxide Ag_2O_3 is obtained by anodic oxidation of Ag^+ in alkaline solution. However, in the presence of complexing agent in alkaline solution Ag^{III} complexes are obtained. The separation of Ag^I and Ag^{III} can be made by the reaction.

$$4AgO + 6KOH + 4KIO_3 \longrightarrow 2K_5H_2\ [Ag(IO_6)_2]$$
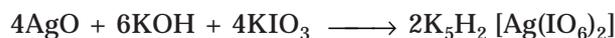
The complexes of Ag^{III} are also prepared by the oxidation of Ag_2O in strongly alkaline solution by $S_2O_8^{2-}$. For example $K_6H[Ag(IO_6)_2].10H_2O$ and $Na_6H_3[Ag(TeO_6)_2].18H_2O$.

Salts of the tetrafluoroaurate ion are obtained by the action of BrF_3 on a mixture of gold and an alkali chloride, K $[AuF_4]$ is isomorphous with K $[BrF_4]$ and has a square AuF_4 ion.
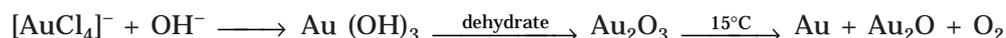
When gold is dissolved in aqua-regia or Au_2Cl_6 is dissloved in HCl and the solution of $AuCl_4^-$ is evaporated. Chloroamic acid can be obtained as yellow crystals $[H_3O]^+\ [AuCl_4]^-$.$3H_2O$.

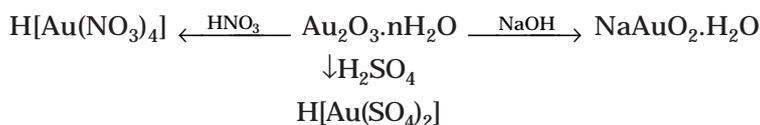$$Au + HNO_3 + HCl \longrightarrow H_3O^+\ [AuCl_4]^-.3H_2O \longrightarrow AuCl_3$$

Other water soluble salts such as $KAuCl_4$ and $NaAuCl_4.2H_2O$ are readily obtained. A number of other complexes are also known. For example, $[AuCl_2Py_2]Cl$, $[Au(phen)Cl_2]Cl$, $[Au(CN)_4]^-$, $[Au(NO_3)_4]^-$, $[Au(dian)_2I_2]$ I and $[Au(dian)_2I]^{2+}$.

Gold (III) alkyls are also usually stable only when other ligands such as triphenyl phosphine are present as in $(CH_3)_3 AuPPh_3$.

$AuCl_4^-$ decompose to metal quite readily on heating

$$[AuCl_4]^- + OH^- \longrightarrow Au(OH)_3 \xrightarrow{\text{dehydrate}} Au_2O_3 \xrightarrow{15°C} Au + Au_2O + O_2$$

Hydrate gold oxide is amphotene.

$$H[Au(NO_3)_4] \xleftarrow{\quad HNO_3 \quad} Au_2O_3.nH_2O \xrightarrow{\quad NaOH \quad} NaAuO_2.H_2O$$
$$\downarrow H_2SO_4$$
$$H[Au(SO_4)_2]$$

Au_2Cl_6 is dimeric.

Ag (+II) is known as the fluoride AgF_2. This is brown solid and is prepared by heating Ag in F_2. AgF_2 is a strong oxidizing agent and a good fluorinating. It decomposes on heating

$$AgF_2 \xrightarrow{\text{heat}} Ag F + \frac{1}{2}F_2$$
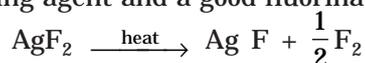
Ag (II) is more stable in complexes such as $[Ag(Py)_4]^{2+}$, $[Ag(dipy)_2]^{2-}$ and $[Ag(o\text{-phen})_2]^{2+}$ which form stable salts with nonreducing anion such as NO_3^- and ClO_4^-. They are usually prepared by oxidizing a solution of Ag^+ and the ligands with $K_2S_2O_8$. The complexes are square planar and paramagnetic.

A black oxide of formula AgO is formed by strong oxidation of Ag_2O in alkaline solution. Au (II) is found in dithiolene compounds and in $[Au[B_9C_2H_{11})_2]^{2-}$, but otherwise it only exists as a tansient intermediate.
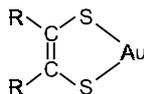
(+1) State

It might be expected that the (+1) state would be the most common and most stable because of the extra stability resulting from a full d shell. Surprisingly this is not so. However, Ag^+ is stable state in both the solid state and solution Au^+ disproportionate in water. Au^+ compounds that are stable to water are either insoluble or present as complexes for example $[R_3P\text{-}Au\text{-}Cl]$, $[R_3P\text{-}Au\text{-}CH_3]$, $[NC\text{-}Au\text{-}CN^2]^-$.

As discussed above that the +1 oxidation is most stable for Ag. A number of ionic compounds are known of Ag^+. Almost all the salts of Ag^+ are insoluble in water but exception are $AgNO_3$ AgF and $AgClO_4$ which are soluble. Except $AgF_2.4H_2O$, all other salts are found in anhydrous form. Ag^+ forms 2-coordinate complexes such $[Ag(H_2O)_2]^+$, or $[Ag(NH_3)_2]^+$. $AgNO_3$ is the most important salts. Ag_2O is mainly basic dissolving in acids. Moist Ag_2O absorbs CO_2 and forms Ag_2CO_3.

The silver halides are used in photography. On addition of ammonia AgCl is dissolve completely. AgBr dissolve partially but AgI is not soluble. The solubility in ammonia is due to the formation of complex $[Ag(NH_3)_2]^+$. A few silver compounds milk colourless anions are coloured. For example Ag_3PO_4, Ag_2S, AgI. It is due to small size and high polarizing power

of Ag^+. The leads to some covalent character. Ag^+ forms of varity of complexes. Most simple ligands results 2-coordination and linear. Stability sequence of halides I > Br > Cl > I. It is unusual. Bidentate ligands form polynuclear complexes. II-acceptor ligands such as phosphine may form two and four coordinate complexes. Au^+ is less stable. By heating gently AuX_3, AuCl and AuBr can be obtained. Au_2O is also known. AuI is precipitated by adding I^- in AuI_3. Gold can form a number of linear complexes with Π-acceptor ligands. An important use of Au (+1) is in drugs to treat rheumatoid arthritis. The drugs are thought to be linear complexes of the type RS→Au→SR or R_3P→Au→PR_3. Au can exist as an amide ion (Au^-).

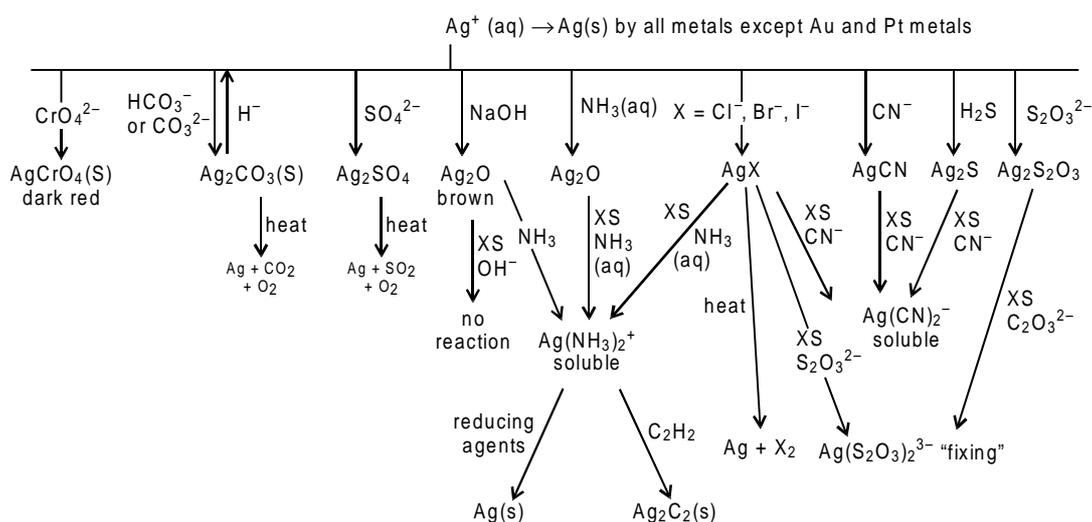Reactions of Ag^+ (aq) are given in below


Fig. 2.16

CADMIUM AND MERCURY

Cd and Hg are quite rare. Inspite of this elements are familiar because their extraction and purification are simple. Cd is found as traces in Zn ores and it is extracted from these. Hg is mined as the rather scarce ore cinnabar Hgs mainly in USSR, Spain, Mexico & Algeria.

Cd is found as traces (2–3 parts per thousand) in most Zn ores, and is extracted from these. The ore is treated with H_2SO_4 that yields a solution of $ZnSO_4$ containing small amount of $CdSO_4$. Cd is recovered by adding a more electro-positive metal to displace it from the solution. Zn powder is added to the $ZnSO_4/CdSO_4$. solution when the Zn dissolves and Cd metal is precipitated. Zn is higher in the electrochemical series than Cd, and elements high in the series displace elements lower in the series.

$$Zn\ (s) + Cd^{2+}_{(solution)} \longrightarrow Zn^{2+}_{(solution)} + Cd\ (s) \qquad E° = 0.36eV$$
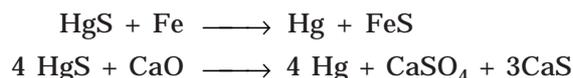
The Cd concentrate so obtained is then dissolved in H_2SO_4 and purified by electrolysis. The Zn is recovered from the $ZnSO_4$ solution by electrolysis.

Hg is mined bright red coloured ore cinnabar HgS. The ore is crushed and as HgS has a very high density (8.1 gcm^{-3}) it is separated from other rocks and con^n by sedimentation.

$$HgS + O_2 \xrightarrow{\ 600°C\ } Hg + SO_2$$
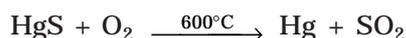
Rich ores are heated with scrap iron or quicklime.

$$HgS + Fe \longrightarrow Hg + FeS$$

$$4\ HgS + CaO \longrightarrow 4\ Hg + CaSO_4 + 3CaS$$

Very pure Hg is obtained by blowing air through the metal at 250°C when traces of other metals form oxides. Hg can be purified and separated from the other metals and oxides by distillation.

Properties and uses

Cd and Hg show few properties associated with typical transition elements. This is because they have a complete d shell, which is not available for bonding.

Cd does not show variable valency whereas Hg exists in (+I) and (+II) oxidation states.

Most of the compounds are white (due to d^{10} electronic configuration) but some compounds of Hg(II) and Cd(II) are highly coloured due to charge transfer.

The metals are soft as compared to other transition metals. It is probably because the d-electrons do not participate in metallic bonding.

The melting and boiling points are very low. This explains why the metal are more reactive than copper group, even though the ionization energies for the two groups suggest the reverse.

Mercury is the only metal which is liquid at room temperature. The reason for this is that the very high ionization energy makes it difficult for electrons to participate in metallic bonding. The liquid has a appreciable vapour pressure at room temperature. Thus exposed mercury surfaces should always be covered to prevent a vaporization and hence poisoning. The gas is unusual because it is monatomic like noble gas.

Cd is a silvery solid which tarnish rapidly in moist air. Hg is a silvery liquid and does not tarnish readily. Cd dissolve in dil. nonoxidizing acids liberating H_2, but Hg does not. Both the metals react with oxidizing acids such as con^n HNO_3 and conc. H_2SO_4 forming salts and evolving a mixture of oxide of nitrogen and SO_2. Hg forms Hg^{II} in air but with dil. HNO_3, $Hg_2\ (NO_3)_2$ containing Hg^{+1} ion.

Both the metals form oxide (MO) sulphide (MS) and halide (MX_2) by heating the elements.

$$Hg + O_2 \xrightarrow{\ 350°C\ } HgO \xrightarrow{\ 400°C\ } Hg + O_2$$

Cd is used to protect steel from corrosion. Cd absorbs very well neutrons and is used as control rod in nuclear reactors. CdS is used as yellow pigment in paints, It is also used for alkaline Ni/Cd storage batteries.

The largest use of mercury is in electrolytic cells for the production of NaOH and Cl_2. Vapour of mercury are used for street light. It is also used for the extraction of Ag and Au as amalgam organic compounds for example phenyl mercuric acetate has fungicidal and germicidal properties. Hg_2Cl_2 is used to treat club root, a disease in brassicas (the cabbage family of plants) $HgCl_2$ is used to make organato derivatives and HgO in antifouling paints for ships etc. Almost all the compounds of Hg are toxic, but the organic compounds are extremely dangerous and have ecological effects. Small scale use of Hg include thermometer, barometer and manometers.

Compounds

The elements in this group all have two s-electrons beyond a completed d shell. (+II) oxidation state is characteristic of the group. However Hg also shows (+I) oxidation states. This oxidation state is more important. Univalent Hg^+ ion does not exist as mercureous compounds are dimerized as Hg_2Cl_2 $(Hg\text{-}Hg)^{2-}$. Cd^+ does not exist. Oxidation states higher than (+II) do not exist. They differ in their size Cd^{2+} (95 pm) Hg^{2+} (102pm). Therefore, they are not similar in properties as Zr and Hf.

CdO and HgO are known. CdO reacts with NaOH to give $Cd(OH)_2$. Due to formation of complexes is soluble in strong alkali $Na_2[Cd(OH)_4]$ or ammonia $[Cd(NH_3)_4]^{2+}$ HgO is basic. Both the oxides are formed either by heating nitrate or direct combination of metal with Air.

$$2 \ Hg\ (NO_3)_2 \longrightarrow 2 \ HgO + 4 \ NO_2 + O_2$$
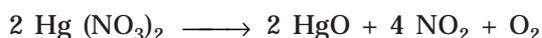
CdO sublime showing that it is appreciably covalent. Hgo does not sublime and decomposes on heating.

$$2 \ HgO \xrightarrow{\ 7400°C\ } 2 \ Hg + O_2$$
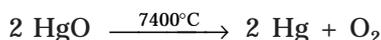
Due to lattice defects on heating they turns to yellow or green (CdO) and red or yellow (HgO).

(X = FCl Br or I)

All the dihalides MX_2 are known. Due to ionic character fluorides have higher melting points than other halides. The melting points of other halides are fairly low. This indicates that these are covalent

CdF_2 1049°C	HgF_2 645°C
$CdCl_2$ 568°C	$HgCl_2$ 276°C
$CdBr_2$ 567°C	$HgBr_2$ 236°C
CdI_2 387°C	HgI_2 259°C.

They have coordination number 8 with a fluorite (CaF_2) structure. The CdX_2 compounds are close packed arrays of halide ions with Cd^{2+} occupying half of the octahedral holes. $CdCl_2$ and CdI_2 form slightly different layer lattice in which Cd^{2+} ions occupy all the octahedral holes in one layer. $HgCl_2$ solid contains linear Cl–Hg–Cl molecules with a bond length Hg–Cl of 225 pm. $Hg Br_2$ and HgI_2 form layer lattices. All the halides are white except $CdBr_2$ which is pale yellow, and HgI_2 which exists in red and yellow forms. The colour is due to charge transfer. Cd salts are hydrated whereas Hg salts are usually anhydrous. Cd salts do not ionize completely in water and may undergo self complexing. Thus CdI_2 may give a mixture of hydrated Cd^{2+}, CdI^+, $CdI_2 \rightarrow [CdI_4]^{2-}$. Hg salts do not ionize. $HgCl_2$ (corrosive sublimate) can be prepared by heating $HgSO_4$ and NaCl and has been used as an antiseptic. However Hg_2Cl_2 (calomel) is used in medicine as a powerful laxative.

Complexes

Cd^{2+} forms complexes with O donor ligands and also N and S donor ligands whereas Hg^{2+} forms complexes with N-P and S donor ligands. Hg^{2+} is reluctant to bond to O. Complexes of Hg^{2+} ion are more stable than Cd^{2+} ion.

They do not form complexes with π-acceptor ligands. Hg^{2+} complexes are often coloured because of change transfer.

Generally geometry of Cd^{2+} is tetrahedral (four-coordinate). For example $[Cd\,(NH_3)_4]^{2+}$. To a lesser extent a six-coordinate octahedral complex of Cd^{2+} also known for example $[Cd(Phen)_3]^{2+}$ or $[Cd(en)_3]^{2+}$.

Most Hg^{2+} ion complex and octahedral. They are appreciably distorted with two short and four long bonds. Hg^{2+} also forms some tetrahedral complexes for example $[Hg\,(SCN)_4]^{2-}$.

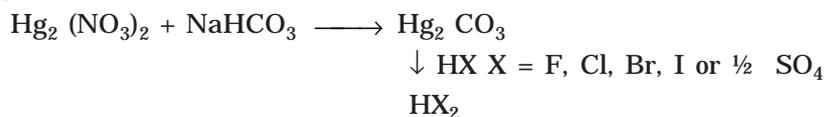### (+1) Oxidation state

Only a few Hg (I) compounds are known. They contain $[Hg–Hg]^{2+}$ not Hg^+. The two Hg atoms are bonded together using the $6s^1$ orbital.

They can be prepared by reducing Hg^{2+} salts with metal

$$Hg^{2+} + Hg \longrightarrow Hg_2{}^{2+}$$
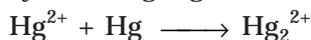
$Hg_2\,(NO_3)_2$ can be made by dissolving Hg in dil. HNO_3. Other salts are prepared by using $Hg_2\,(NO_3)_2$.

$$Hg_2\,(NO_3)_2 + NaHCO_3 \longrightarrow Hg_2\,CO_3$$
$$\downarrow HX \quad X = F,\ Cl,\ Br,\ I\ or\ \tfrac{1}{2}\ SO_4$$
$$HX_2$$

All the $Hg_2{}^{2+}$ halides are known. Hg_2F_2 is hydrolysed by water

$$Hg_2F_2 + 2H_2O \longrightarrow 2HF + Hg_2\,(OH)_2.$$
$$Hg_2(OH)_2 \xrightarrow{\text{disproportionate}} Hg^{II}O + Hg° + H_2O$$

Other halides i.e. Hg_2Cl_2, $Hg_2\,Br_2$ and $Hg_2\,I_2$ are insoluble in water. However, $Hg_2(NO_3)_2$ and $Hg_2\,(ClO_4)_2$ are soluble and contain the linear $[H_2O\,–Hg–Hg\,(OH_2)]^{2+}$. Oxides, hydroxides and sulphides are not known.

Comparison between the first row and other two rows

IInd row and IIIrd row transition elements differ to that of Ist row.

RADII

The radii of the heavier transition atoms and ions are known only in a few cases.

As already discussed the atomic radii of second row transition elements is large as compared to first row. But due to lanthanide contraction the radii of third row elements is almost same to that of second row.

Abundance

The ten elements of first row are reasonably common and make up 6.79% of earth's crust. The remaining transition elements are very scare. The 20 elements of second and third row together make up only 0.025% of the earth's crust. Tc does not occur in nature. The abundance Zr is 162 ppm, La 31 ppm, Y 31 ppm and Nb 20 ppm.

Metal-Metal bonding

Due to low value of enthalpies or atomization of first row transition elements as compared to other two row transition elements, the tendency to form compounds of M–M bonding is quite rare in first row transition elements. It occurs in a few carbonyl compounds such as $Mn_2(CO)_{10}$, $Co_2(CO)_8$ $Fe_3(CO)_{12}$ and $Co_4(CO)_{12}$. Some others compounds are carboxylate $Cr_2(CH_3COO)_4.2H_2O$ or $Cu_2(CH_3COO)_4.2H_2O$ and in solid dimethylglyoximate nickel (II).

However M–M bonding is more common in second and third row of transition elements.

(a) A number of carbonyls are known of these elements with M–M bonding. For example $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $RH_4(CO)_{12}$ and $Ir_4(CO)_{12}$. A specific carbonyl $Rh_6 (CO)_{16}$ which is not formed by Ist row transition elements.

(b) Line chromium (11) Mo, Ru and Rh form binuclear carboxylate complexes such as $MO_2(CH_3COO)_4(H_2O)_2$.

(c) Halides ions are known which have M-M bonds such as $[Re_2Cl_8]^{2-}$ and $[MO_2Cl_9]^{3-}$.

(d) The lower halides of several elements have a group of three or six metal atoms bonded together and are called cluster compounds. The compounds $[Nb_6 Cl_{12}]^{2+}$ and $[Ta_6Cl_{12}]^{2+}$ have unusual structures. Both contain six metal atoms arranged in a cluster at the corners of an octahedran, with 12 bridging halogen atoms across the corners. There is a extensive M-M bonding within the octahedron. Others examples are MO_6Cl_{12}, $W_6 Br_{12}$, Re_3Cl_9 etc.

Stability of oxidation states

(+II) and (+III) oxidation states are important for all the first row transition elements. M^{2+} and M^{3+} ions are well known for the first row transition elements but these are less important for second and third row elements, which have few ionic compounds. Similarly the first row form a large number of extremely stable complexes such as $[CrCl_6]^{3-}$ and $[Co (NH_3)_6]^{3+}$. No such type of compounds of Mo or W or Rh or Ir are known.

The higher oxidation states are important and stable for second and third row of transition elements as compare to first row elements. Molybdate $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ ions are stable whereas $[CrO_4]^{2-}$ acts as oxidizing agent. Similarly pertechnate $[TCO_4]^{-}$ and perhenate $[ReO_4]$ ions are stable. Some elements also form compounds in higher oxidation states which have no counterparts in the first row, for example WCl_6, ReF_7 RuO_4, OsO_4 and PtF_6.

Magnetism

The elements of first row transition elements are generally of high-spin type (*i.e.* more unpaired electron) whereas the second and third row elements are of low-spin type due the pairing of electrons. In an octahedral complexes the *d*-level split into two sets *i.e.* t_2g and eg The difference in the energy is depend on the nature of ligand and the metal. In case of first row transition elements it is dependent on the nature of ligands. Therefore generally first row transition elements form high-spin complexes. However, energy difference between t_2g and eg depend on the metal ion. This difference is higher for second and third row transition elements. Therefore, they are of low-spin type.

The spin only formula gives reasonable agreement relating the observed magnetic moment of first row transition metal complexes to the number of unpaired electrons. For the second and third row transition metal the orbital contribution is significant and in addition spin-orbit coupling may occur. Thus the spin only approximation is no longer valid, and more complicated equation must be used.

Thus the simple interpretation of magnetic moments in terms of the number of unpaired electrons cannot be extended from the first row of transition elements to the second and third rows. The second and third rows also show extensive temperature dependent (Fig. 2.17) paramagnetism. This is explained by the spin orbit coupling removing the degeneracy from the lowest energy level in the ground state.
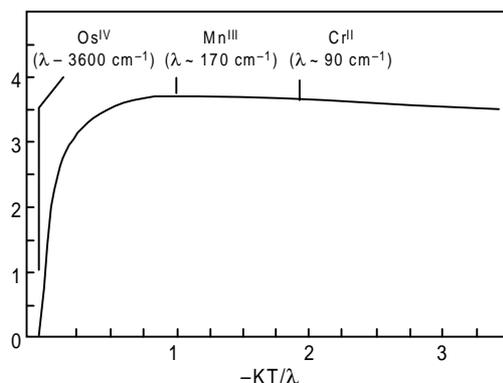
Fig. 2.17. Curve showing the dependence on temperature and on the spin-orbit coupling constant, λ, of the effective magnetic moment of a d^4 ion in octahedral coordination.

Complexes

Most of the transition elements form complexes having coordination 6. The coordination 4 is less common to give tetrahedral and square planar geometry. Coordination number 7 and 8 are uncommon for the first row but are much more common in the early members of the second and third rows. For example $[ZrF_7]^{3-}$, $[ZrF_8]^{4-}$ etc.

SOLVED QUESTIONS

Q.1. *Explain why the physical and chemical properties of Zr and Hf compounds are much more similar than the properties of Ti and Zr.*

Ans. Due to lanthanide contraction the size of Zr and Hf is almost similar. However, the Zr is larger in size than Ti. Therefore, the properties of Zr and Hf are same whereas the properties of Ti and Zr are different.

Q.2. *Oxoanions of 4d and 5d transition elements do not act as oxidizing agent 3d do.*

Ans. Higher oxidation states are more stable for $4d$ and $5d$ transition elements than elements of $3d$ transition series. Therefore, the oxoanions of $4d$ and $5d$ are stable whereas the oxoaions of $3d$ elements act as oxidizing agents.

Q.3. *Elements 4d and 5d transition series tend to give low-spin compounds. Why ?*

Ans. There are two main reasons for this intrinsically greater tendency to spin pairing.

1. The $4d$ and $5d$ orbitals are spatially larger than $3d$ orbitals so that double occupation of an orbital produces significantly less interelectronic repulsion.

2. a given set of ligand atoms produces larger splittings of $5d$ than of $4d$ orbitals and in both cases larger splitting than for $3d$ orbitals.
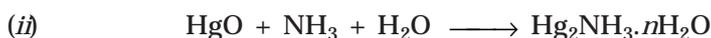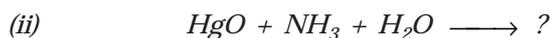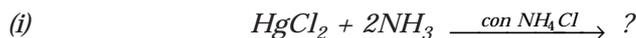
Q.4. *ZrO_2 is almost insoluble in an excess of base ? Whereas TiO_2 is soluble why ?*

Ans. ZrO_2 is more basic than TiO_2 and virtually therefore, insoluble in an excess of base. There is more extensive aqueous chemistry of Zr because of lower tendency toward complete hydrolysis.

**Q.5.** *List out the names of platinum metals.*

Ans. Ru, Os, Rh, Ir, Pd and Pt.

Q.6. *How is Zr extracted from Zircons ?*

Ans. Zircon

$$ZrSiO_4 + 60\% \ ZrO_2 \xrightarrow[\text{Arc furnace}]{\text{(CuO + C) Air}} ZrC + Zrn$$

$$300°C \downarrow Cl_2$$

$$\text{Pure Zr} \xleftarrow[\substack{\text{W Filament} \\ \text{1200-1300°C}}]{\text{Hot}} ZrI_4 \xleftarrow{I_2} Zr \xleftarrow{\text{Mg, 800°C}} ZrCl_4$$

Q.7. *NbF_5 is white but $NbCl_5$ is yellow why ?*

Ans. Nb (V) has $4d^0$ electronic configuration so the compounds of Nb (V) should be white. So $NbCl_5$ is yellow coloured due to change transfer spectra.

Q.8. *Mo/W can be easily separated compared to Zr/Hf and Nb/Ta pairs though all these pairs are under lanthanide contraction effect. Why ?*

Ans. Due to lanthanide contraction these elements show similarity in radii and other physical and chemical properties. However, this effect decrease and remain more effective upto V groups. So Zr/Hf and Nb/Ta are closely similar. Mo/W have difference in their size and also in properties.

Q.9. *Name the scientists who discovered Tc.*

Ans. In 1937 Segre and Perrier produced Tc by bombardment of Mo plate with ^2_1H in a cyclotron :

$$^{96}_{42}Mo + ^2_1H \longrightarrow ^{97}_{43}Tc + ^1_0n$$

Tc which has been isolated by Segre and Perrier showed strong β activity.

Q.10. *Write down the formula of first known transition metal complex with nitrogen.*

Ans. The first transition metal complex of nitrogen is $[Ru(NH_3)_5N_2]^{2+}$

$$[Ru(NH_3)_5H_2O]^{2+} + N_2 \longrightarrow [Ru(NH_3)_5N_2]^{2+}$$

Q.11. *Give the example of platinum compounds useful in cancer chemotherapy.*

Ans. (1) Cis platin   *i.e.*

Q.12. *Discuss the role of AgBr in photogrophy.*

Ans. It has two important roles in photography.

(*i*) Development (negative)

$$C_6H_4(OH)_2 + 2AgBr \xrightarrow[\text{exposed}]{} C_6H_4O_2 + 2Ag + 2HBr$$

(*ii*) Fixing

$$AgBr + Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

Printing is done by negative then extra Ag^+ is washed way with $Na_2S_2O_3$.

Q.13. *Complete following equation.*

(i) $\qquad\qquad HgCl_2 + 2NH_3 \xrightarrow{\ con\ NH_4Cl\ } ?$

(ii) $\qquad\qquad HgO + NH_3 + H_2O \longrightarrow ?$

(iii) $\qquad\qquad Ag_2S + 4NaCN \longrightarrow ?$

Ans. (*i*) $\qquad\qquad HgCl_2 + 2NH_3 \xrightarrow{\ +conc\ NH_4Cl\ } Hg(NH_3)_2Cl_2$

(*ii*) $\qquad\qquad HgO + NH_3 + H_2O \longrightarrow Hg_2NH_3.nH_2O$

(*iii*) $\qquad\qquad Ag_2S + 4NaCN \longrightarrow 2Na[Ag(CN)_2] + Na_2S$

Q.14. *Why is ZrCl$_4$ the most stable chloride of Zirconium, while for palladium it is PdCl$_2$?*

Ans. The third and higher ionization energies of the *d*-block metals increase with increasing atomic number owing to the large Z_{eff} making it more energetically unfavorable to attain oxidation state abvoe +2. Furthermore, the *d*-orbitals become more core-like towards the ends of the transition series, and so are less effective in stablizing higher oxidation states through covalent contributions to bonding. These factors combine to make higher oxidation states less accessible to the right of the *d*-block. In addition , there is a greater loss of exchange energy in creating Pd^{4+} from Pd^{2+} than Zr^{2+} to Zr^{4+}.

**Q.15.** *Write down the oxidation state and valence shell electron configuration of the metal in each of the following ions.*

TaO_4^{3-}, Pr^{3+}, OsO_4, Rh^+, Gd^{3+}, Yb^{2+}, $PaO(OH)^{2+}$, UO_2^{2+}, Pu^{4+}, NO^{2+}.
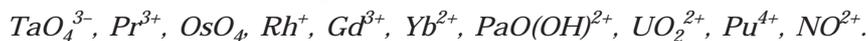
Ans. TaO_4^{3-} (+5) $5d^0$, Pr^{3+} (+3) $4f^2$, OsO_4 (+8) $5d^{10}$, Rh^+ (+1) $4d^8$, Gd^{3+} (+3) $4f^7$, Yb^{2+} (+2) $4f^{14}$, $PaO(OH)^{2+}$ (+5) $5f^0$, UO_2^{2+} (+6) $5f^0$, Pu^{4+} (+4) $5f^4$, NO^{2+} (+2) $5f^{14}$.

UNSOLVED QUESTIONS

Q.1. State the chief differences between the second and third row transiton elements on the one hand and those of the first series on the other hand with respect to (*a*) atomic and ionic radii (*b*) oxidation states (*c*) formation of metal-metal bond (*d*) magnetic properties (*e*) stereochemistry.

Q.2. Why are the chemical and physical properties of Hf and Zr compounds are so similar.

Q.3. What elements characteristically form cluster in their lower oxidation states ? Gives examples of the the three major types, two of which have six metal atoms and the other three.

Q.4. Explain the physical and chemical properties of RuO_4 and OsO_4, including preparations and toxicology.

Q.5. What is the nature of dihalides of Mo and W ?

Q.6. List all the elements in the group called the 'platinum metals.' and show how and where they are arranged in the periodic table.

Q.7. Complete the following

$$Mo + F_2 \longrightarrow$$

$$W + F_2 \longrightarrow$$

$$Mo + Cl_2 \longrightarrow$$

$$W + Cl_2 \longrightarrow$$
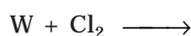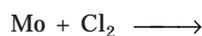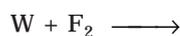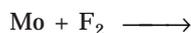
Q.8. How is commerical $RuCl_3.3H_2O$ prepared and what does it octually contain ? Suggest the products when it is (*a*) dissolved in con^n HCl and evaporated (*b*) heated with aqueous hydrazine (*c*) boiled in aquous $NH_4Cl + NH_4OH$ with Zn powder (*d*) heated with triphenyl phosphine in ethanol.

Q.9. Suggest explanations for the following

(*a*) the aquo nickel (II) ion is paramagnetic while the aquo palladium (II) ion is diamagnetic.

(*b*) the $[Ru_2OCl_{10}]^{4-}$ ion has no unpaired electron.

(*c*) there is a important metal-metal bonding in $M_6Cl_{12}^{n+}$ cluster species when M = Nb or Ta but not when M = Pd or Pt.

Q.10. Why is it that compounds such as K_3ZrF_7, $K_4Zr_2F_{12}$ and K_4ZrF_8 can by crystallized from solution which contain all the zirconium as ZrF_6^{2-} ? What is the structure of $Zr_2F_{12}^{4-}$?

Q.11. Write balanced equations for the following processes;

(*a*) leaching of metallic gold by CN^- in the presence of oxygen.

(*b*) reaction of AgI with a solution of thiosulphate.

(*c*) reaction of $AgNO_3$ with $S_2O_8^{2-}$ in the presence of excess pyridine　　　　[Hint $Ag(Py)_4]^{2+}$

Q.12. Write down the oxidation state and valence shell electron configuration of the metal in each of the following ions:

$$OsO_4 \; Rh^+, \; TaO_4^{3-} \; Ru^{2+}$$

Q.13. What evidence is there that the mercurous ion Hg_2^{2+} rather than Hg^+ ?

Q.14. When mercury is oxidized with a limited amount of oxidizing agent then Hg^I compounds are formed. If there is an excess of oxidizing agent then Hg^{II} compounds are formed. Explain this.

Q.15. Suggest reasons why the noble metals are relatively unreactive.

Q.16. Give examples of Mo (V) and W (V) oxo species. Comment on the structure of the species of Mo (V) and W (V), one for each.

Q.17. Ru (II) complex with ammonia used in N_2 fixation. How this complex is prepared ? Discuss its structure.

Q.18. Discuss the position of platinum in the periodic table.

Q.19. Describe the chemistry of photography.

Q.20. Suggest structures of $Os_2(CO)_9$ and $Os_3(CO)_{12}$.

Q.21. Draw the structures of (*a*) $[Re_2Cl_8]^{2-}$, $[RhH_9]^{2-}$ and Re_3Cl_9.

Q.22. What are hetero and isopolyacids of Mo and W ? Explain with example.

Q.23. Explain the method of preparation of the following

(*a*) $[Mo_6Cl_8]^{4+}$, (*b*) $(NH_4)_6MO_7O_{24}.4H_2O$, (*c*) $WO_3.nH_2O$, (*d*) ReO_4^- (*e*) RuO_4^- (*f*) Molybdenum blue.

Q.24. Discuss the Parke's process for extraction of Ag from argentiferrus lead.