

# Chapter 2

CHEMISTRY OF  
ELEMENTS OF  
SECOND AND THIRD  
TRANSITION SERIES

# HEAVY METALS

- Second and Third Transition Series elements are also called **Heavy metals**

IIIB	IVB	VB	VIB	VIB	VII		IB	IB	
21 Sc	22 Ti	23 Y	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg

# ELECTRONIC CONFIGURATION

- ⦿ Second transition series

- ⦿ Yttrium (  $z = 39$  ) to Cadmium (  $Z = 48$  )

- ⦿ 4d orbital's are gradually filled

- ⦿ Third Transition Series

- ⦿ Lanthanum (  $Z = 57$  ) to Hafnium (  $Z=72$  ) to Mercury (  $Z=80$  )

- ⦿ 5d orbital's are gradually filled

# SECOND TRANSITION SERIES

elements	Atomic Number	Symbol	Electronic configuration
<u>Ytterium</u>	39	Y	[Kr] 4d <sup>1</sup> 5s <sup>2</sup>
Zirconium	40	<u>Zr</u>	[Kr] 4d <sup>2</sup> 5s <sup>2</sup>
Niobium	41	<u>Nb</u>	[Kr] 4d <sup>4</sup> 5s <sup>1</sup>
Molybdenum	42	Mo	[Kr] 4d <sup>5</sup> 5s <sup>1</sup>
Technetium	43	<u>Tc</u>	[Kr] 4d <sup>5</sup> 5s <sup>2</sup>
Ruthenium	44	<u>Ru</u>	[Kr] 4d <sup>7</sup> 5s <sup>1</sup>
Rhodium	45	<u>Rh</u>	[Kr] 4d <sup>8</sup> 5s <sup>1</sup>
Palladium	46	Pd	[Kr] 4d <sup>10</sup> 5s <sup>0</sup>
Silver	46	Ag	[Kr] 4d <sup>10</sup> 5s <sup>1</sup>
Cadmium	48	<u>Cd</u>	[Kr] 4d <sup>10</sup> 5s <sup>2</sup>

# SERIES

Element	Atomic number	Symbol	Electronic configuration
Lanthanum	57	La	[Xe] 5d <sup>1</sup> 6s <sup>2</sup>
Hafnium	72	Hf	[Xe] 4f <sup>14</sup> 5d <sup>2</sup> 6s <sup>2</sup>
Tantalum	73	Ta	[Xe] 4f <sup>14</sup> 5d <sup>3</sup> 6s <sup>2</sup>
Tungsten	74	W	[Xe] 4f <sup>14</sup> 5d <sup>4</sup> 6s <sup>2</sup>
Rhenium	75	Re	[Xe] 4f <sup>14</sup> 5d <sup>5</sup> 6s <sup>2</sup>
Osmium	76	Os	[Xe] 4f <sup>14</sup> 5d <sup>6</sup> 6s <sup>2</sup>
Iridium	77	Ir	[Xe] 4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>
Platinum	78	Pt	[Xe] 4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>
Gold	79	Au	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup>
Mercury	80	Hg	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>

# GENERAL CHARACTERISTICS

- Elements show a strong similarity in their chemistry with in a group but show large differences from the elements of the first transition series .
- This similarity is due to filling of 4f orbital in the elements that's lie between these two rows of elements (i.e. period 5 and 6)

# ATOMIC AND IONIC RADII

- As we move down there is a increase in the size increases from first to second but from second to third transition series increase in negligible

## CONTD

- ⦿ There are 14 elements called lanthanides 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  $\text{Hf}^{4+}$  are actually smaller than the corresponding value of Zr



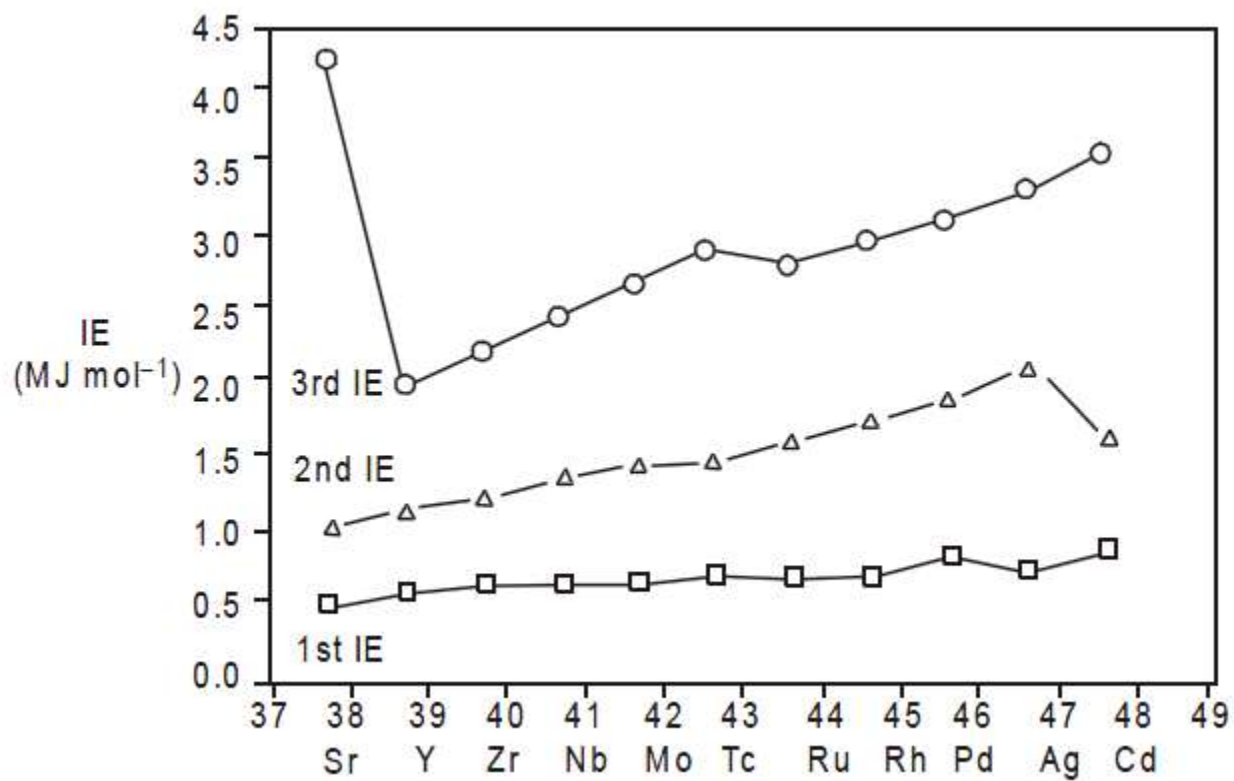
## CONTD

- 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  $\text{Sc} \rightarrow \text{Y} \rightarrow \text{La}$
- . 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

# IONIZATION ENERGY

- ◉ Due to almost same size of second and third row transition series, they show almost same value of ionization energy
- . 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 sub shells.

# IONIZATION ENERGY



# 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  $\text{OsO}_4$  and  $\text{RuO}_4$
- 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

# CONTD

- ⦿ State stoichiometric oxides and fluorides of the second and third row elements are given in Tables.
- ⦿ Binary compounds with less electronegative element chlorine might be expected to show a slightly different range of oxidation states.
- ⦿ The elements of second and third rows show maximum oxidation state for example  $\text{MO}_4$  ( $M = \text{Os}$  or  $\text{Ru}$ ) with oxygen and  $\text{Re}(+\text{VII})$  in  $\text{ReF}_7$  with fluorine

# THE MOST COMMON OXIDATION NUMBERS OF THE TRANSITION METALS

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

# THE MOST COMMON OXIDATION NUMBERS OF THE TRANSITION METALS

<i>La</i>	<i>Hf</i>	<i>Ta</i>	<i>W</i>	<i>Re</i>	<i>Os</i>	<i>Ir</i>	<i>Pt</i>	<i>Au</i>	<i>Hg</i>
								+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					

# REACTIVITY

- Elements of first transition are more reactive than the elements of second and third
- The lanthanide contraction is mainly responsible for the low reactivity of 2<sup>nd</sup> and 3<sup>rd</sup> transition series
- Eg. Gold and Platinum are least reactive



# STABILITY OF THE COMPLEXES

- Transition metals have the ability to form complexes this is due to **small size , highly charged ions and availability of vacant d orbital's**
- The elements of first transition series form stable complexes with hard donors viz N , O and F , where as elements of 2<sup>nd</sup> and 3<sup>rd</sup> transition series form stable complexes with P , s and heavier Chalcogen donors

# MAGNETIC PROPERTIES

- Magnetic moments are close to spin only value , in first transition series but elements of 2<sup>nd</sup> and 3<sup>rd</sup> transition metal ions often observed a complex behavior
- Compounds of 1<sup>st</sup> transition series show High spin nature , the compound of 2<sup>nd</sup> and 3<sup>rd</sup> are low spin nature .

There are two main reasons for this ,

1. 4d and 5d orbital's are spatially larger than 3d orbital's so that the presence of 2 electrons in an orbital produces less electronic repulsion .
2. A given set of ligand produces large splitting of d orbital's in case of 5d then of 4d than of 3d .

# METAL -METAL BONDING

- Metal -metal bonding is very rare in first transition series except in Metal carbonyls such as  $\text{Mn}_2(\text{CO})_{10}$   $\text{Fe}_2(\text{CO})_9$   $\text{Co}_4(\text{CO})_{12}$  and in carboxylate complex such as  $\text{Cr}_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2$
- On the other hand metal -metal bonding is very common among the heavier elements for example they form carbonyl with M-M bonds similar to those of 1<sup>st</sup> transition series VIZ  $\text{Ru}_3(\text{CO})_{12}$   $\text{Os}_3(\text{CO})_{12}$
- Metals such as Mo, Ru and Rh form Binuclear carboxylate complexes such

# CONTD

- ⊙ 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. Forexample*  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Os}_3(\text{CO})_{12}$ ,  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Ir}_4(\text{CO})_{12}$ . A specific carbonyl  $\text{Rh}_6(\text{CO})_{16}$  which is not formed by Ist row transition elements.

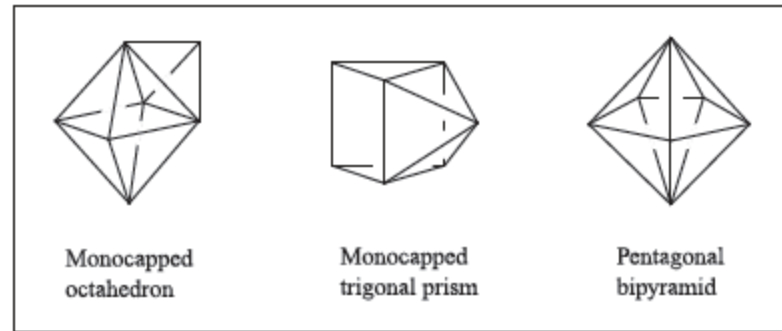
- ⊙ (b) Line chromium (11) Mo, Ru and Rh form binuclear carboxylate complexes such as  $\text{MO}_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2$
- ⊙ (c) Halides ions are known which have M-M bonds such as  $[\text{Re}_2\text{Cl}_8]_{2-}$  and  $[\text{MO}_2\text{Cl}_9]^-$

- ⊙ (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  $[\text{Nb}_6\text{Cl}_{12}]_{2+}$  and  $[\text{Ta}_6\text{Cl}_{12}]_{2+}$  have unusual structures. Both contain six metal atoms arranged in a cluster at the corners of an octahedron, with 12 bridging halogen atoms across the corners. There is an extensive M-M bonding within the octahedron. Other examples are  $\text{Mo}_6\text{Cl}_{12}$ ,  $\text{W}_6\text{Br}_{12}$ ,  $\text{Re}_3\text{Cl}_9$  etc.*

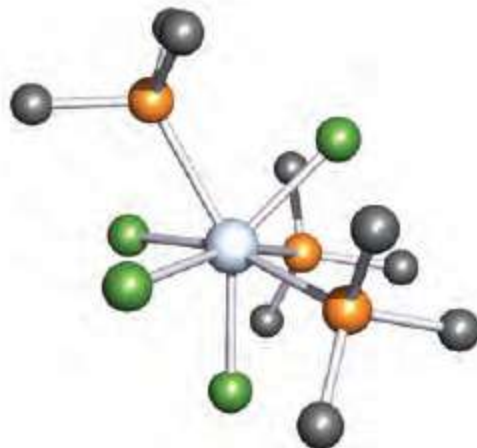
# COORDINATION NUMBER

- ◉ The coordination Number 6 is commonly found giving octahedral structure .
- ◉ Complexes with coordination number higher than 6 is less common in first transition series but common among second and third transition series .
- ◉ There are few compounds in which coordination number is 7 .

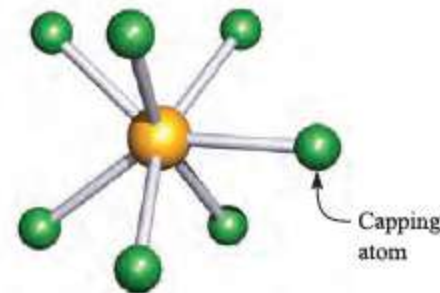
# GEOMETRY ADOPTED BY COORDINATION NUMBER 7



(a) The coordination spheres defined by the donor atoms in idealized 7-coordinate structures.



(b)



(c)



Comparative study of  
elements of 2<sup>nd</sup> and 3<sup>rd</sup>  
transitional series

# ZIRCONIUM (ZR) AND HAFNIUM (HF)

- ◉ 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.
- ◉ Their chemical properties are almost same. Separation of two elements is difficult.

# EXTRACTION IS DIFFICULT DUE TO

- ⦿ The sizes of Zr and Hf are nearly the same due to Lanthanide contraction .
- ⦿ They possess similar electronic configuration
- ⦿ But now they can be separated effectively by ion exchange or solvent extraction

# PROPERTIES AND USES

- Like titanium both Zr and Hf are metal, hard and corrosion resistant and their melting point  $1855^{\circ}\text{C}$  and  $2222^{\circ}\text{C}$  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  $\text{Zr}_2\text{ON}_2$ .
- 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 HF AND ZR

- 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  $ZrO_2 \cdot nH_2O$  is formed. Where  $n$  is variable.
- $ZrO_2$  and  $HfO_2$  are stable white solids, non-volatile and rendered refractory by strong ignition.
- $ZrO_2$  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  $1000^\circ C - 2500^\circ C$ . Zirconates and hafnates are formed

# HALIDES

- ⊙ All the halides of the type  $MX_4$  (where  $M = \text{Zr}$  or  $\text{Hf}$  and  $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) are known.
- ⊙  **$\text{ZrCl}_4$ . It can be prepared by the chlorination of heated Zirconium, Zirconium carbide and a mixture of  $\text{ZrO}_2$  and charcoal. It is white solid, subliming at  $331^\circ\text{C}$ .**
- ⊙ It fumes in moist air and hydrolyzed vigorously by water. Hydrolysis proceeds only partway at room temperature, affording the stable oxide chloride.
- ⊙  $\text{ZrCl}_4 + 9\text{H}_2\text{O} \rightarrow \text{ZrOCl}_2 \cdot 8\text{H}_2\text{O} + 2\text{HCl}$

# AQUEOUS CHEMISTRY AND COMPLEXES

- ◉  $\text{ZrO}_2$  is more basic as compared to  $\text{TiO}_2$ , therefore it is virtually insoluble in an excess base.
- ◉ The aqueous chemistry of  $\text{Zr}^{4+}$  is well known since it is doubtful that hydrolysis of  $\text{Zr}^{4+}$  takes place.
- ◉ The hydrolyzed ion is often known as Zirconyl ion and written  $\text{ZrO}_2^+$ .
- ◉ The most important Zirconyl salt is  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  which crystallizes from dil. HCl and contain  $[\text{Zr}_4(\text{OH})_8]_{20}\text{O}_{16}]^{8+}$ .
- ◉



## NIOBIUM(NB)AND TANTALUM(TA)

- ◉ 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 columbit-tantalite( $\text{FeMnNb}_2\text{O}_6$ ) ( $\text{Fe,MnTa}_2\text{O}_6$ ) series of minerals.
- ◉ The most important mineral is Pyrochlorite  $\text{CaNaNb}_2\text{O}_6\text{F}$ .
- ◉ 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 HF Nb forms a soluble  $\text{K}_2[\text{NbOF}_5]$  and Ta forms insoluble  $\text{K}_2[\text{TaF}_7]$ .

# PROPERTIES AND ITS USES

- ◉ Nb and Ta are silvery colored 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.  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  are amphoteric.
- ◉ They have only weak acidic properties. Niobates and tantalates are only formed by fusing with NaOH.

# CONTI...

- ◉ 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  $3800^{\circ}\text{C}$ ).

# COMPOUNDS

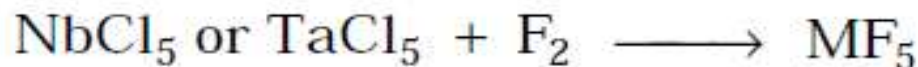
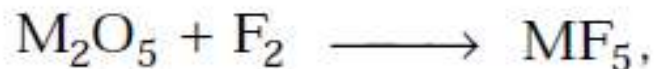
- Nb and Ta react with all of the halogens on heating to give pentahalides  $MX_5$
- . The range of halides is given in Table
- All the halides are volatile, covalent and hydrolyzed by water.

# HALIDES OF NIOBIUM

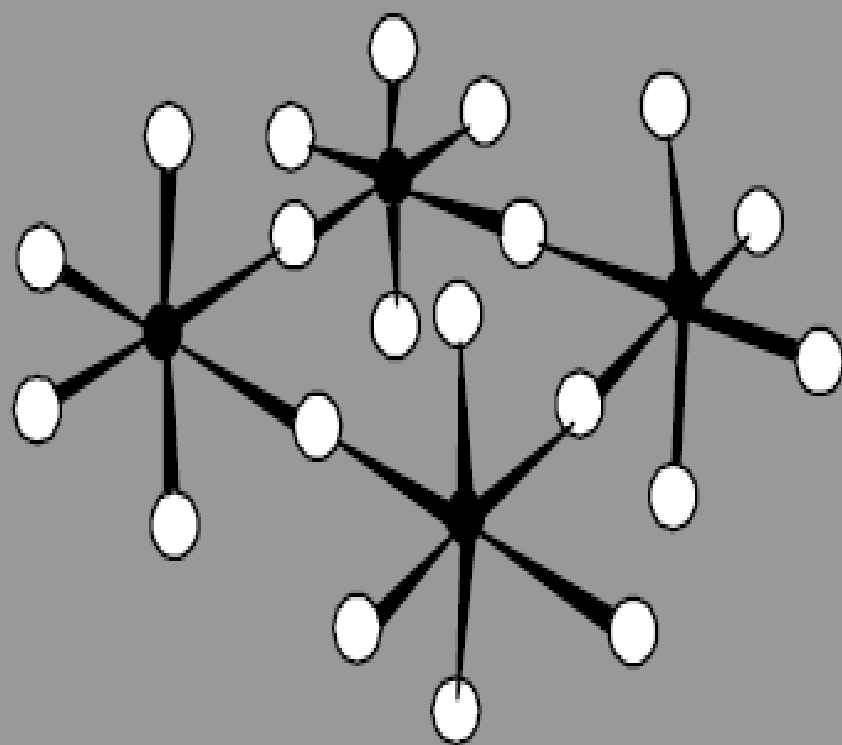
<i>+III</i>	<i>+IV</i>	<i>+V</i>
NbF <sub>3</sub>	NbF <sub>4</sub>	NbF <sub>5</sub>
NbCl <sub>3</sub>	NbCl <sub>4</sub>	NbCl <sub>5</sub>
NbBr <sub>3</sub>	NbBr <sub>4</sub>	NbBr <sub>5</sub>
NbI <sub>3</sub>	NbI <sub>4</sub>	NbI <sub>5</sub>
	--	TaF <sub>5</sub>
TaF <sub>3</sub>	TaCl <sub>4</sub>	TaCl <sub>5</sub>
TaCl <sub>3</sub>	TaBr <sub>4</sub>	TaBr <sub>5</sub>
TaBr <sub>3</sub>	TaI <sub>4</sub>	TaI <sub>5</sub>

## +V HALIDES

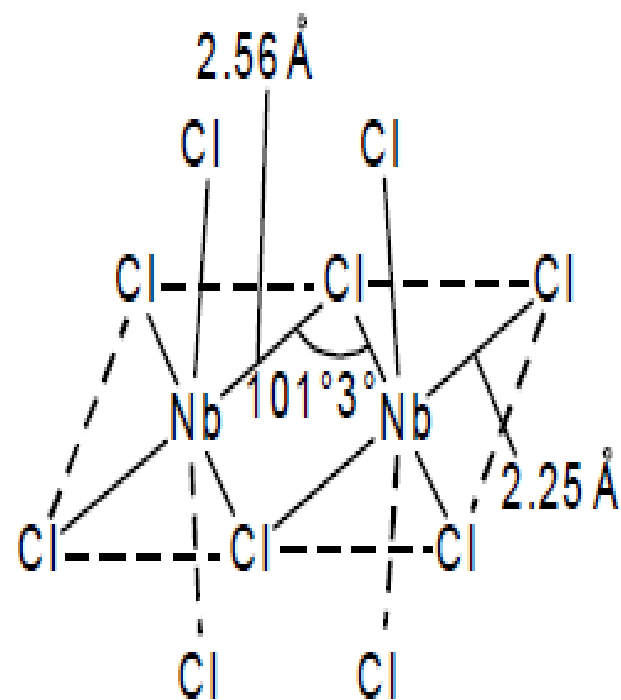
- ⊙ Nb and Ta form penta halides. These may be formed by direct reaction of the elements or by the reaction oxides.
- ⊙  $\text{NbF}_5$  and  $\text{TaF}_5$  form cyclic tetramers with four octahedra joined in this way (Fig.2)
- ⊙ Solid  $\text{NbCl}_5$  and  $\text{TaCl}_5$  are dimeric with two octahedral joined by sharing two corners



FIG



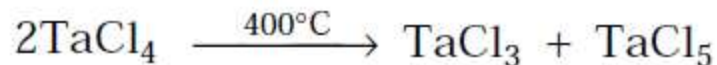
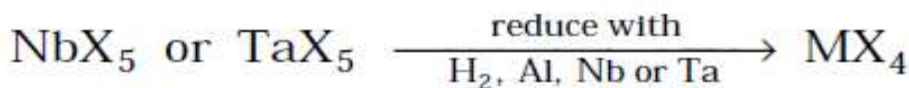
(a)



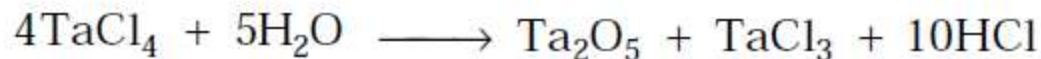
(b)

## (+IV) HALIDES

- The tetrahalides are formed by the reduction of pentahalides with H<sub>2</sub>, Al, Nb or Ta.
- NbF<sub>4</sub> is black paramagnetic nonvolatile solid made up of regular octahedral joined in chain by their edges. Other tetrahalides are brown-black solids and are diamagnetic. This suggests extensive metal-metal interaction. NbI<sub>4</sub> the structure is a chain of octahedral joined by their edges. NbCl<sub>4</sub> is similar. Tetrahalides tend to dispr



They hydrolyze by water





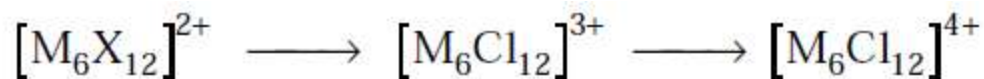
## (+III) HALIDES

- All the trihalides are known except  $TaI_3$ . They are reducing, have a *d<sup>1</sup> 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.

- High temperature reduction of the pentahalides.  $\text{NbX}_5$  and  $\text{TaX}_5$  with Na or Al give a series of lower halides such

- $\text{M}_6\text{Cl}_{14}$ ,  $\text{M}_6\text{I}_{14}$ ,  $\text{Nb}_6\text{F}_{15}$ ,  $\text{Ta}_6\text{Cl}_{15}$ ,  $\text{Ta}_6\text{Br}_{15}$  and  $\text{Ta}_6\text{Br}_{17}$

- These are be oxidized.



# OXIDES

- The metals all react with  $O_2$  at elevated temperatures and give pentaoxide  $M_2O_5$ .
- The main oxides formed are shown

<i>(+II)</i>	<i>(+III)</i>	<i>(+IV)</i>	<i>(+V)</i>
NbO	–	NbO <sub>2</sub>	Nb <sub>2</sub> O <sub>5</sub>
TaO	–	TaO <sub>2</sub>	Ta <sub>2</sub> O <sub>5</sub>

# MOLYBDENUM(MO) AND TUNGSTEN(W)

- 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  $\text{MoS}_2$ , but also as molybdates such as Wulfenite ( $\text{PbMoO}_4$ ) or  $\text{MgMoO}_4$ .
- Tungsten is found almost exclusively in the form of tungstate, the chief ore being Wolframite ( $\text{FeWO}_4$  and  $\text{MnWO}_4$ ), scheelite ( $\text{CaWO}_4$ ) and stolzite ( $\text{PbWO}_4$ ).

# PROPERTIES AND USES

- The metals are hard and have very high melting and low volatility .
- 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  $2610^{\circ}\text{C}$  and  $3418^{\circ}\text{C}$  respectively

## CONT...

- ⊙ 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  $W$ ).



# HALIDES

- ⦿ They also combine with  $\text{Cl}_2$  to give  $\text{MCl}_6$ . They react with  $\text{F}_2$  at room temperature to
- ⦿ form  $\text{MF}_6$
- ⦿  $\text{Mo} + 3\text{Cl}_2 \rightarrow \text{MoCl}_6$

# PREPARATION OF MOLYBDENUM CHLORIDES AND CHLORO COMPLEXES

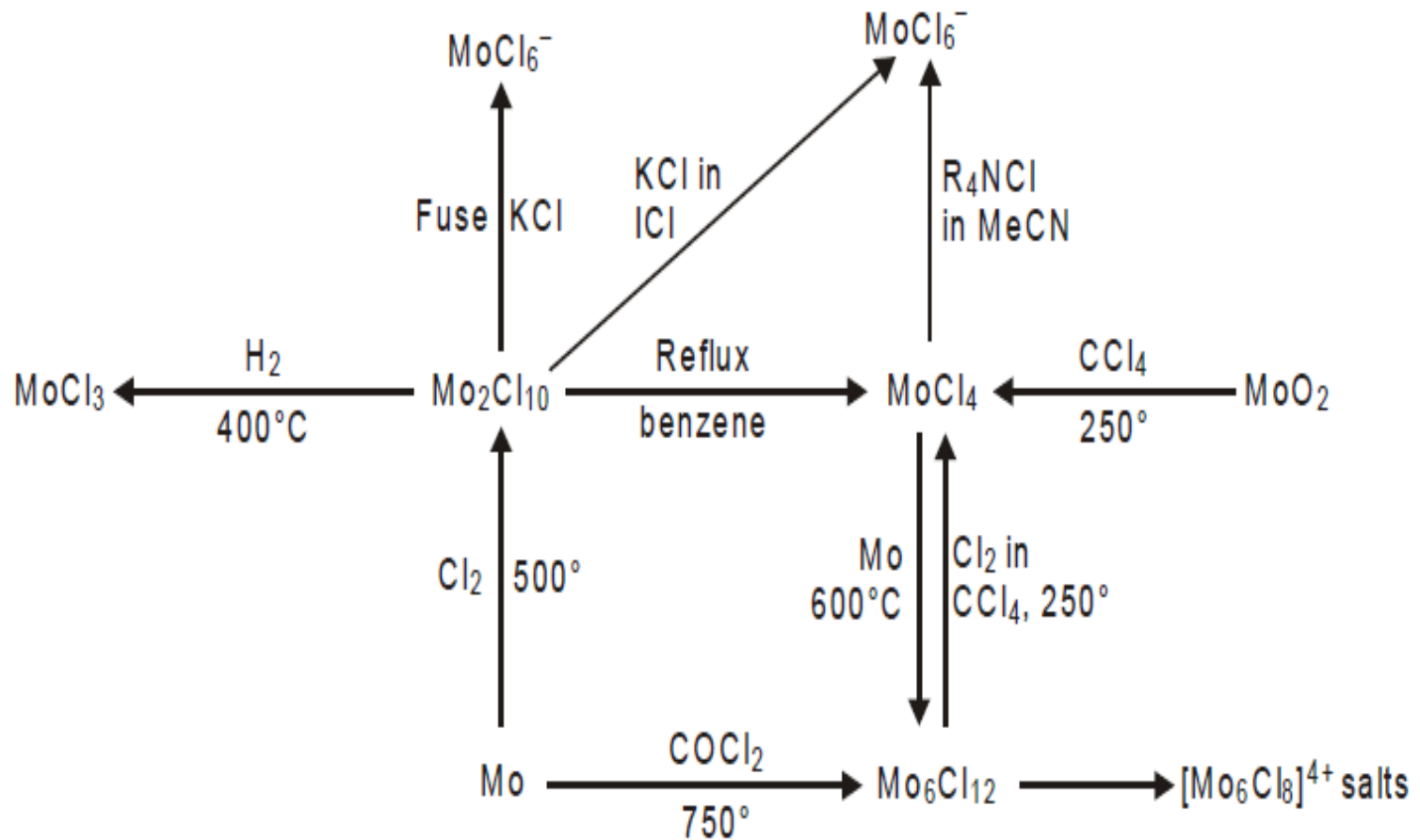


Fig. 2.1. Preparation of molybdenum chlorides and complexes.



- Treatment of molybdenum carbonyl with fluorine diluted in nitrogen at  $-75^{\circ}\text{C}$  gives a product of composition  $\text{Mo}_2\text{F}_9$ . On heating  $\text{Mo}_2\text{F}_9$  at  $150^{\circ}\text{C}$  gave the nonvolatile  $\text{MoF}_4$  as a residue and volatile  $\text{MoF}_5$  which condenses in a cooler region of the apparatus.
- $\text{MoF}_5$  is also obtained by the reactions.
- $5\text{MoF}_6 + \text{Mo}(\text{CO})_6 \text{ -----} \rightarrow 6\text{MoF}_5 + 6\text{CO}$  (at  $25^{\circ}\text{C}$ )
- $\text{Mo} + 5\text{MoF}_6 \rightarrow 6\text{MoF}_5$
- $\text{Mo} + \text{F}_2$  (dil)  $\rightarrow \text{MoF}_5$  ( at  $400^{\circ}\text{C}$ )

# TECHNETIUM (TC ) AND RHENIUM (RE)

- Technetium does not occur in nature and was the first manmade element
  - . All the isotopes are radioactive.  $^{99}\text{Tc}$  is one of the fission products of uranium. It is a  $\beta$  emitter with half-life of  $2.1 \times 10^5$  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  $\text{Tc}_2\text{O}_7$  which is volatile.

# CONTI..

- Rhenium is a very rare element, and occurs in small amounts in molybdenum sulphide ores. Re is recovered as  $\text{Re}_2\text{O}_7$  from the flue dust from roasting these ores.
- This is dissolved in NaOH, giving a solution containing  $\text{ReO}_4^-$  ion.
- The solution is concentrated and then KCl added to precipitate  $\text{KReO}_4$ . The metal is obtained by reducing  $\text{KReO}_4$  or  $\text{NH}_4\text{ReO}_4$  with  $\text{H}_2$ .
- 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. ( $3180^\circ\text{C}$ ) it is used in thermocouple, electric furnace windings and mass spectrometer filaments.

# PROPERTIES

- Tc and Re are less reactive. They do not react with  $\text{H}_2\text{O}$  or non-oxidizing acids.

They do not dissolve in  $\text{HCl}$  and  $\text{HF}$ , but they react with oxidizing acids, such as conc.  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  forming pertechnic acid  $\text{HTeO}_4$  and perhenic acid  $\text{HReO}_4$ .

Tc and Re undergo similar reaction with  $\text{H}_2\text{O}_2$  and bromine water. They get tarnish slowly in moist air, but powder metal is more reactive. Heating with  $\text{O}_2$  gives  $\text{Tc}_2\text{O}_7$  and  $\text{Re}_2\text{O}_7$  which are low melting point (119.5°C and 300°C respectively) and volatile

- . On heating with  $\text{F}_2$  gives  $\text{MF}_6$  and  $\text{MF}_7$  ( $\text{M} = \text{Tc}$  or  $\text{Re}$ ).

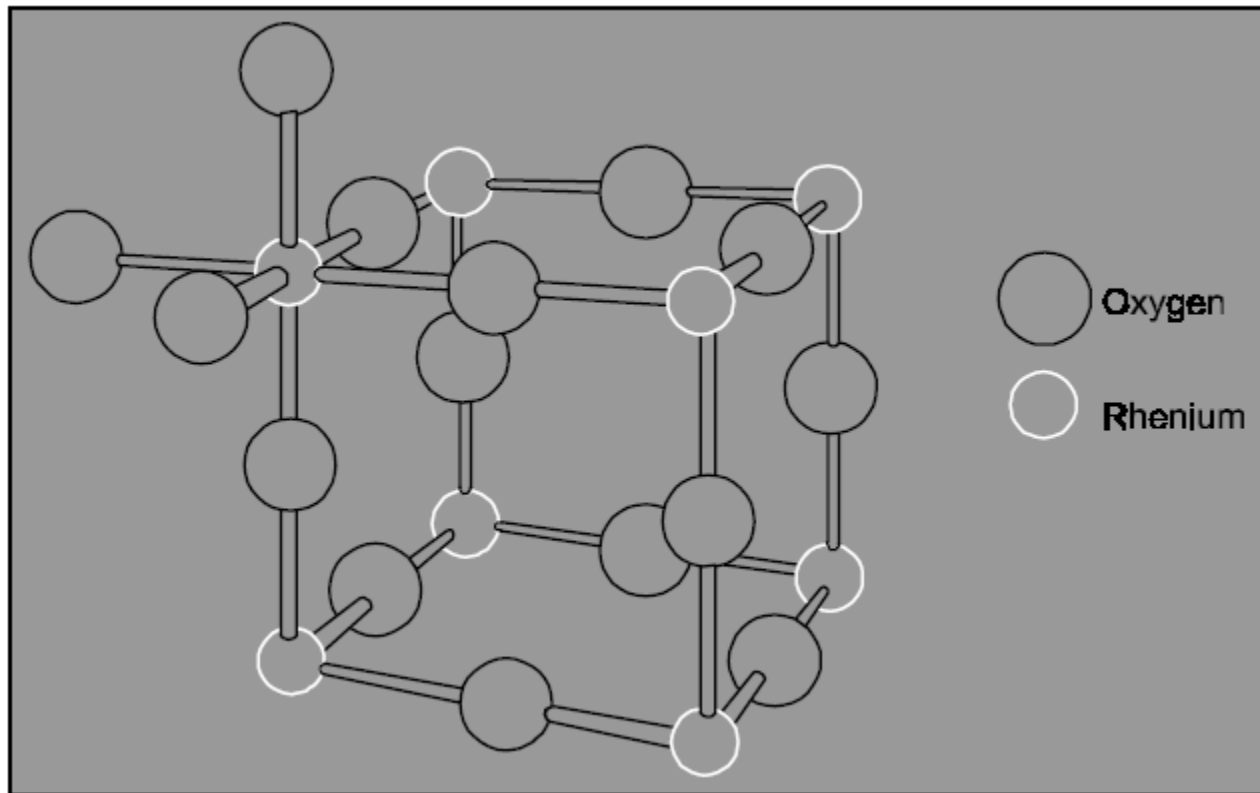
# OXIDES

- ⊙ Many compounds such as  $M_2O_7$ ,  $M_2S_7MO_3$ 
  - -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  $120^\circ C$  and  $220^\circ C$  respectively.  $Tc_2O_7$  is more oxidizing than  $Re_2O_7$ .

# HALIDES

- On heating Re with fluoroine to form  $\text{ReF}_7$ . Tc forms only  $\text{TcF}_6$ . Several oxohalides are formed such as  $\text{ReOF}_5$ ,  $\text{ReO}_2\text{F}_3$ ,  $\text{ReO}_3\text{F}$ ,  $\text{TeO}_3\text{F}$  and  $\text{TcO}_3\text{Cl}$ . These are pale yellow or colourless compounds. They exist either as low melting solid or liquid.

# THE STRUCTURE OF $\text{ReO}_3$ .



# HALIDES OF GROUP 7

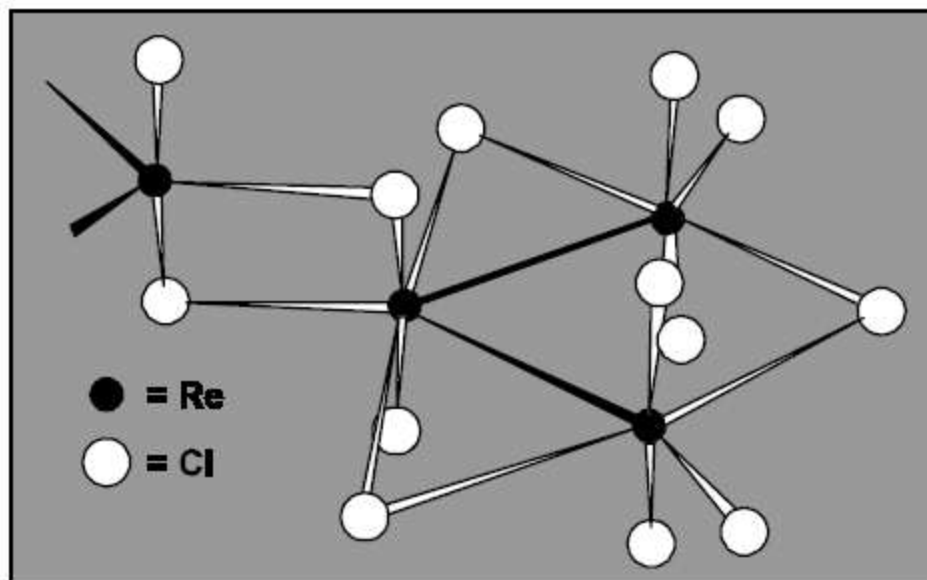
<i>State</i>	<i>Fluorides</i>	<i>Chlorides</i>	<i>Bromides</i>	<i>Iodides</i>
+7	ReF <sub>2</sub> yellow mp 48.3°, bp 73.7°			
+6	TcF <sub>6</sub> yellow mp 37.4°, bp 55.3° ReF <sub>6</sub> yellow mp 18.5°, bp 33.7°	TcCl <sub>6</sub> green mp 25° ReCl <sub>6</sub> red-green mp 29° (dichroic)		
+5	TcF <sub>5</sub> yellow mp 50°, bp (d) ReF <sub>5</sub> yellow-green mp 48°, bp(extrap) 221°	ReCl <sub>5</sub> brown-black mp 220°	ReBr <sub>5</sub> dark brown (d 100°)	
+4	- ReF <sub>4</sub> blue (subl > 300°)	- TcCl <sub>4</sub> red(subl > 300°) ReCl <sub>4</sub> purple-black (d 300°)	- (?TcBr <sub>4</sub> ) (red-brown) ReBr <sub>4</sub> dark red	ReI <sub>4</sub> black (d above rt)
+3	-	- [ReCl <sub>3</sub> ] <sub>3</sub> dark red (subl 500°) (d)	- [ReBr <sub>3</sub> ] <sub>3</sub> red-brown	- [ReI <sub>3</sub> ] <sub>3</sub> lustrous black (d on warming)



## + (III) STATES

- Tc(III) is unstable but  $\text{Re}_2\text{O}_3 \cdot (\text{H}_2\text{O})_n$  and the heavier halides are known. The chloride, bromide, and iodide have been structurally characterized and their true molecular formulas are  $\text{Re}_3\text{X}_9$ . They are not isomorphous but all consist of  $\text{Re}_3\text{X}_9$  units connected by sharing of X atoms as shown in Fig.  $\text{Re}_3\text{X}_9$  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 experimentally.

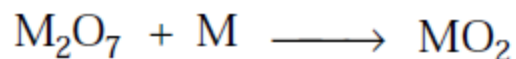


## (+IV) STATES

- It is second most stable state for Tc and Re.
- The oxides  $\text{TcO}_2$  and  $\text{ReO}_2$  can be prepared by using the following methods.
- By burning the metal in a limited supply of oxygen.



- By heating  $\text{M}_2\text{O}_7$  with M.



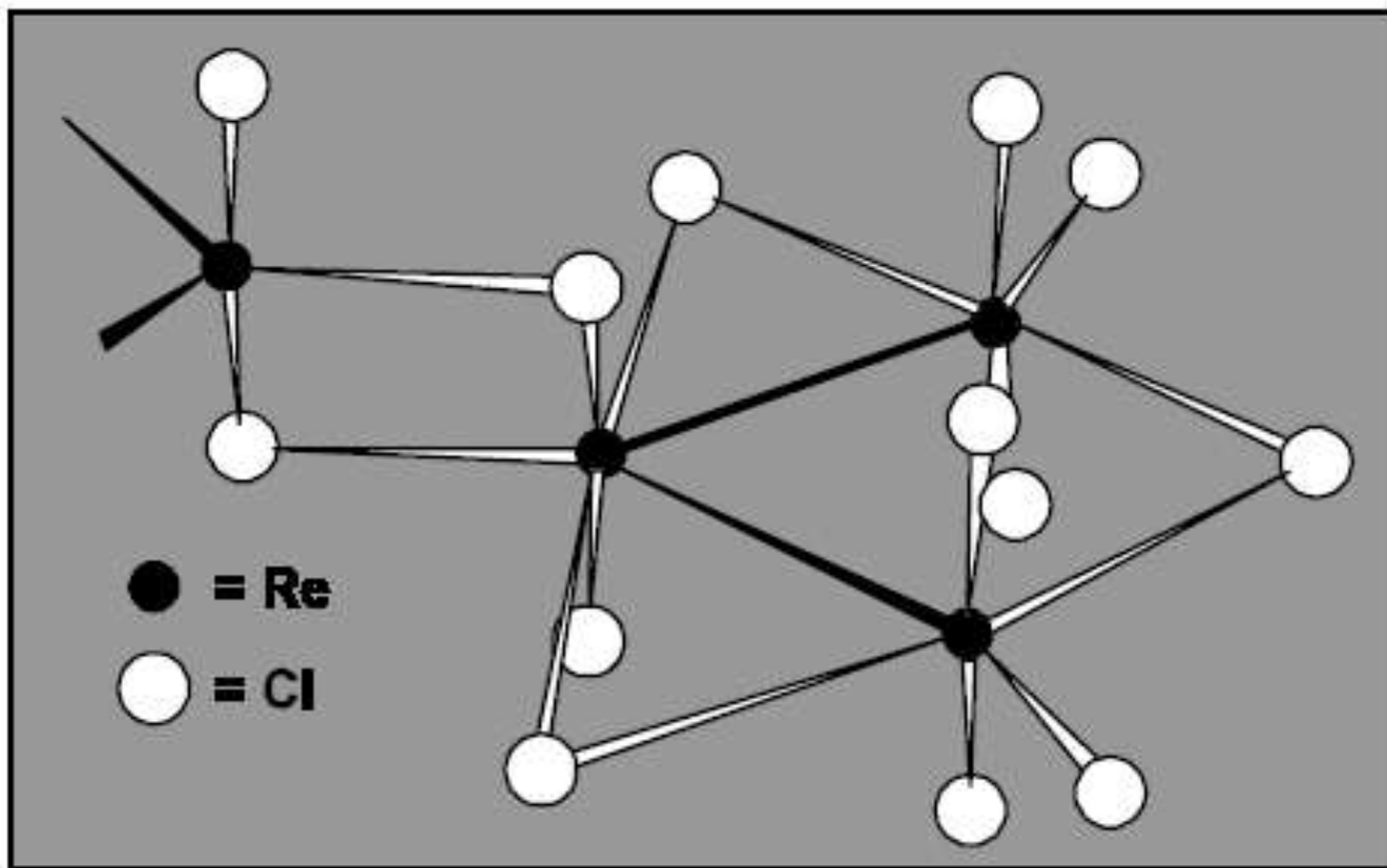
# SULPHIDES

- ⦿ The sulphides  $\text{TcS}_2$  and  $\text{ReS}_2$  are known. These are obtained by heating hepta sulphides with sulphur in vacuum. They have the advantage over heterogeneous platinum metal catalysts in that they are not poisoned by sulphur compounds.

# HAI IDES

<i>State</i>	<i>Fluorides</i>	<i>Chlorides</i>	<i>Bromides</i>	<i>Iodides</i>
+7	ReF <sub>2</sub> yellow mp 48.3°, bp 73.7°			
+6	TcF <sub>6</sub> yellow mp 37.4°, bp 55.3° ReF <sub>6</sub> yellow mp 18.5°, bp 33.7°	TcCl <sub>6</sub> green mp 25° ReCl <sub>6</sub> red-green mp 29° (dichroic)		
+5	TcF <sub>5</sub> yellow mp 50°, bp (d) ReF <sub>5</sub> yellow-green mp 48°, bp(extrap) 221°	ReCl <sub>5</sub> brown-black mp 220°	ReBr <sub>5</sub> dark brown (d 100°)	
+4	– ReF <sub>4</sub> blue (subl > 300°)	– TcCl <sub>4</sub> red(subl > 300°) ReCl <sub>4</sub> purple-black (d 300°)	– (?TcBr <sub>4</sub> ) (red-brown) ReBr <sub>4</sub> dark red	ReI <sub>4</sub> black (d above rt)
+3	–	– [ReCl <sub>3</sub> ] <sub>3</sub> dark red (subl 500°) (d)	– [ReBr <sub>3</sub> ] <sub>3</sub> red-brown	– [ReI <sub>3</sub> ] <sub>3</sub> lustrous black (d on warming)

# CLUSTER OF $\text{RE}_3\text{CL}_9$ .



# RUTHENIUM (RU) AND OSMIUM (OS)

- 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.

# PROPERTIES AND USES

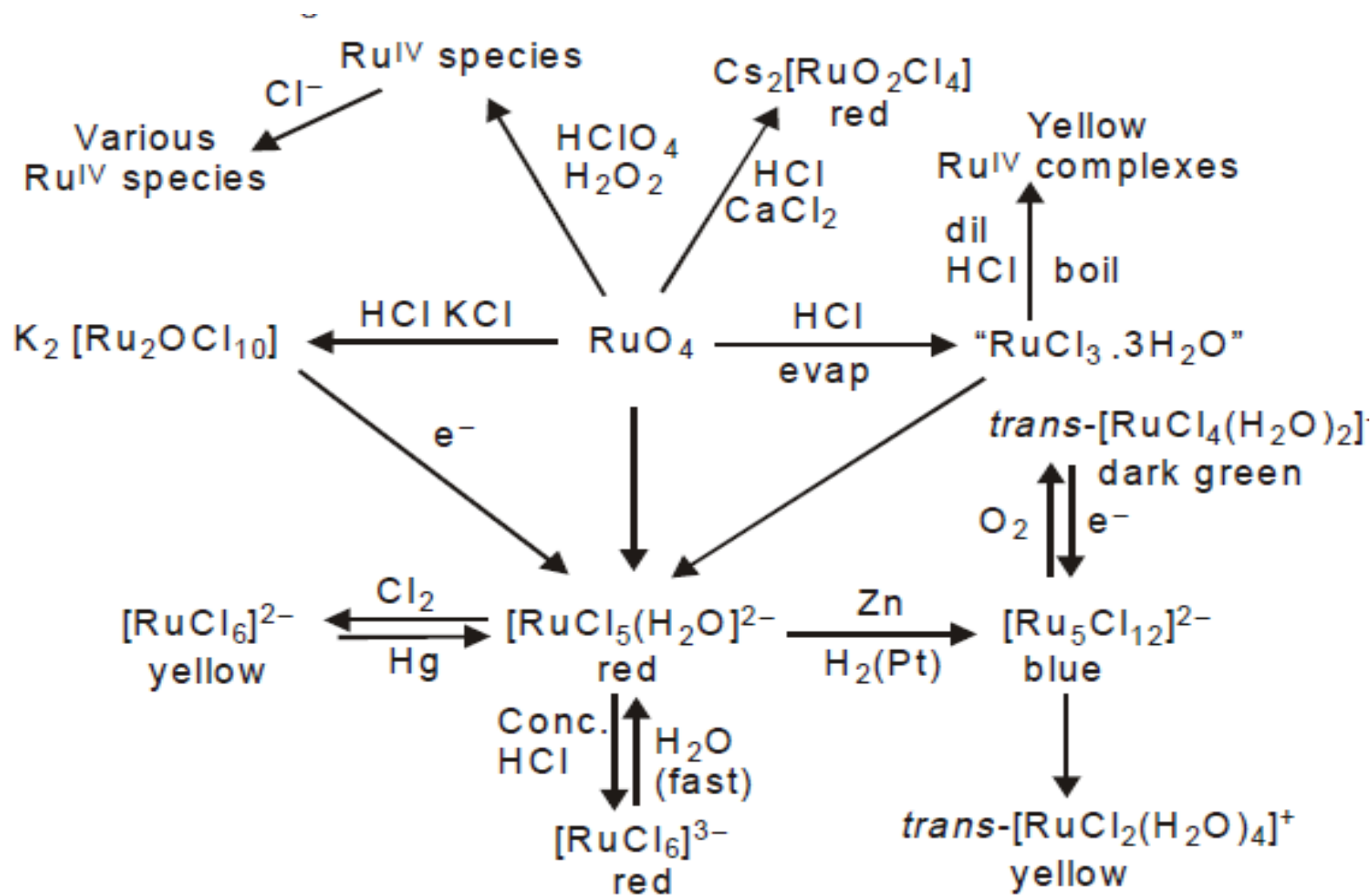
- ⦿ Ru and Os are unaffected by mineral acids below  $\sim 100^{\circ}\text{C}$  and are best dissolved by alkaline oxidizing fusion for example  $\text{NaOH} + \text{Na}_2\text{O}_2$ ,  $\text{KClO}_3$  etc.
- ⦿ Os is oxidized to  $\text{OsO}_4$  by aqua-regia .
- ⦿ The effect of lanthanide contraction 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.



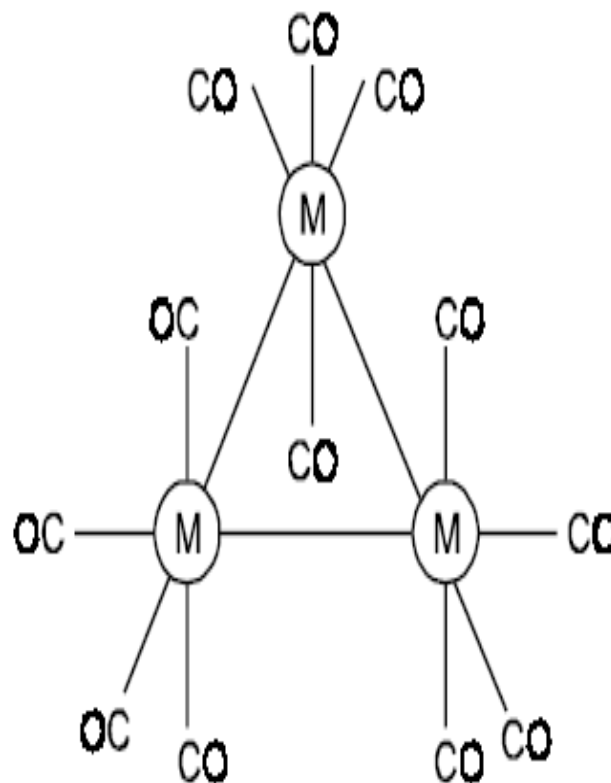
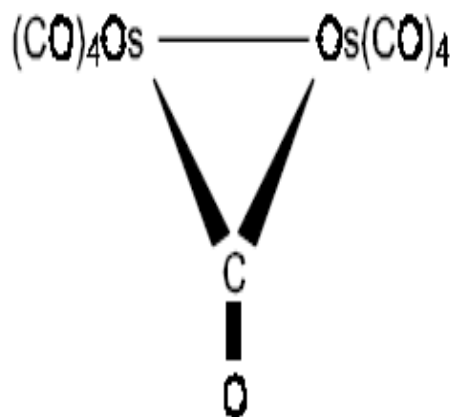
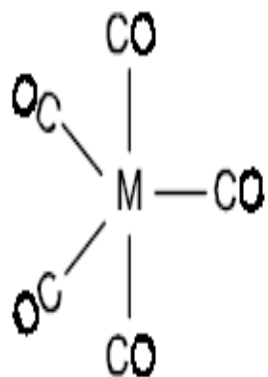
# COMPOUNDS

- ⦿ Ru and Os form  $\text{RuO}_4$  and  $\text{OsO}_4$  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.

# SOME REACTIONS OF RUTHENIUM CHLORO COMPLEXES



# STRUCTURE OF METAL CARBONYLS



# RHODIUM (RH) AND IRIDIUM (IR)

- ◉ Rhodium



# RHODIUM (RH) AND IRIDIUM (IR)

- 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.

# PROPERTIES AND USES

- ⦿ Rh and Ir are hard metals.
- ⦿ They are noble and unreactive.
- ⦿ Ir has highest density,  $22.61 \text{ gcm}^{-3}$ .
- ⦿ Rh and Ir are resistant to acids, but react with  $\text{O}_2$  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).
- ⊙ Some Compounds are shown in Table

Oxidation state	Fluorides	Chlorides	Bromides	Iodides
+6	RhF <sub>6</sub> black (70)			
	IrF <sub>6</sub> yellow (44) bp 53			
+5	[RhF <sub>5</sub> ] <sub>4</sub> dark red			
	[IrF <sub>5</sub> ] <sub>4</sub> yellow (104)			
+4	RhF <sub>4</sub> purple-red			
	IrF <sub>4</sub> dark brown	IrCl <sub>4</sub> ?	IrBr <sub>4</sub> ?	IrI <sub>4</sub> ?
+3	RhF <sub>3</sub> red	RhCl <sub>3</sub> red	RhBr <sub>3</sub> red-brown	RhI <sub>3</sub> black
	IrF <sub>3</sub> black	IrCl <sub>3</sub> red	IrBr <sub>3</sub> red-brown	IrI <sub>3</sub> dark brown



# CONTD

- ⊙ There is a fairly extensive chemistry of Rh (+I) and Ir (+I) complexes with  $\pi$  -bonding ligands such as CO,  $\text{PH}_3$ ,  $\text{PR}_3$  and alkene.
- ⊙ There are two important compounds of Rh (I) and Ir(I) i.e.  $[\text{Rh}(\text{Cl})(\text{PPh}_3)_3]$  *Wilkinson catalyst* and *trans*  $[\text{IrClCO}(\text{PPh}_3)_2]$ .

- ⊙ **Wilkinson Catalyst.** This red-violet compound which is readily obtained by refluxing ethanolic  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  with an excess  $\text{PPh}_3$  was discovered in 1965.
- ⊙ It undergoes a variety of reactions, most of which involve either replacement of a phosphine ligand with  $\text{CO}$ ,  $\text{CS}$ ,  $\text{C}_2\text{H}_4$  or  $\text{O}_2$  giving trans products or oxidative addition with  $\text{H}_2$  or  $\text{MeI}$  to form  $\text{Rh}_{\text{III}}$ .
- ⊙ 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.**

# PALLADIUM (PD) AND PLATINUM (PT)



## Group 10 (the nickel group )

### PALLADIUM (PD) AND PLATINUM (PT)

- ⦿ Pd and Pt are rare elements, but they are appreciably more abundant than the other platinum group metals. Even though 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.

# PROPERTIES

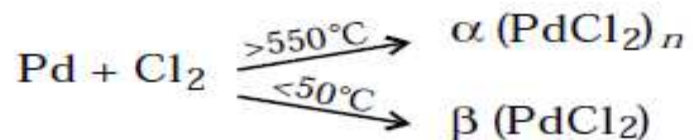
- Palladium and platinum are both rare and expensive.
- They are noble and not very reactive, but are slightly more reactive than the other platinum group metals.
- Both are used as catalyst.
- The most common oxidation state as Pd(II) and Pt(II) and Pt(IV).

# COMPOUNDS

- ⦿ Pd (II) and Pt (II) exist as oxides, halides, nitrates and sulphates.
- ⦿ Generally anhydrous solids are not ionic.
- ⦿ PdO is found in anhydrous form whereas PtO is only known as an unstable hydrated form.
- ⦿ Except PtF<sub>2</sub>, all the halides are known. PdF<sub>2</sub> is ionic.

# CONTD

- ⊙ All the complexes for example  $[\text{Pd}(\text{OH})_4]_{2-}$  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 prepared from the elements. They exist in two different forms depending upon the conditions used.



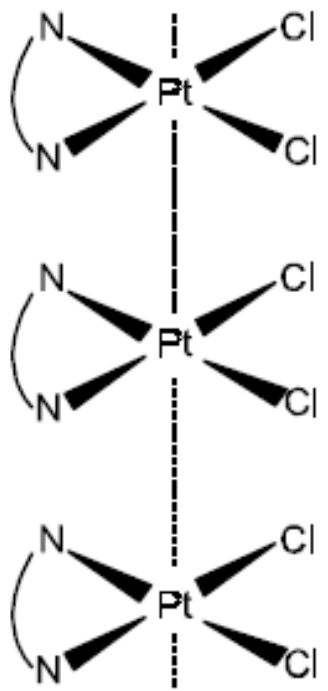
# CONTD

- ⊙  $\alpha$  forms of  $\text{PdCl}_2$  and  $\text{PtCl}_2$  are dark-red and olive green in colour respectively.
- ⊙  $\alpha$   $\text{PdCl}_2$  is hygroscopic and soluble in water and has a polymeric chain type structure.
- ⊙  $\alpha$   $\text{PtCl}_2$  is insoluble in water and dissolve in  $\text{HCl}$  due to formation of  $[\text{PtCl}_4]_{2-}$ .

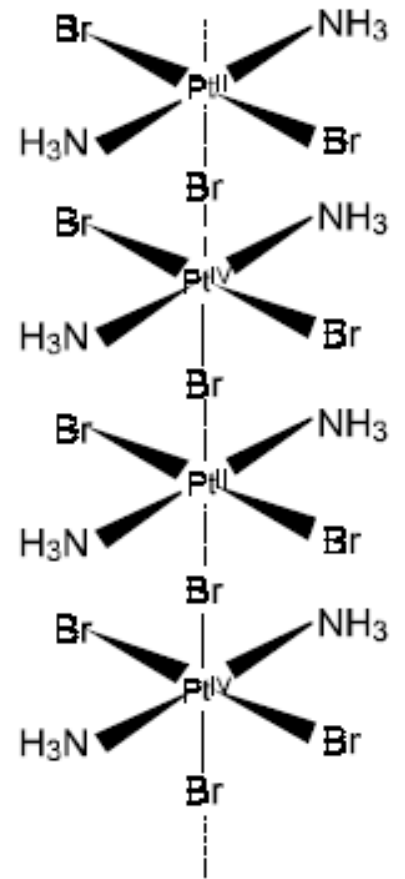


- β forms of PdCl<sub>2</sub> or PtCl<sub>2</sub> have an unusual molecular structure. This is based on
- Pd<sub>6</sub>Cl<sub>12</sub> or Pt<sub>6</sub>Cl<sub>12</sub> unit.

Stacks of square planar [Pt(ethylenediamine)Cl<sub>2</sub>] molecules



Structure of [Pt(NH<sub>3</sub>)<sub>2</sub>Br<sub>3</sub>]



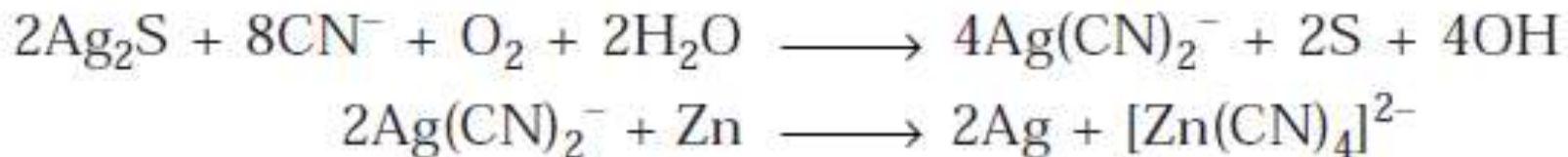
# SILVER (AG) AND GOLD (AU)



## Group 11 (the copper group )

# SILVER (AG) AND GOLD (AU)

- ◉ Silver is found as sulphide ores  $\text{Ag}_2\text{S}$  (argentite), as the chloride  $\text{AgCl}$  (horn silver) and as the native metal. There are three process of extraction.
  1. It is obtained mostly as a bi product 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.



# OCCURRENCE

- 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.

# USES

- ⦿ 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  $\frac{9}{24}$ ,  $\frac{18}{24}$ ,  $\frac{22}{24}$  carats gold respectively.

# NOBLE CHARACTER

- ⦿ The metals in the group have the highest electrical and thermal conductivities known.
- ⦿ They are the most malleable 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  $E^\circ$  values and are thus below hydrogen in the electrochemical series

# COMPOUNDS

- ⊙ The most common oxidation states are Ag (+1) and Au (+III) and the two
- ⊙ elements differ widely in their Chemistries.
- ⊙ 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<sub>+</sub> is stable state in both the solid state and solution Au<sub>+</sub> disproportionate in
- ⊙ water. Au<sub>+</sub> compounds that are stable to water are either insoluble or present as complexes
- ⊙ for example [R<sub>3</sub>P-Au-Cl], [R<sub>3</sub>P-Au-CH<sub>3</sub>], [NC-Au-CN<sub>2</sub>]<sup>1-</sup>.

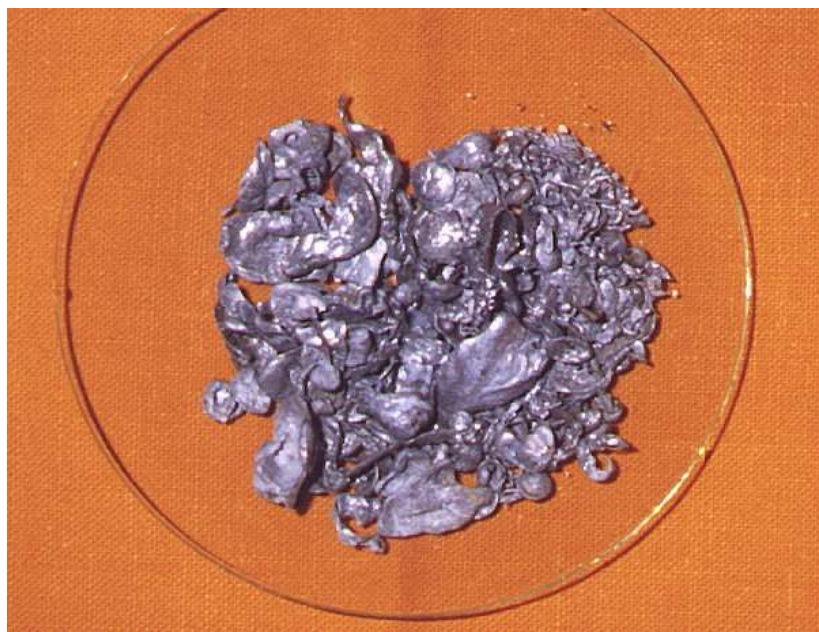
- ⦿ The silver halides are used in photography. On addition of ammonia AgCl is dissolve completely.
- ⦿ AgBr dissolve partially but AgI is not soluble. The solubility in ammonia is due to the formation of complex  $[\text{Ag}(\text{NH}_3)_2]^+$ .



CADMIUM

AND

MERCURY



Group 12 zinc (heavier elements )

## CADMIUM (CD) AND MERCURY (HG)

- ⦿ Cd and Hg are quite rare. In spite of these 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.

# PROPERTIES

- 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<sup>10</sup> electronic configuration) but some compounds of Hg(II) and Cd(II) are highly coloured due to charge transfer.

# CONTD

- 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 morereactive 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.

# USES

- ⦿ 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.

# USES OF HG

- ⦿ The largest use of mercury is in electrolytic cells for the production of NaOH and Cl<sub>2</sub>.
- ⦿ Vapour of mercury are used for street light. It is also used for the extraction of Ag and Au as amalgam organic compounds
- ⦿ Hg<sub>2</sub>Cl<sub>2</sub> is used to treat club root, a disease in brassicas (the cabbage family of plants)
- ⦿ HgCl<sub>2</sub> is used to make organato derivatives and HgO in antifouling paints for ships etc.

## CONTD

- ⦿ 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.