

## Transition Elements

### Electron configurations

The energy levels of different orbitals are changed depending upon the population of other levels in multi-electron atoms. Since, the penetration power of the orbitals run as  $s > p > d > f$ , the ns orbitals are experienced highest effective nuclear charge than the np or nd orbitals. That's why, in between 4s and 3d orbital, 4s orbital have lower energy than 3d orbital. Therefore, last electrons in K and Ca enter the 4s orbital after Ar.

In case of first transition elements, electron starts to fill 3d orbital giving ground state configuration  $3d^1 4s^2$  for scandium. Thus from Sc to Cu, two electrons is in the 4s orbital and an incomplete 3d level. Similarly, in second and third transition series electrons start to fill the 4d and 5d level after the corresponding ns level has been filled with two electrons.

With filling of electron in 3d orbital, its energy is lowered down to 4s orbital. Hence, the ground state configuration of  $M^{n+}$  ion is  $[Ar]3d^{m-(n-2)} 4s^0$  rather than  $[Ar]3d^{m-n} 4s^2$ . For example, configuration of  ${}_{23}V$  is  $[Ar]3d^3 4s^2$  so, configuration of  $V^{2+}$  will be  $[Ar]3d^3 4s^0$  rather than  $[Ar]3d^1 4s^2$ .

The stability of an electronic configuration is determined by the net effect of the forces of nuclear-electronic, shielding of one electron by the others, inter-electronic repulsions and the exchange energy force. The interplay of these forces and their sensitivity largely depends on the nuclear charge and the number of electrons present. That's why it is not possible to predict electron configuration solely by the order of orbital energies. The ultimate configuration will have always lower total energy for the whole configuration.

For most of the d-block elements, due to inter electron interaction the ground state configuration become  $(n-1)d^n ns^2$ , that is ns orbital remains fully occupied despite of individual (n-1)d orbitals have lower energy. At the same ground the energy difference between (n-1)d and ns orbitals are less when  $n = 5$  or  $6$  than when  $n = 4$ . Consequently, the ground state configuration of the 4d and 5d transition elements differ from the corresponding 3d element. But, cation of ( $M^{n+}$ ) all d-block elements exhibit  $d^n$  configurations because in ions, the energy of (n-1)d orbitals fall well below that of ns orbitals. The electron configurations of the transition elements are given below: The few exceptions of general trends of configuration are highlighting here.

	Gr. 3	Gr. 4	Gr. 5	Gr. 6	Gr. 7	Gr. 8	Gr. 9	Gr. 10	Gr. 11	Gr. 12
3d	${}_{21}Sc$ $3d^1 4s^2$	${}_{22}Ti$ $3d^2 4s^2$	${}_{23}V$ $3d^3 4s^2$	${}_{24}Cr$ $3d^5 4s^1$	${}_{25}Mn$ $3d^5 4s^2$	${}_{26}Fe$ $3d^6 4s^2$	${}_{27}Co$ $3d^7 4s^2$	${}_{28}Ni$ $3d^8 4s^2$	${}_{29}Cu$ $3d^{10} 4s^1$	${}_{30}Zn$ $3d^{10} 4s^2$
4d	${}_{39}Y$ $4d^1 5s^2$	Zr $4d^2 5s^2$	Nb $4d^4 5s^1$	Mo $4d^5 5s^1$	Tc $4d^5 5s^2$	Ru $4d^7 5s^1$	Rh $4d^8 5s^1$	Pd $4d^{10} 5s^0$	Ag $4d^{10} 5s^1$	Cd $4d^{10} 5s^2$
5d	${}_{57}La$ $5d^1 6s^2$	${}_{72}Hf$ $5d^2 6s^2$	${}_{73}Ta$ $5d^3 6s^2$	W $5d^4 6s^2$	Re $5d^5 6s^2$	Os $5d^6 6s^2$	Ir $5d^7 6s^2$	Pt $5d^9 6s^1$	${}_{79}Au$ $5d^{10} 6s^1$	${}_{80}Hg$ $5d^{10} 6s^2$

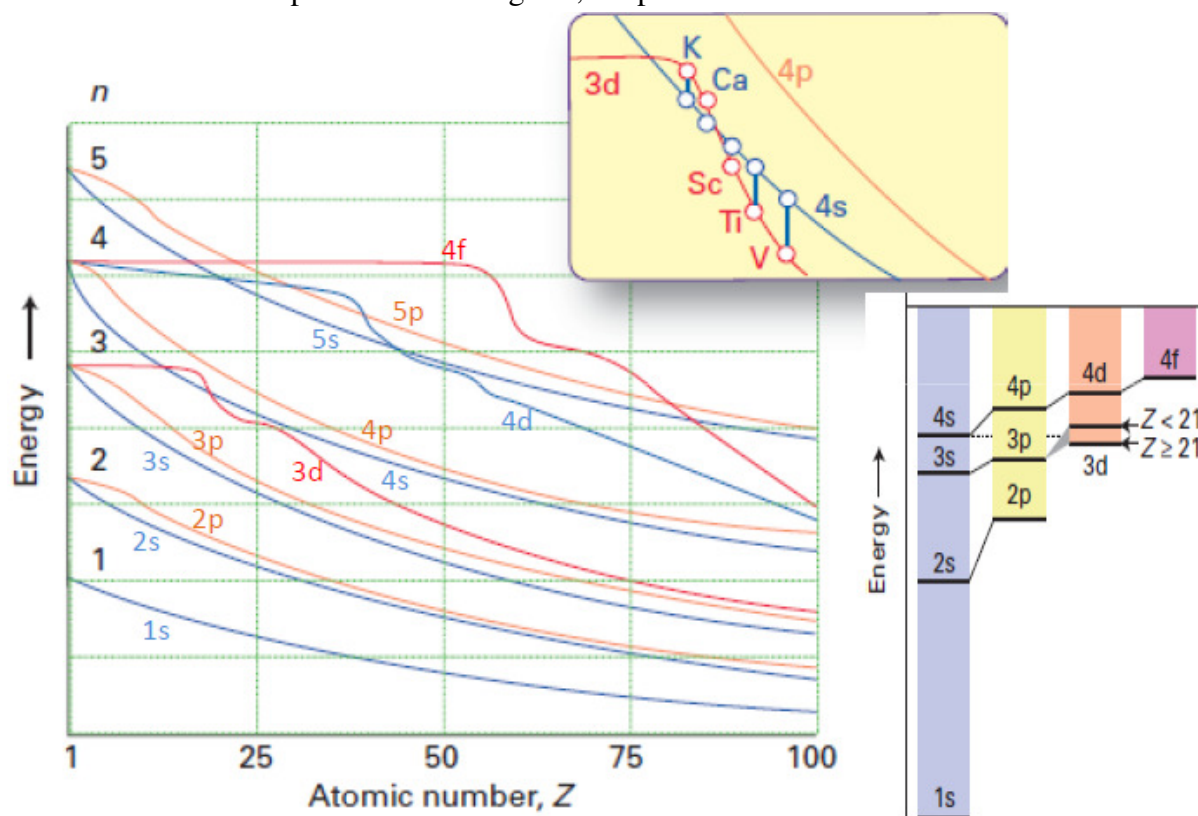
The exception in configurations which can be explained by considering (a) the energy gap between the ns and (n-1)d orbitals (b) pairing energy for the electrons in s-orbital (c) inter-electronic repulsions and the exchange energy force.

(i) In case of Gr. 6 (Cr) and Gr. 11 (Cu), transfer of electron from s orbital to d orbital due to attainment of half filled ( $d^5$ ) and full filled ( $d^{10}$ ) configuration leading to extra stabilization by way of greater exchange energy. From same ground, Pd adopted the configuration  $4d^{10}5s^0$ .

(ii) In 4d series, from niobium, presence of electron in d orbitals appears to be preferred than being shared in s orbitals. Between the available s and d orbitals, the electron can either go for sharing in s-orbital or excited to d-orbital. Obviously, the choice depends on the repulsive energy arises on sharing in s-orbital and the energy gap between the s and d-orbitals.

In the 4d series, s and d-orbital have the almost same energy, because of which electrons prefer to occupy the d-orbital. So from niobium, s-orbital has mostly only one electron.

(iii) The 5d series metals has more paired s configuration even at the expense of half-filled orbitals (Tungsten- $6s^25d^4$ ). This is happen due to lanthanide contraction as the series comes after filling up of 4f orbitals. The energy gap between the 6s and 5d orbitals is increased due to reduced in size that results pairing energy is less than the excitation. Excitation of the electron does not take place even in tungsten, in spite of the half-filled stabilization.



### Oxidation state

	Gr. 3	Gr. 4	Gr. 5	Gr. 6	Gr. 7	Gr. 8	Gr. 9	Gr. 10	Gr. 11
3d	Sc <b>3</b>	Ti (2), <b>3</b> , <b>4</b>	V 2, 3, <b>4</b> , 5	Cr 2, <b>3</b> , (4), (5), 6	Mn <b>2</b> , (3), <b>4</b> , (5), (6), 7	Fe <b>2</b> , <b>3</b> , (4), (5), (6)	Co 2, <b>3</b> , (4), (5)	Ni <b>2</b> , (3), (4)	Cu 1, <b>2</b> , (3)
4d	Y <b>3</b>	Zr (3), <b>4</b>	Nb (2), (3), (4), <b>5</b>	Mo 2, 3, <b>4</b> , <b>5</b> , <b>6</b>	Tc <b>4</b> , (5), <b>7</b>	Ru <b>2</b> , <b>3</b> , <b>4</b> , (5), <b>6</b> , (7), (8)	Rh 2, <b>3</b> , 4, (5), (6)	Pd <b>2</b> , (3), <b>4</b> , (6)	Ag <b>1</b> , (2), (3), (4)
5d	La <b>3</b>	Hf (3), <b>4</b>	Ta (2), (3), (4), <b>5</b>	W 2, (3), <b>4</b> , <b>5</b> , <b>6</b>	Re (1), (2), 3, <b>4</b> , <b>5</b> , (6), 7	Os 2, 3, <b>4</b> , <b>6</b> , <b>8</b>	Ir 2, <b>3</b> , <b>4</b> , (5), (6)	Pt <b>2</b> , (3), <b>4</b> , (5), (6)	Au 1, <b>3</b> , 5

\*Most stable oxidation states are shown in bold and unstable states are shown in parentheses.

- All s-electrons and some or all the d-electrons take part in the valency resulting variable oxidation states of the transition elements.
- The stability of any oxidation state depends upon combining atom, solvent, nature of ligand etc.
- The highest oxidation state of transition metal is eight, shown by Ru and Os.
- Size and the relative stabilities of different oxidation states of the element in any group are generally differ between first (3d) and heavier members (4d, 5d).
- Due to lanthanide contraction the size of 4d and 5d elements in a particular group are comparable. As a result, chemical properties of 4d and 5d elements in any group are similar. But, the similarity disappears on proceeding towards right along the period. This is because, size factor is not only governing factor to determine the properties, other factor such as ionisation energy, crystal field stabilization of d-orbitals and their spacial extension seems to control the chemical behaviour of the element. Thus, last two elements of Gr. 4 and 5 have similar properties but in platinum metals and, Ag and Au have more dissimilarities than similarities.

➤ In any period, the number of different oxidation states first increases, becomes maximum at the middle of the series and then decreases.

(i) The minimum and lower oxidation states at the two extreme ends due to either few electrons to lose or share or due to many d electrons only fewer orbitals open to sharing electrons with ligands for higher valency.

(ii) The stability of high oxidation states toward the end of the transition series is decreased as the filling of d-orbital results steady increase in effective nuclear charge. The energy of d-orbital is lowered down and thus d-electron is more reluctant to participate in bonding. For example, zinc shows only +2 state. Ni(II) and Cu(II) are stable but Ni(III), Cu(III) are oxidizing.

(iii) On the other hand, for lighter elements all ns and (n-1)d electrons take part in valency as effective nuclear charge is not high for lighter elements. So, it is easy to utilize all ns and (n-1)d-electrons to form complexes. For example, +3 state for Sc and +4 state for Ti.

➤ The maximum oxidation states of reasonable stability occur equal to sum of s and d electron upto  $d^5$ , ( $Ti^{IV}O_2$ ,  $V^{V}O_2^+$ ,  $Cr^{VI}O_4^{2-}$ ,  $Mn^{VII}O_4^-$ ) but once the  $d^5$  configuration is crossed, the stability of the higher oxidation state is decreased abruptly. It is observed in iron(II,III), cobalt(II, III), nickel(II) and copper(II) groups except, Os(VIII) and Ru(VIII).

➤ The heavier elements have a tendency to attain higher oxidation states because of larger size, lower binding energy towards outer electron and lower energy difference of ns and (n-1)d orbitals, more d-electron can participate in bonding in case of the heavier elements.

➤ The +2 oxidation state is known for all elements of the first transition series except scandium. Cadmium shows only +2 oxidation state and  $Hg^{II}$ ,  $Pd^{II}$  and  $Pt^{II}$  are other important dipositive species. Chromium(III) is most stable but Mo(III) and W(III) are strongly reducing. Cr(VI) is strong oxidizing but Mo(VI) and W(VI) are quite stable.  $[ReO_4]^-$  is not a strong oxidizing agent like  $[MnO_4]^-$ . Similarly, iron shows the common oxidation state +2 and +3 while ruthenium and osmium readily form compounds of +4, +6 and +8 oxidation states. Although  $Co^{II}$  and  $Co^{III}$  are known, rhodium and iridium are essentially shown +3 oxidation state. Further,  $Pd^{IV}$ ,  $Pt^{IV}$ ,  $Au^{III}$  are relatively stable from the lighter congeners.

➤ With the increase of the oxidation state of the metal ion acidity of the metal oxides increases because of higher affinity to accept the electron. Elements in their lower oxidation states will be ionic and basic ( $TiO$ ,  $VO$ ,  $CrO$ ,  $MnO$ ,  $TiCl_2$  and  $VCl_2$ ). Elements exists in-between states are amphoteric ( $Ti_2O_3$ ,  $V_2O_3$ ,  $Mn_2O_3$ ,  $Cr_2O_3$ ,  $TiCl_3$ ,  $VCl_3$ ) and higher oxidation states are covalent and acidic ( $TiO_2$ ,  $V_2O_5$ ,  $CrO_3$ ,  $MnO_3$ ,  $Mn_2O_7$ ,  $VCl_4$  and  $VOCl_3$ ).

➤ The oxidizing power increases in the series  $Sc(III) < Ti(IV) < V(V) < Cr(VI) < Mn(VIII)$ . Conversely, reducing power increases as  $Cr(II) < V(II) < Ti(II)$ . This is happen because in case of first transition series, the stability of higher oxidation state decreases gradually.

➤ Higher oxidation state of the metal is stabilized by small, hard ligands with  $\sigma$ -donor properties like fluoride and oxide. For example, highest oxidation state of V, Cr, Mn ( $VO_4^{3-}$ ,  $CrO_4^{2-}$ ,  $MnO_4^-$ ), oxidation state higher than +3 in iron, cobalt ( $FeO_4^{2-}$ ,  $Ba_2CoO_4$ ,  $Cs_2CoF_6$ ), oxidation state higher than +2 in nickel, copper ( $NiO(OH)$  or  $Ni_2O_3 \cdot 2H_2O$ ,  $K_2NiF_6$ ,  $CsCuF_4$ ,  $KCuO_2$ ).



➤ Lower oxidation states of the metals are stabilized by (i) large saturated ligands like iodide and sulphide which are good reducing agent and (ii) ligands with  $\pi$ -acceptor capacity like CO,  $\text{NO}^+$ ,  $\text{PR}_3$ , dipyrindyl, *o*-phenanthroline. In these complexes ligand to metal  $\sigma$ -donation is reinforced by metal to ligand  $\pi$  back donation to the  $\pi^*$  MO or vacant d-orbital to stabilizing the complex.

(i) The neutral CO molecule forms complexes with metals in zero state e.g.  $\text{Cr}(\text{CO})_6$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{Ni}(\text{CO})_4$ . Even negative oxidation state (-I) is also found as in  $\text{Na}[\text{Co}(\text{CO})_4]$ ,  $\text{Na}[\text{Mn}(\text{CO})_5]$ .

(ii) Metal nitrosyl ( $\text{NO}^+$ ) complex:  $[\text{Mn}^{\text{III}}(\text{CO})(\text{NO}^+)_3]$ ,  $[\text{Fe}^{\text{II}}(\text{CO})_2(\text{NO}^+)_2]$ ,  $[\text{Co}^{\text{I}}(\text{CO})_3(\text{NO}^+)]$

➤ Oxides of the metals from titanium to cobalt in their highest oxidation states form oxo-anions salts with alkali because of high acidic character the metal ions in higher oxidation state have high affinity to accept oxide ions.  $\text{TiO}_2$  forms titanates ( $\text{TiO}_4^{4-}$ ),  $\text{V}_2\text{O}_5$  forms vanadates ( $\text{VO}_4^{3-}$ ) and  $\text{CrO}_3$  forms chromates ( $\text{CrO}_4^{2-}$ ). On the other side, the oxides of metals in their +2 oxidation state are only basic and dissolve in acids to form aqua ions.

### Atomic and ionic radii:

Generally, down in any group the radius is increased as electron is placed to the new shell having higher principal quantum. This is happen prominently for 's' and 'p' block elements. But, in case of 'd' block element the vertical variation is not so prominent because of poor shielding of the 4f orbital causing lanthanide contraction in the 5d elements. As a result, the 4d and 5d elements in a particular group in the d-block have almost identical radii.

Atomic radii								Ionic radii	
Ti	132		V	122		Cr	117	$\text{Ti}^{4+}$	68
Zr	145		Nb	134		Mo	129	$\text{Zr}^{4+}$	74
Hf	144		Ta	134		W	130	$\text{Hf}^{4+}$	75
Radii are in pm unit									

Such comparability in size results similar characteristic between the 4d and 5d elements in a vertical group. For example, ionisation potential, solvation energies, redox behaviour, lattice energy etc. For this similarity, their overall chemical behaviour is also similar. Thus, each group has two parts, chemistry of 3d element and chemistry of heavier (4d, 5d) elements. The main differences between these two parts are the size and relative stabilities of the different oxidation states.

The poor shielding by successive d-electrons is resulted a gradual decrease of size along the each transition series. The last member in each series i.e. Cu, Ag, Au has somehow larger radius than the expected value. The atoms are smaller than the Group-1 and 2 elements since the electrons are added to the penultimate shell. The overall decrease in size between the successive elements along the transition series is often small. That's why in many instances the chemical properties are similar e.g., the chemistry of  $\text{V}^{3+}$  and  $\text{Ti}^{3+}$ . The chemistry of Fe(II), Co(II) and Ni(II) are also similar in many cases.

### Metallic properties:

The transition elements are typical metals having high tensile strength, ductile, malleable, thermal and electrical conductor and lustre.

## Redox Chemistry

❖ Metal ions present in lower oxidation states expected to be reducing and in higher oxidation states expected to be oxidizing in nature but it is not true always. The stability of different oxidation states can be accounted by considering the electron configuration of the metal ions. The relative stability of different oxidation states of the transition metals are known from the relevant electrode potential data.

+7	+6	+5	+4	+3	+2	+1	0								
			$\text{TiO}^{2+}$	$\xrightarrow{0.1}$	$\text{Ti}^{3+}$	$\xrightarrow{-0.37}$	$\text{Ti}^{2+}$	$\xrightarrow{-1.63}$	Ti						
							$\xrightarrow{-1.21}$								
			$\text{Zr}^{4+}$				$\xrightarrow{-1.529}$		Zr						
			$\text{Hf}^{4+}$				$\xrightarrow{-1.529}$		Hf						
+7	+6	+5	+4	+3	+2	+1	0								
			$\text{VO}_2^+$	$\xrightarrow{1.00}$	$\text{VO}^{2+}$	$\xrightarrow{0.34}$	$\text{V}^{3+}$	$\xrightarrow{-0.26}$	$\text{V}^{2+}$	$\xrightarrow{-1.13}$	V				
							$\xrightarrow{0.67}$								
			$\text{Nb}_2\text{O}_5$				$\xrightarrow{0.035}$	$\text{Nb}^{3+}$	$\xrightarrow{-1.10}$	Nb					
							$\xrightarrow{-0.644}$								
			$\text{Ta}_2\text{O}_5$				$\xrightarrow{-0.812}$			Nb					
+7	+6	+5	+4	+3	+2	+1	0								
			$\text{Cr}_2\text{O}_7^{2-}$	$\xrightarrow{0.55}$	$\text{Cr}^{5+}$	$\xrightarrow{1.34}$	$\text{Cr}^{4+}$	$\xrightarrow{2.10}$	$\text{Cr}^{3+}$	$\xrightarrow{-0.42}$	$\text{Cr}^{2+}$	$\xrightarrow{-0.90}$	Cr		
							$\xrightarrow{1.38}$				$\xrightarrow{-0.74}$				
			$\text{H}_2\text{MoO}_4$	$\xrightarrow{0.4}$	$\text{MoO}_2^+$	$\xrightarrow{0.0}$	$\text{Mo}^{3+}$	$\xrightarrow{-0.20}$				Mo			
							$\xrightarrow{0.0}$								
			$\text{WO}_3$	$\xrightarrow{-0.03}$	$\text{W}_2\text{O}_5$	$\xrightarrow{-0.04}$	$\text{WO}_2$	$\xrightarrow{-0.15}$	$\text{W}^{3+}$	$\xrightarrow{-0.11}$		W			
							$\xrightarrow{-0.09}$				$\xrightarrow{-0.12}$				
+7	+6	+5	+4	+3	+2	+1	0								
			$\text{MnO}_4^-$	$\xrightarrow{0.56}$	$\text{MnO}_4^{2-}$	$\xrightarrow{0.27}$	$\text{MnO}_4^{3-}$	$\xrightarrow{4.27}$	$\text{MnO}_2$	$\xrightarrow{0.95}$	$\text{Mn}^{3+}$	$\xrightarrow{1.5}$	$\text{Mn}^{2+}$	$\xrightarrow{-1.18}$	Mn
							$\xrightarrow{1.51}$				$\xrightarrow{1.23}$				
			$\text{TcO}_4^-$	$\xrightarrow{0.7}$				$\text{TcO}_2$	$\xrightarrow{0.6}$	$\text{Tc}^{2+}$	$\xrightarrow{0.4}$		Tc		
							$\xrightarrow{0.6}$				$\xrightarrow{0.5}$				
			$\text{ReO}_4^-$	$\xrightarrow{0.4}$	$\text{ReO}_3$	$\xrightarrow{0.6}$	$\text{ReO}_2$	$\xrightarrow{0.2}$	$\text{Re}^{3+}$	$\xrightarrow{0.3}$			Re		
							$\xrightarrow{0.362}$								



**d<sup>0</sup> configuration:** Metal ions having d<sup>0</sup> configuration are not reducing as there is no electron to lose. They have little tendency to behave as oxidizing agent except [CrO<sub>4</sub>]<sup>2-</sup>, CrO<sub>3</sub>Cl<sup>-</sup>, CrO<sub>2</sub>Cl<sub>2</sub>, [MnO<sub>4</sub>]<sup>-</sup>. [VO<sub>4</sub>]<sup>3-</sup> is mild oxidizing, converts to vanadium(IV) which is most stable oxidation state.

**d<sup>1</sup> configuration:** Ti(III) is reducing in nature as Ti(IV) is most stable oxidation state. VO<sup>2+</sup> is stable in aqueous solution. Cr<sup>V</sup>, Mn<sup>VI</sup> is disproportionate to the more stable state as follows.



**d<sup>2</sup> configuration:** Ti(II), V(III) is reducing because +IV state is most stable where as Fe(VI) very strongly oxidizing as it is easily reduced to Fe(III) or Fe(II).

**d<sup>3</sup> configuration:** V(II) is reducing and Mn(IV) is oxidizing. Cr<sup>3+</sup> is stable in aqueous solution. Mn<sup>IV</sup>O<sub>2</sub> is stable because it's insolubility.

**d<sup>4</sup> configuration:** Cr(II) is reducing. Mn(III) is oxidizing and is subject to disproportionation. Complex of Mn<sup>III</sup> are relatively unstable with the exception of [Mn(CN)<sub>6</sub>]<sup>3-</sup>.

**d<sup>5</sup> configuration:** Mn<sup>2+</sup>, Fe<sup>3+</sup> is quite stable. Fe<sup>3+</sup> may be reduced to Fe<sup>2+</sup> with suitable reducing agents.

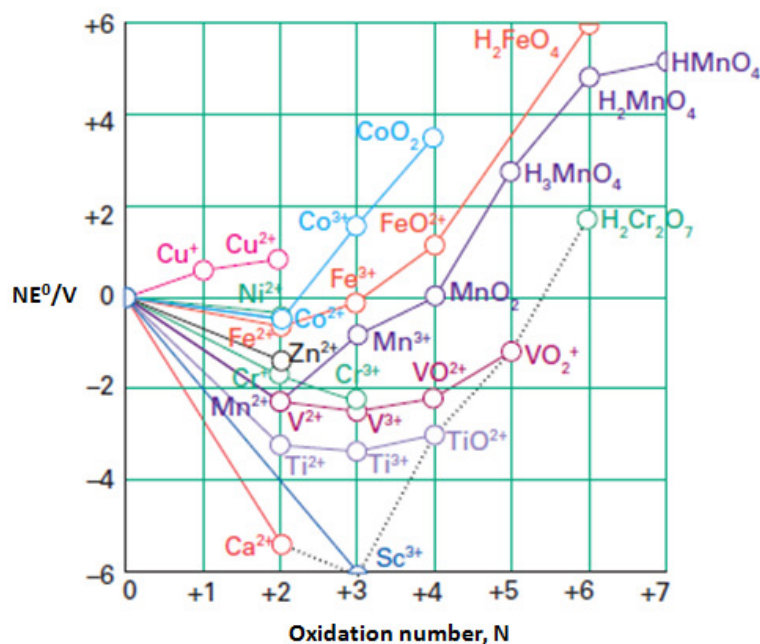
**d<sup>6</sup> configuration:** Fe(II) is quite stable. Co(III) is extremely stable in presence of strong field ligand but strong oxidizing agent in absence of strong field ligands. Ni(IV) is strongly oxidizing as Ni(II) is most stable.

**d<sup>7</sup> configuration:** Co(II) is stable but in presence of strong field ligand it is easily oxidized to Co(III) complexes as it form low spin complex having large CFSE. Ni(III) is strongly oxidizing.

**d<sup>8</sup> configuration:** Ni(II) is stable. Cu(III) is oxidizing as Cu(II) is most stable.

**d<sup>9</sup> configuration:** Cu(II) is stable.

**d<sup>10</sup> configuration:** Cu(I) is reducing. Zn(II) is stable.



- ❖ The plots of  $nE^0$  vs.  $N$  for all elements from Ti to Co show a sharp downward slope at the beginning, reaching minima at +2 and +3 oxidation states and then rise steadily. Hence, higher and lower oxidation states are expected to convert to these (+2 and +3) oxidation states on reaction.
- ❖ The +1 oxidation state is not common except copper, silver, mercury. Cu(I) is also susceptible to disproportionation because of the difference of hydration energy between  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  becomes dominant over 2<sup>nd</sup> ionisation energy. In silver the reverse is true.
- ❖ The potential for higher oxidation states rise steadily after the minima at +2 or +3 that means higher oxidation states become increasingly unfavourable. Therefore, elements become gradually more oxidizing in higher oxidation states. Permanganate is stronger oxidizing than chromate while chromates are stronger oxidizing agents than vanadates.
- ❖  $M^{2+}/M$  potential suggest that all the metals except copper would liberate  $\text{H}_2$  from acids.
- ❖  $\text{Ti}^{2+}$ ,  $\text{V}^{2+}$ ,  $\text{Cr}^{2+}$  are expected to liberate  $\text{H}_2$  from acidic aqueous solutions. Reducing power decreases from left to right in the transition series. In voltammetric analysis,  $\text{Fe}^{2+}$  is a common reducing agent.  $\text{Cr}^{2+}$ ,  $\text{V}^{2+}$ ,  $\text{Ti}^{2+}$  are stronger reducing agents. The  $\text{Co}^{3+}/\text{Co}^{2+}$  couple may also liberate  $\text{H}_2$  from aqueous solution in presence of cyanides which strongly complex with Co(III).
- ❖ The heavier elements show greater stability in higher oxidation states and also have a tendency to attain higher coordination number. This is because of larger size and lower binding energy towards outer electron and lower energy difference of ns and (n-1)d orbitals, more d-electron can participate in bonding. That's why Cr(VI) is strong oxidizing while Mo(VI) and W(VI) are quite stable. Similarly, iron shows the common oxidation state +2 and +3 while ruthenium and osmium readily form compounds of +4, +6 and +8 oxidation states.

❖ The stabilization of a higher oxidation state through complexation reveals the decrease of reduction potentials. As for example:

Redox couple	E <sup>0</sup> (volt)
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + e \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	0.77
$[\text{FeF}_6]^{3-} + e \rightleftharpoons [\text{FeF}_6]^{4-}$	0.40
$[\text{Fe}(\text{CN})_6]^{3-} + e \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$	0.36
$[\text{Fe}(\text{oxinate})_3] + e \rightleftharpoons [\text{Fe}(\text{oxinate})_3]^-$	-0.20
$[\text{Mn}(\text{H}_2\text{O})_6]^{3+} + e \rightleftharpoons [\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	1.50
$[\text{Mn}(\text{CN})_6]^{3-} + e \rightleftharpoons [\text{Mn}(\text{CN})_6]^{4-}$	0.22
$[\text{Co}(\text{H}_2\text{O})_6]^{3+} + e \rightleftharpoons [\text{Co}(\text{H}_2\text{O})_6]^{2+}$	1.84
$[\text{Co}(\text{dipy})_3]^{3+} + e \rightleftharpoons [\text{Co}(\text{dipy})_3]^{2+}$	0.31
$[\text{Co}(\text{en})_3]^{3+} + e \rightleftharpoons [\text{Co}(\text{en})_3]^{2+}$	0.18
$[\text{Co}(\text{CN})_6]^{3-} + e \rightleftharpoons [\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$	-0.8

❖ The stabilization of a lower oxidation state through complexation reveals the increase of reduction potentials. As for example:

Redox couple	E <sup>0</sup> (volt)
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + e \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	0.77
$[\text{Fe}(\text{dipy})_3]^{3+} + e \rightleftharpoons [\text{Fe}(\text{dipy})_3]^{2+}$	0.96
$[\text{Fe}(\text{o-phen})_3]^{3+} + e \rightleftharpoons [\text{Fe}(\text{o-phen})_3]^{2+}$	1.12

In this cases, dipyriddy and o-phenanthroline form low spin complexes with both Fe(III) and Fe(II), but Fe(II) is a good  $\pi$  donor while Fe(III) is expected to be poorer  $\pi$  donor.

(However, CN<sup>-</sup>, a potential  $\pi$  acid ligand stabilizes Fe(III) rather than Fe(II) resulting decrease of reduction potential. It is established that a large negative entropy of hydration of  $[\text{Fe}(\text{CN})_6]^{4-}$  ion is responsible for that. The highly charged anion arranged the water molecule in more ordered phase in its vicinity.)



**Group 3: Scandium (Sc): Electronic configuration: [Ar]3d<sup>1</sup>4s<sup>2</sup>**

**Chemistry of scandium:** Scandium has only common oxidation state is +3. Sc(II) is highly reducing in nature and virtually unknown. As it is first transition metal, d-orbital is not stabilized enough, so that all three electron are easily ionised.

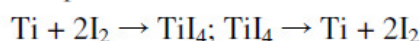
In fact, Sc lacks the characteristic of transition elements and usually occurs with lanthanides. The chemistry of scandium resembles that of aluminium very closely. Scandium occurs as Sc<sub>2</sub>O<sub>3</sub> with lanthanide and actinide ores.

**Group 4: Titanium(Ti)[Ar]3d<sup>2</sup>4s<sup>2</sup>, Zirconium(Zr)[Kr]4d<sup>2</sup>5s<sup>2</sup> and Hafnium(Hf)[Xe]4f<sup>14</sup>5d<sup>2</sup>6s<sup>2</sup>****Chemical Reactivity:**

The most important oxidation state of Gr. – 4 elements is +4, particularly exists as dioxide and tetrahalides. Titanium shows many similarities with tin which has same size. Lower oxidation states are not so stable for Zr, Hf and not even for Ti. Lower oxidation state compounds are readily oxidized to +4 state.

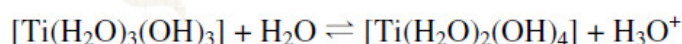
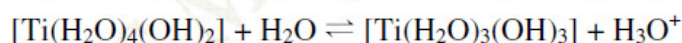
**Titanium (Ti): Electronic configuration: [Ar]3d<sup>2</sup>4s<sup>2</sup>**

Titanium is extracted and purified by van Arkel–de Boer method through the formation of volatile TiI<sub>4</sub>. TiI<sub>4</sub> is decomposed in contact with hot tungsten at 1300 °C.



**Chemistry of titanium(IV):** The highest and most stable oxidation state of titanium is +IV and it is consistent with valence shell electron configuration. The of lower oxidation state (0, II, III) are readily oxidized to Ti(IV). Since, the fourth ionization energy is very high to form Ti<sup>4+</sup> ion (8800 kJ mol<sup>-1</sup>) the compounds are mostly covalent. The known principal compounds of Ti(IV) are the dioxide TiO<sub>2</sub>, tetrahalides TiX<sub>4</sub> (X = F – I), disulphide TiS<sub>2</sub>, disulphate Ti(SO<sub>4</sub>)<sub>2</sub>.

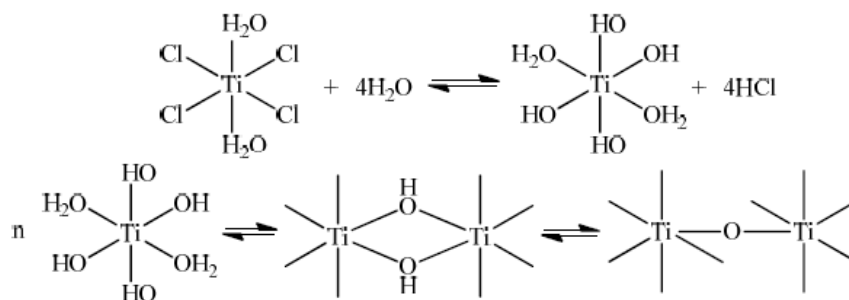
**Aqueous chemistry of Ti(IV):** In aqueous solution Ti(IV) ion does not exist as [Ti(H<sub>2</sub>O)<sub>6</sub>]<sup>4+</sup>. Due to high ionic potential (charge/size ratio), it is hydrolyzed in solution.



There is no evidence for formation of Ti(OH)<sub>4</sub>. The composition of TiO<sub>2</sub>.xH<sub>2</sub>O is [Ti(H<sub>2</sub>O)<sub>2</sub>(OH)<sub>4</sub>]. The monomeric oxido titanium, [TiO(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup>, is not form in aqueous solution but, oxido vanadium(IV), [VO(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup>, is the predominant species. This is due to smaller size of V(IV) than Ti(IV) that results the formation of stable V=O bond.

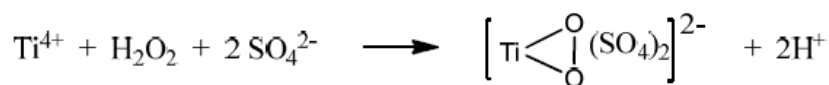
**Hydrolysis of Ti(IV) in aqueous solution:**

TiCl<sub>4</sub> is hydrolysed in the following way. First, there will be saturation in coordination to TiCl<sub>4</sub>.2H<sub>2</sub>O and then splitting off four HCl molecules producing [Ti(H<sub>2</sub>O)<sub>2</sub>(OH)<sub>4</sub>]. At high temperature or alkaline medium or prolong standing it converted to hydroxo and oxo-bridged polymeric species.



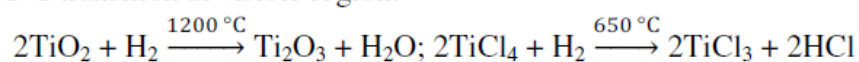
### Peroxo complex:

In mild acidic medium, aqueous solution of Ti(IV) produce an intense orange colour with  $\text{H}_2\text{O}_2$  due to formation of peroxotitanic acid,  $\text{Ti}(\text{OOH})(\text{OH})_3$ . In sulphuric acid solution, the colour is due to the peroxidic anion furnished by the free peroxodisulfatotitanic acid. In presence of  $\text{F}^-$  ions, colour is discharged due to formation of stable  $\text{TiF}_6^{2-}$  ion.



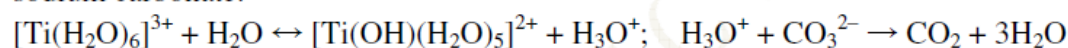
### Chemistry of Ti(III):

Unlike Ti(IV), Ti(III) compounds are paramagnetic and coloured. In aqueous solution  $\text{Ti}^{\text{III}}$  can be prepared by reduction of  $\text{Ti}^{\text{IV}}$ , either with Zn and dilute acid or electrolytically. In dilute acid solutions, it exists as the octahedral hexaaqua ion  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ . The solution is violet due to d–d transition at visible region.



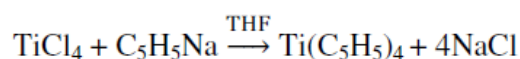
### Aqueous chemistry of Ti(III):

The violet colour of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  disappears in air due to oxidation of Ti(III) to Ti(IV) by air and must be kept under inert atmosphere. The violet solution is acidic, liberating  $\text{CO}_2$  from sodium carbonate.

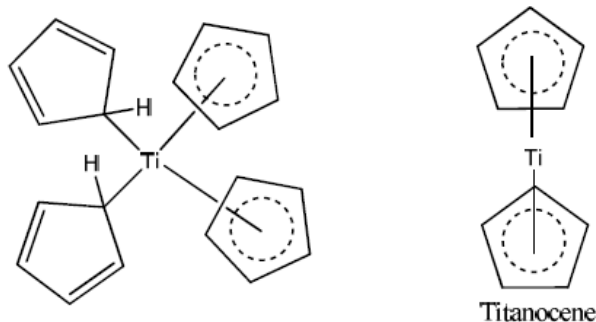


### Organometallic compounds:

$\text{Ti}(\text{Me})_4$  is thermally unstable organometallic compound decomposes at  $-40^\circ\text{C}$ . Titanium does not form stable binary carbonyl compounds, presumably due to inadequate back bonding due less d–electron density. A few carbonyl complexes are known with other  $\pi$ -bonding ligands, e.g.,  $[(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2]$  and  $[(\pi\text{-C}_6\text{H}_6)\text{Ti}(\text{CO})_4]\text{Br}$ . The stable  $\pi$ -cyclopentadienyl compound,  $\text{Ti}(\text{C}_5\text{H}_5)_4$ , is prepared by the reaction of  $\text{C}_5\text{H}_5\text{Na}$  with  $\text{TiCl}_4$ . ( $\text{Cp} = \text{-C}_5\text{H}_5$ )



X–ray diffraction study of green black solid shows that the compound contains two  $\sigma$ -bonded monohapto,  $\eta^1\text{-C}_5\text{H}_5$ , bonded through only one carbon atom and two  $\pi$ -bonded pentahapto,  $\eta^5\text{-C}_5\text{H}_5$ , bonded through all five C–atoms. The compound is thus  $[\text{Ti}(\eta^1\text{-C}_5\text{H}_5)_2(\eta^5\text{-C}_5\text{H}_5)_2]$ . Reaction of  $\text{NaC}_5\text{H}_5$  and  $\text{TiCl}_4$  also produces  $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_3]$  and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2]$ . Both are orange crystalline diamagnetic compounds stable in dry air. Reduction of  $\text{Cp}_2\text{TiCl}_2$  produces a compound with formula  $\text{TiCp}_2$  is called titanocene, an analogue of ferrocene.



## Zirconium (Zr) [Kr]4d<sup>2</sup>5s<sup>2</sup> and Hafnium (Hf) [Xe]5d<sup>2</sup>6s<sup>2</sup>

The very pure zirconium and hafnium are produced by the van Arkel process through decomposition of ZrI<sub>4</sub> and HfF<sub>4</sub> respectively.

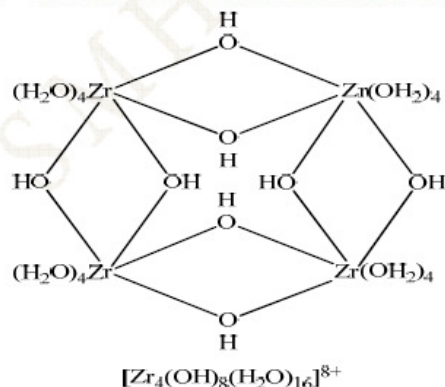
### Chemistry of Zr(IV) and Hf(IV):

The most common oxidation state of zirconium and hafnium is +IV. Lower oxidation state is not common. Zr<sup>III</sup> and Hf<sup>III</sup> are strongly reducing. Since, they reduce water, they have no aqueous chemistry. Only trihalides and their derivatives are known.

The M<sup>4+</sup>/M potentials indicate the greater reducing power of Zr and Hf than Ti: E°(V): Ti (-0.89), Zr (-1.56), Hf (-1.70). This is because the higher oxidation state is stable for heavier elements compared to lighter elements.

The hydroxide M(OH)<sub>4</sub> are obtained as white gelatinous precipitate on adding alkali to M(IV) solutions having compositions MO<sub>2</sub>.nH<sub>2</sub>O. These give dioxide on strong heating. The oxides and hydroxides reacts with acids produce MOX<sub>2</sub> compound (X = Cl, Br, I, NO<sub>3</sub>, ½SO<sub>4</sub>). These halides are readily hydrolyzed at room temperature giving oxohalides which are stable to further hydrolysis. ZrCl<sub>4</sub> + 9H<sub>2</sub>O → ZrOCl<sub>2</sub>.8H<sub>2</sub>O + 2HCl

**Aqueous Chemistry:** Due to larger size, Zr(IV) and Hf(IV) are hydrolyzed less extensively than Ti(IV). The main species in aqueous solution may be ZrO<sup>2+</sup>, HfO<sup>2+</sup>. In low concentration and highly acidic medium, the principal species appears to be [M(OH)<sub>n</sub>]<sup>(4-n)-</sup> and tri or tetrameric species. As concentration increases and acidity decreases, the polymeric species are produced. ZrOCl<sub>2</sub>.8H<sub>2</sub>O actually consists of the tetrameric ion [Zr<sub>4</sub>(OH)<sub>8</sub>(H<sub>2</sub>O)<sub>16</sub>]<sup>8+</sup>. The strong polarizing nature of M<sup>4+</sup> ion disfavoured the formation of simple ionic compound.





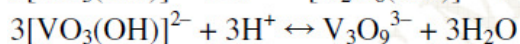
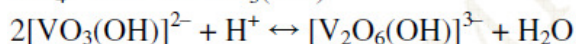
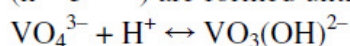
**Group 5: Vanadium(V)[Ar]3d<sup>3</sup>4s<sup>2</sup>, Niobium(Nb)[Kr]4d<sup>4</sup>5s<sup>1</sup> and Tantalum(Ta)[Xe]4f<sup>14</sup>5d<sup>3</sup>6s<sup>2</sup>**  
 Group oxidation state is +5, but each element shows formal oxidation states from +5 to -1. Stability of lower oxidation state is decreased down the group. In the case of vanadium, +4 is the most stable and +3 and +2 oxidation states are strongly reducing whereas for niobium and tantalum +5 oxidation state is mainly observed.

**Vanadium (V): Electronic configuration: [Ar]3d<sup>3</sup>4s<sup>2</sup>**

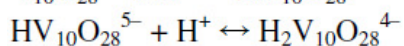
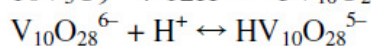
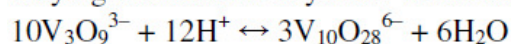
Vanadium has a total five valence electrons and shows all oxidation states from -I to +V. Vanadium(V) is mild oxidizing and exists as oxo species and fluoride. Its aqueous chemistry is characterized by polymeric species commonly known as isopolyvanadates. Vanadium(IV) is the most stable state under normal conditions and is represented by the halides and the vanadyl ion VO<sup>2+</sup>. Vanadium(III) is a milder reducing compared to titanium(III). But, Vanadium(II) is strongly reducing and rapidly oxidized in air and water. Compounds containing vanadium in IV, III, II oxidation states are normally coloured and paramagnetic. VO<sup>2+</sup> (blue) → V<sup>3+</sup> (green) → V<sup>2+</sup> (violet)

**Vanadates:**

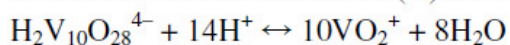
V<sub>2</sub>O<sub>5</sub> dissolves in strong bases forming ‘vanadates’ which have different compositions at different pH. In strongly basic solution (pH > 12.6), the main species is colourless monomeric tetrahedral ion VO<sub>4</sub><sup>3-</sup>. On gradual lowering of pH, it starts to condense – first a dinuclear species (pH = 12–9), and then tri and tetra nuclear species (pH = 9–7) are formed. These are also colourless. On further lowering of pH, red to red brown polynuclear species (n ~ 5 – ∞) are formed until V<sub>2</sub>O<sub>5</sub>.xH<sub>2</sub>O is precipitated at pH ~ 6.



The precipitates is dissolved in more acidic solution (pH = 6–2). The colour of the solution is varying from brown to yellow where the main species is orange coloured decavanadate ion.



The monomeric dioxovanadium(V) ion is formed at pH below 2.2.



**Halides and oxohalides:**

VF<sub>5</sub> is the only pentahalide of V(V) because V(V) oxidizes the other halides to halogen due to its strong oxidizing nature. The VOX<sub>3</sub> (X = F, Cl, Br), VO<sub>2</sub>F, VO<sub>2</sub>Cl are known. The thermal stability of the oxohalides decreases from VOF<sub>3</sub> to VOB<sub>3</sub>, because reducing power of the halide ion increases in the order F<sup>-</sup> < Cl<sup>-</sup> < Br<sup>-</sup>. VOB<sub>3</sub> liberating Br<sub>2</sub> at RT. All the oxohalides are readily hydrolyzed in moist air producing copious brown fumes of V<sub>2</sub>O<sub>5</sub>.

Reaction of vanadium metal with fluorine, chlorine and bromine separately produce VF<sub>5</sub>, VCl<sub>4</sub> and VBr<sub>3</sub> respectively. This is because, the oxidizing power of vanadium ions increases as V(III) < V(IV) < V(V) and reducing power of X<sup>-</sup> ion is increases as F<sup>-</sup> < Cl<sup>-</sup> < Br<sup>-</sup> that means Br<sup>-</sup> is easily oxidizable whereas F<sup>-</sup> is hard to oxidize to corresponding halogen.

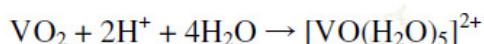
Therefore, V(V) ion oxidises  $\text{Cl}^-$  and  $\text{Br}^-$  quite easily but not  $\text{F}^-$  whereas V(IV) oxidizes only  $\text{Br}^-$  and V(III) does not oxidize  $\text{Br}^-$ ,  $\text{Cl}^-$  or  $\text{F}^-$ . So, V(V) is stable only with fluoride and V(IV) is stable with both fluoride and chloride, and vanadium(III) is stable with fluoride, chloride and also bromide.

### Complexes of vanadium(V):

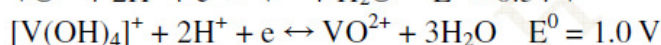
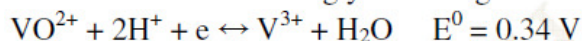
Various peroxo complexes of V(V) are produced due to addition of  $\text{H}_2\text{O}_2$  to aqueous solution of vanadium(V) under varying acidic condition. In acid solution, the red-brown peroxo species,  $[\text{V}(\text{O}-\text{O})]^{3+}$  is formed. In alkaline solution, yellow complexes of the type  $[\text{V}(\text{O}-\text{O})_2\text{O}_2]^{3-}$  are formed. In strongly alkaline medium, the high concentration (~100 volume) of  $\text{H}_2\text{O}_2$  solution producing blue  $[\text{V}(\text{O}_2)_4]^{3-}$  and  $[\text{V}(\text{O}_2)_3]^-$  ions.

### Aqueous chemistry of vanadium(IV):

The  $\text{V}^{4+}$  ion has a high charge density and the  $[\text{V}(\text{H}_2\text{O})_6]^{4+}$  ion is extremely acidic, not exist in aqueous solution. Instead, the aqueous chemistry of vanadium(IV) is dominated by the oxovanadium(IV) cation,  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$  or simply  $\text{VO}^{2+}$  (vanadyl) ion. It is formed by dissolving  $\text{VO}_2$  in acids.



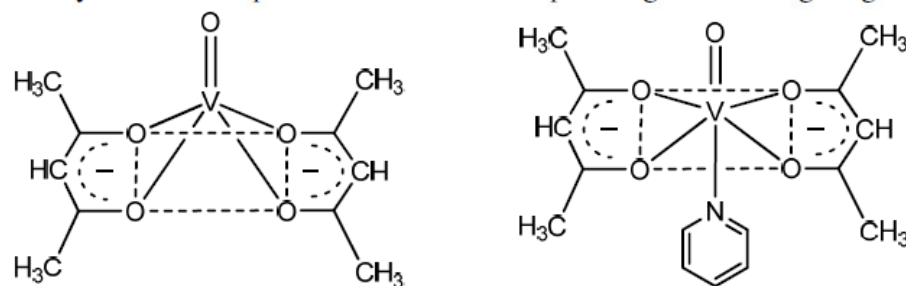
The cationic species of  $\text{V}^{4+}$  are virtually unknown,  $[\text{V}(\text{en})_3]\text{F}_4$  being a rare example. The  $\text{VO}^{2+}$  grouping is very stable since the V–O bond is very close to a double bond resulting from  $\pi$ -overlap of a filled 2p orbital on oxygen to an empty 3d orbital on vanadium. The  $\text{VO}^{2+}$  ion is neither strongly oxidizing nor reducing:



**Complexes of V(IV):** The  $\text{VO}^{2+}$  ion forms numerous oxovanadium(IV) complexes which may be anionic, cationic and neutral. These may be prepared easily by reduction of  $\text{V}_2\text{O}_5$ .



Similarly,  $\text{V}_2\text{O}_5$  is dissolved in hot oxalic acid solution producing  $[\text{VO}(\text{C}_2\text{O}_4)_2]^{2-}$  ion. The complexes are usually 5-coordinate square pyramidal with the oxygen of the VO unit occupying an apex. The V atom is often slightly above the base. The 5-coordinate complexes may become 6-coordinate by picking up an extra ligand as in  $[\text{VO}(\text{acac})_2\text{py}]$ . Since, V(IV) is a  $d^1$  system, these species are one electron paramagnetic having magnetic moment ~1.7 B.M.





**Aqueous chemistry of vanadium(III):**

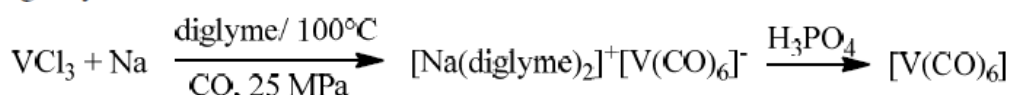
$[\text{V}(\text{H}_2\text{O})_6]^{3+}$  is obtained from dissolving  $\text{V}_2\text{O}_3$  in acid or  $\text{VX}_3$  in water.



The  $[\text{V}(\text{CN})_7]^{4-}$  ion is an example of rare seven coordination species of vanadium having pentagonal bipyramid structure. It is obtained by adding excess of KCN solution to dilute HCl solution of  $\text{V}^{\text{III}}$ . On standing in absence of air, the deep blue colour of the solution is changed to wine red and  $\text{K}_4[\text{V}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$  precipitates on addition of methanol.

**Lower oxidation state of vanadium:**

Vanadium(0) is present in  $[\text{V}(\text{CO})_6]$  and  $[\text{V}(\text{CO})_5(\text{NO})]$ .  $[\text{V}(\text{CO})_6]$  is prepared in the following way.



Vanadium(I) is present in the nitrosyl cyanide complex  $\text{K}_3[\text{V}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ . The N–O stretching frequency around  $1530 \text{ cm}^{-1}$  suggests that NO present as  $\text{NO}^+$ .

**Niobium (Nb):  $[\text{Kr}]4d^45s^1$  and Tantalum (Ta):  $[\text{Xe}]5d^36s^2$** 

The normal oxidation state is +V but it also shows lower oxidation states those are less stable than +V oxidation states and are strongly reducing. Though, V(V) forms only  $\text{V}_2\text{O}_5$  and  $\text{VF}_5$  due to oxidizing nature of V(V) other pentahalide are unknown, but Nb(V) and Ta(V) forms all halide  $\text{MX}_5$  and  $\text{M}_2\text{O}_5$ .

Oxides are white, high melting solids and chemically inert, insoluble in water and acids, attackable only by HF or fusion by hydroxide. Like vanadates, various niobates and tantalates like metaniobates ( $\text{NbO}_3^-$ ) and metatantalates ( $\text{TaO}_3^-$ ), polyanions having two, five or six metal atoms like  $\text{Nb}_2\text{O}_7^{4-}$ ,  $\text{Ta}_6\text{O}_{19}^{8-}$  etc are known.



**Group 6: Chromium(Cr)[Ar]3d<sup>5</sup>4s<sup>1</sup>, Molybdenum(Mo)[Kr]4d<sup>5</sup>4s<sup>1</sup> and Tungsten(W)[Xe]4f<sup>14</sup>5d<sup>4</sup>6s<sup>2</sup>**

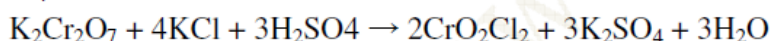
Gr. 6 elements exhibit +6 to -2 oxidation state but the stability of higher oxidation increases down to the group. Chromium (III) state is most stable oxidation state whereas +5 and +4 are unstable. Chromium(II) is strongly reducing ( $\text{Cr}^{3+}/\text{Cr}^{2+}$ ,  $E^\circ = -0.41 \text{ V}$ ) while Cr(VI) is oxidizing. On contrast, the chemistry of molybdenum and tungsten in oxidation states +5 to +2 is dominated by clusters and multiple bonded species.

**Chemistry of chromium(VI):**

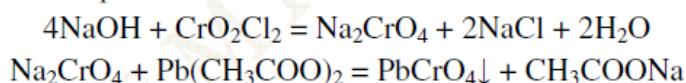
The important Cr(IV) compounds are  $\text{CrO}_3$ , the oxohalides  $\text{CrOX}_4$  ( $X = \text{F}, \text{Cl}$ ),  $\text{CrO}_2\text{X}_2$  and  $\text{CrO}_3\text{X}^-$  ( $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ); oxoions  $\text{Cr}_n\text{O}_{3n+1}^{2-}$  ( $n = 1, 2, 3, 4$ ) and the peroxy compounds.

The aqueous solution of  $\text{CrO}_3$  is strongly acidic and red in colour, mainly contains  $\text{H}_2\text{CrO}_4$  as main species at  $\text{pH} < 1$  but at  $\text{pH} 2-6$ ,  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions predominate. The  $\text{CrO}_4^{2-}$  ion becomes the main species above  $\text{pH} 6$ .  $\text{CrO}_3$  is a powerful oxidizing agent.

**$\text{CrO}_2\text{Cl}_2$ , chromyl chloride:**  $\text{CrO}_2\text{Cl}_2$ , chromyl chloride is the most important oxohalides of chromium(VI). It is formed when an ionic chloride is heated with potassium dichromate and concentrated  $\text{H}_2\text{SO}_4$ .

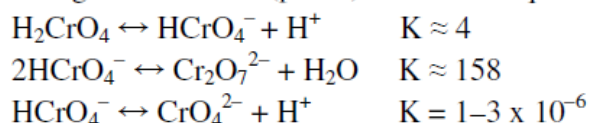


Bromides, iodides evolve free halogens under identical condition and hence this reaction is used as a specific test for chlorides. The reddish brown fume of  $\text{CrO}_2\text{Cl}_2$  evolved is collected in dilute sodium hydroxide solution. Then the resulting solution is acidified with acetic acid and treated with lead acetate solution – a yellow precipitates of lead chromate indicates the presence of chloride in sample.

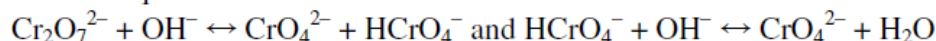


**Aqueous solution chemistry of Cr(VI):**

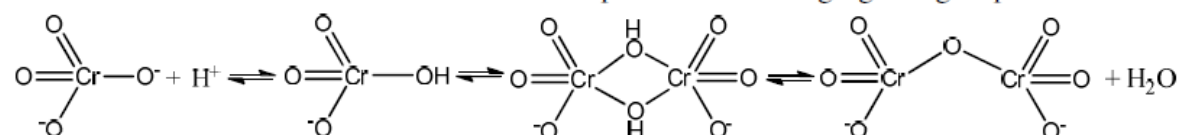
The chromate ion,  $\text{CrO}_4^{2-}$  (yellow) and dichromate ion (orange) are the main Cr(VI) species in aqueous solution. The  $\text{CrO}_4^{2-}$  ion predominates in alkaline solution ( $\text{pH} > 6$ ) while  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  exist in equilibrium between  $\text{pH} 2$  and  $6$ .  $\text{H}_2\text{CrO}_4$  appears to be main species in strong acid medium ( $\text{pH} < 1$ ). The main equilibria in acid medium are:



And the equilibria in alkaline medium are



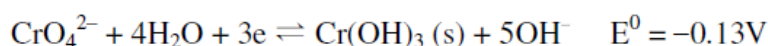
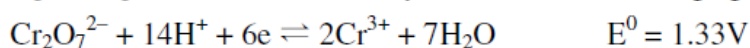
The conversion of  $\text{CrO}_4^{2-}$  ions to  $\text{Cr}_2\text{O}_7^{2-}$  ions proceeds via bridging OH groups.



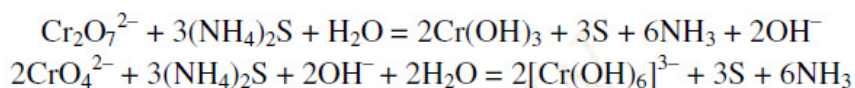
The chromate ion is tetrahedral and two tetrahedral  $\text{CrO}_4$  units linked by sharing an O-atom form the dichromate ion.

**Vanadate ( $\text{VO}_4^{3-}$  vs Chromate ( $\text{CrO}_4^{2-}$ ):** In aqueous solution, the  $\text{VO}_4^{3-}$  ion forms a large series of poly-vanadates, but the  $\text{CrO}_4^{2-}$  ion condenses mainly upto the  $\text{Cr}_2\text{O}_7^{2-}$  ion inspite of  $d^0$  configuration. As, chromium is present in +VI oxidation state, it's size is smaller and has higher effective nuclear charge compare to vanadium(V). That's why  $\text{Cr}=\text{O}$   $\pi$ -bond is strong enough. So, chromium prefers to form  $\text{Cr}=\text{O}$   $\pi$ - bond instead of  $\text{Cr}-\text{O}-\text{Cr}$  bond. On the other side, vanadium prefers  $\text{V}-\text{O}-\text{V}$  bond in contrast to  $\text{V}=\text{O}$  bond.

**Oxidizing nature of  $\text{CrO}_4^{2-}$ :** The dichromate ion is a strong oxidizing agent in acid medium, but the chromate ion is much milder oxidizing agent. Since, in acidic medium  $\text{Cr}_2\text{O}_7^{2-}$  is the main species, so only in acidic medium it is act as oxidizing agent. But, in alkaline medium  $\text{CrO}_4^{2-}$  is the main species present in solution only acts as mild oxidizing agent.

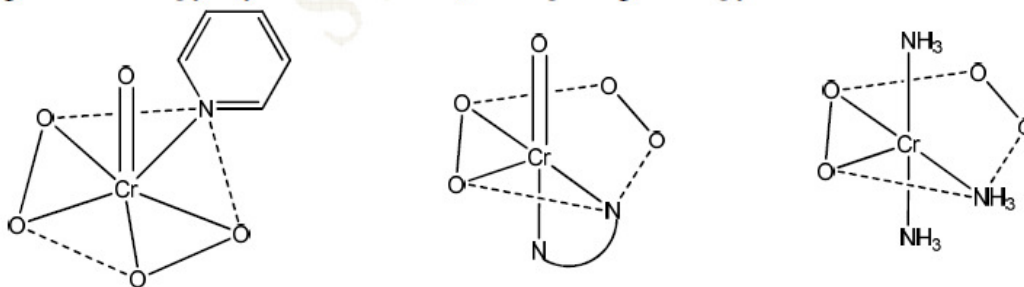


In neutral medium,  $\text{Cr}(\text{OH})_3$  is precipitated and in alkaline medium the anionic complex  $[\text{Cr}(\text{OH})_6]^{3-}$  is formed.



#### Peroxo complexes of chromium:

When acidified potassium dichromate solution is treated with  $\text{H}_2\text{O}_2$ , solution becomes deep blue due to formation of peroxo species,  $\text{CrO}_5$ . Colour disappears gradually with evolution of oxygen. If the solution is shaken in ether, the colour concentrates in the ether layer where it is more soluble. Addition of pyridine to this ether solution gives the explosive solid adduct 'pyridine perchromate',  $[\text{CrO}(\text{O}_2)_2(\text{py})]$ . It dissolves as a monomer in benzene and it is diamagnetic. The dipyridyl adduct of  $\text{CrO}_5$  has a pentagonal bipyramid structure.



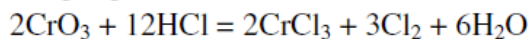
In faintly acidic or neutral medium,  $\text{H}_2\text{O}_2$  reacts with dichromate solution giving violet explosive salts like  $\text{KHCrO}_6$  which is diamagnetic, supposed to be a  $[\text{Cr}^{\text{VI}}\text{O}(\text{O}_2)_2\text{OH}]^-$  anion.

When alkaline potassium dichromate solution is treated with 30%  $\text{H}_2\text{O}_2$  then the red-brown paramagnetic species of chromium(V),  $\text{K}_3\text{CrO}_8$  is obtained. It exists as  $[\text{Cr}(\text{O}_2)_4]^{3-}$  which have dodecahedron structure. Treating this red complex with aqueous ammonia at  $50^\circ\text{C}$  produces a dark red-brown Cr(IV) complex,  $[\text{Cr}(\text{O}_2)_2(\text{NH}_3)_3]$  which adopts pentagonal bipyramidal geometry. This compound may also be obtained by adding  $\text{H}_2\text{O}_2$  to an ammoniacal solution of  $(\text{NH}_4)_2\text{CrO}_4$ .

### Compounds of Cr(III):

This is most stable and common oxidation state of chromium. Cr(III) forms the most stable trivalent cation in aqueous solution. The important compounds are  $\text{Cr}_2\text{O}_3$ ,  $\text{CrX}_3$  ( $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) and different stable complexes.

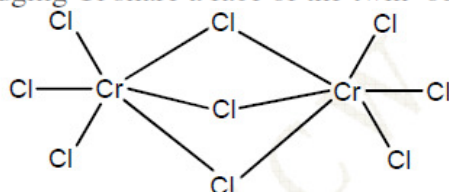
A green solution of  $\text{CrCl}_3$  is obtained when  $\text{CrO}_3$  is boiled with concentrated  $\text{HCl}$ . The crystalline hydrate  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  may exist as three hydrate isomers.  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (violet),  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (light green) and  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  (dark green, trans),



### Adduct formation:

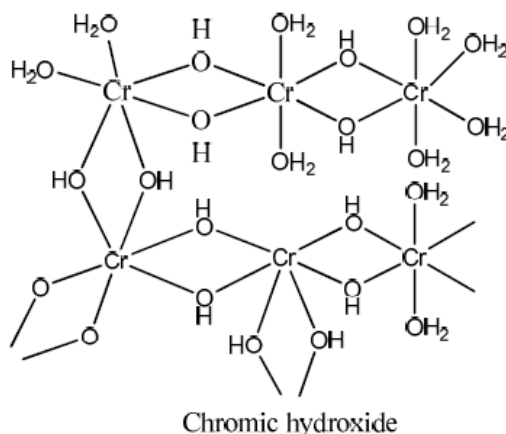
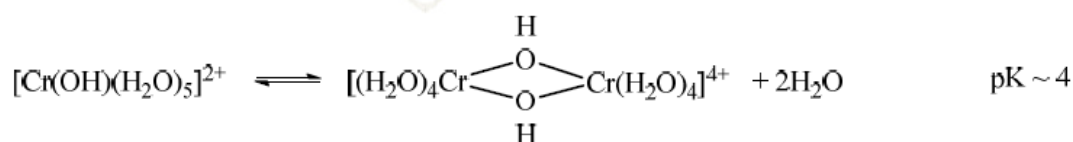
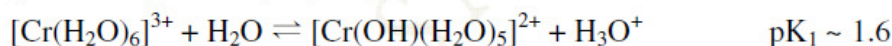
$\text{CrCl}_3$  forms a large number of adducts e.g.,  $\text{CrCl}_3 \cdot 3\text{py}$  and  $\text{CrCl}_3 \cdot 3\text{THF}$ . Trimethylamine forms a 5-coordinate adduct with trans-trigonal bipyramidal structure,  $\text{CrCl}_3(\text{NMe}_3)_2$ .

Two series of halide complexes are generated with alkali metal chlorides –  $\text{M}_3\text{CrCl}_6$  and  $\text{M}_3\text{Cr}_2\text{Cl}_9$ . These are paramagnetic showing the presence of three unpaired electrons per chromium. There is no spin pairing between the two chromium centres. The skeleton of  $\text{Cr}_2\text{Cl}_9^{3-}$  shows that three bridging Cl share a face of the twin-octahedra.



### Aqueous chemistry of Cr(III):

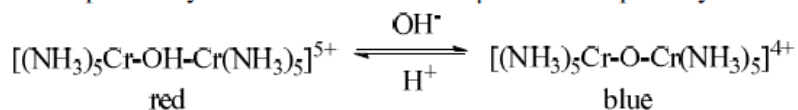
The hexaaqua ion is largely acidic. The hydroxide ion readily condenses to a dimeric hydroxo bridged species. With the increase in pH, greyish-blue hydrated chromium(III) oxide (chromic hydroxide) is precipitated.



Chromic hydroxide



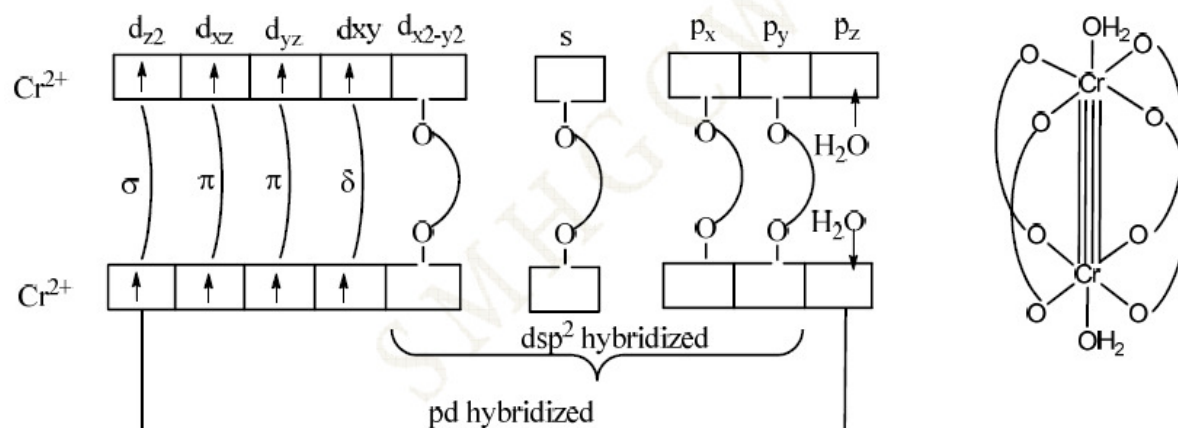
A dinuclear hydroxo-bridge ammine complexes and ethylenediamine complexes are known which shows temperature dependent paramagnetic moment is lower than the expected for octahedral Cr(III), suggesting partial pairing of spin via OH bridges. The red  $\mu$ -hydroxo bis pentaammine complex may be converted to blue  $\mu$ -oxo complex by the action of alkali.



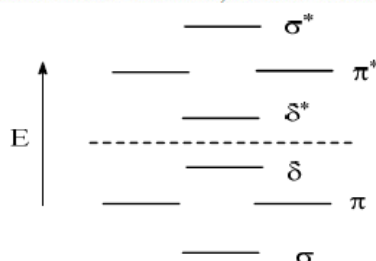
Magnetic moment of the blue complex at room temperature is  $\sim 1.3$  B.M., indicating greater spin pairing between the two chromium centres via  $d\pi$ - $p\pi$  bonds in linear oxo-bridge whether the hydroxo bridge complex has bent structure.

### Chromium(II) acetate dehydrate, $\text{Cr}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ :

Treating Cr(II) solution with saturated solution of sodium acetate under nitrogen produces a red precipitate of chromium(II) acetate dehydrate. The precipitate is oxidized in air but less readily than the other Cr(II) salts. The compound is actually diamagnetic with dimeric structure  $\text{Cr}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$ , having a Cr-Cr quadruple bond,  $1\sigma + 2\pi + 1\delta$  bond. The all four unpaired electron are involved in quadruple bond. Therefore, no unpaired electron is present. So it becomes diamagnetic.

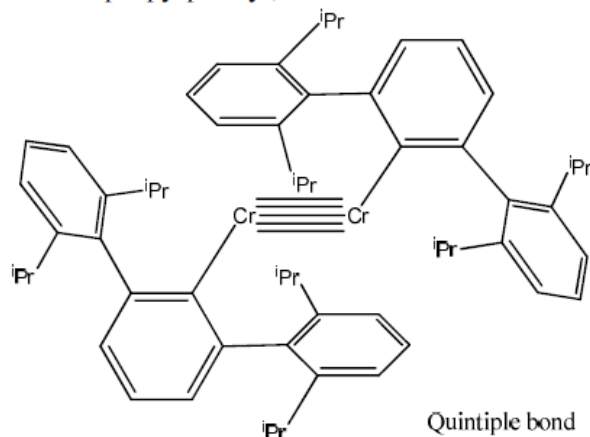


Each  $\text{Cr}(\text{OAc})_2$  unit is square planner. Cr uses  $dsp^2$  ( $d_{x^2-y^2}$ ,  $s$ ,  $p_x$ ,  $p_y$ ) hybrid orbital to form bond with  $\text{OAc}^-$ . The  $pd$  ( $d_z^2$ ,  $p_z$ ) hybrid orbital overlap each other to form Cr-Cr  $\sigma$ -bond and form bond with  $\text{H}_2\text{O}$ . The  $d_{xz}$ ,  $d_{yz}$  orbitals on each Cr atom can undergo sideways overlap to produce two  $d\pi$ - $d\pi$  bonds and the  $d_{xy}$  orbital undergo a face on overlap of four lobes to produce  $\delta$ -bond. Due to  $\delta$ -bond two  $\text{CrO}_4$  units becomes eclipsed configuration. Because of the  $\delta$ -bond formation between two metal centres, M-M bond distances become shorter.



Two Cr(II) ( $d^4$  system), has total eight electron, occupy bonding molecular orbital, giving electron arrangement  $\sigma^2\pi^4\delta^2$ . The  $\text{Cr}_2^{4+}$ ,  $\text{Mo}_2^{4+}$ ,  $\text{W}_2^{4+}$ ,  $\text{Re}_2^{6+}$  species forms  $\delta$ -bond. For example,  $\text{Cr}_2(\text{RCO}_2)_4$ ,  $\text{Re}_2\text{Cl}_8^{2-}$ ,  $\text{Re}_2(\text{RCO}_2)_2\text{Cl}_4$ ,  $\text{Mo}_2\text{Cl}_8^{4-}$ ,  $\text{Mo}_2(\text{RCO}_2)_4$ .

Similarly, quintuple bond (Bond Order = 5,  $\sigma + 2\pi + 2\delta$ ) also exists. For example,  $\text{Cr}_2\text{L}_2$  where HL = 2,6-bis(2,6-di-isopropylphenyl)benzene. It contains two Cr(I) ( $d^5$ ) system.



**Molybdenum (Mo):**  $[\text{Kr}]4d^54s^1$  and **Tungsten (W):**  $[\text{Xe}]4f^{14}5d^46s^2$

+VI oxidation state is most stable for molybdenum and tungsten but +V and +IV state is also shown but III and II state is strongly reducing.

#### Oxidation state VI:

The oxides, hexafluorides, hexachlorides for both metals are known. Hexabromides are unknown except  $\text{WBr}_6$  because of lower electronegativity and larger size it is difficult to accommodate six bromide and iodide around metal atom. In the Cr(VI)–Mo(VI)–W(VI) series, there is a marked increase in stability of compounds as shown by the  $\Delta G_f^\circ$  values.

$\text{CrO}_3$  (s): –506,  $\text{MoO}_3$  (s): –668,  $\text{WO}_3$  (s): –764

$\text{CrO}_2\text{Cl}_2$  (l): –524,  $\text{MoO}_2\text{Cl}_2$  (l): –623,  $\text{WO}_2\text{Cl}_2$  (s): –753

$\text{CrO}_4^{2-}$  (aq): –730,  $\text{MoO}_4^{2-}$  (aq): –916,  $\text{WO}_4^{2-}$  (aq): –920

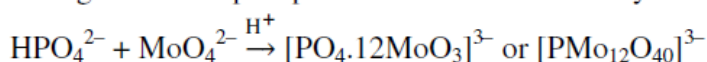
#### Isopoly and heteropoly oxometallates (iso and hetero–poly acids and salts):

Polyoxometallates and their corresponding protonated species are called isopoly acids and their salts. The species formed by condensation of oxometals with another hetero oxo ion like  $\text{PO}_4^{3-}$ ,  $\text{SiO}_4^{4-}$  are called heteropoly acids and their salts. In strongly basic medium, the  $\text{MO}_4^{2-}$  ions of Mo(VI) and W(VI) show a prominent tendency to form various polyoxoanions in solution as well as in solid state. This tendency is shown though in limited extent by V(V), Nb(V), Ta(V) and U(VI) but not for Cr(VI). Cr(VI) has smaller size always prefers to form  $\text{M}=\text{O}$  instead of  $\text{M}-\text{O}-\text{M}$ .

The principal isopolyoxometallates for Mo(VI) and W(VI) in solution are:  $\text{Mo}_7\text{O}_{26}^{6-}$  (pH $\approx$ 6),  $\text{Mo}_8\text{O}_{26}^{4-}$  (pH < 6),  $\text{H}_2\text{W}_6\text{O}_{22}^{6-}$ ,  $\text{W}_7\text{O}_{24}^{6-}$ ,  $\text{H}_2\text{W}_{12}\text{O}_{42}^{10-}$ .

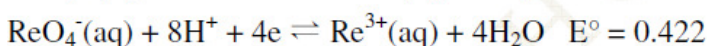
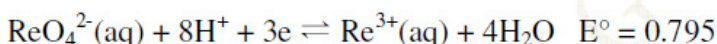
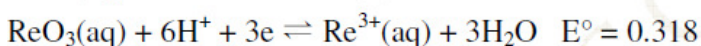
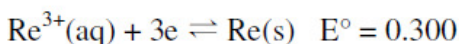
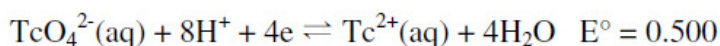
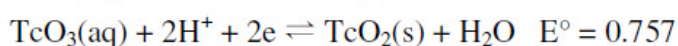
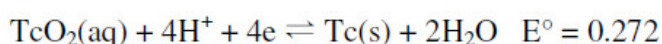
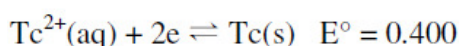
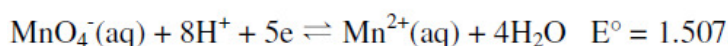
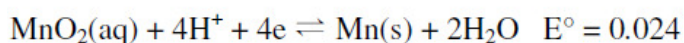
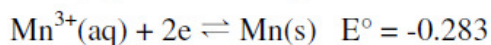
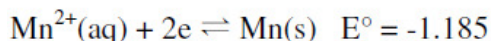
In solid,  $\text{Mo}_2\text{O}_7^{2-}$  exists as infinite chain of  $\text{MoO}_6$  octahedra and  $\text{MoO}_4$  tetrahedral units but in solution it readily rearranges to  $\text{Mo}_7\text{O}_{24}^{6-}$  and  $\text{Mo}_8\text{O}_{26}^{4-}$ .

Heteropoly oxometallates are readily formed by condensation of two oxoanions as observed during the test of phosphate with ammonium molybdate solution.



**Group 7: Manganese (Mn)[Ar]3d<sup>5</sup>4s<sup>2</sup>, Technetium(Tc)[Kr]4d<sup>6</sup>5s<sup>1</sup> and Rhenium(Re)[Xe]4f<sup>14</sup>5d<sup>5</sup>6s<sup>2</sup>**

The relative stabilities of different oxidation states in aqueous, acidic solutions may be idealized from the redox potential data as summarized below.



❖ Gr. 7 elements shows wide range of the oxidation states because of the presence of many d electrons, as the d orbitals have not sunk energetically into the inert electron core. The number of d electrons available for bonding is consequently maximized, and not only are high oxidation states possible, but back donation of electrons from metal to ligand is also facilitated with resulting stabilization of low oxidation states.

❖ The Mn<sup>II</sup> cation is most stable. This may be taken as an indication of the stability of the symmetrical d<sup>5</sup> electron configuration.

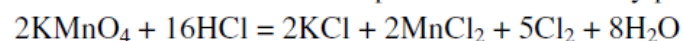
❖ The manganate(VII) (permanganate) ion is an extremely strong oxidizing agent but TcO<sub>4</sub><sup>-</sup> and ReO<sub>4</sub><sup>-</sup> show only mild oxidizing properties.

**Manganese (Mn): Electron configuration: [Ar]3d<sup>5</sup>4s<sup>2</sup>**

The stable oxidation state is +II, consistent with the half filled configuration. In alkaline medium, it is readily oxidized to MnO<sub>2</sub>. The highest oxidation state shown is +VII, which is very strong oxidizing.

**Chemistry of Mn(VII):**

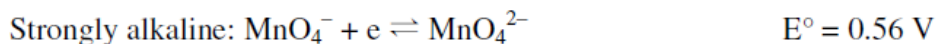
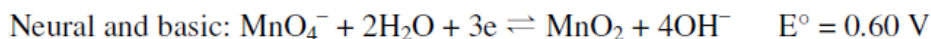
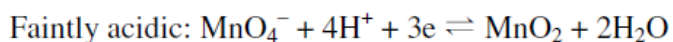
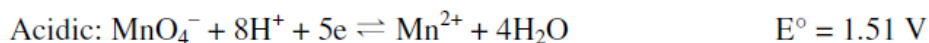
KMnO<sub>4</sub>, consists permanganate ion acts as strong oxidizing agent. HMnO<sub>4</sub> and Mn<sub>2</sub>O<sub>7</sub> is also important compound of Mn(VII). Permanganate cannot be used in hydrochloric acid medium since chloride ions are susceptible to oxidation by permanganate. (E<sup>o</sup><sub>Cl<sub>2</sub>/Cl<sup>-</sup></sub> = 1.36 V)



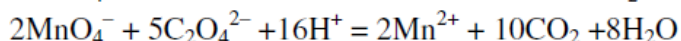
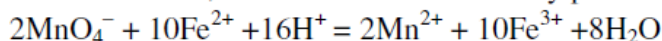


### Aqueous solution chemistry of Mn(VII):

The permanganate ion ( $\text{MnO}_4^-$ ) is very strong oxidizing agent in acid medium and moderately oxidizing in neutral and alkaline medium.



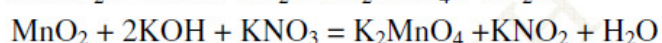
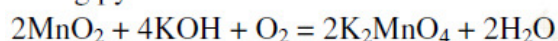
In acid solution, most oxidation reaction by permanganate is quantitative:



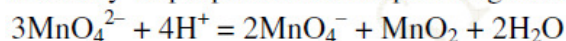
It is worth to mention that, Zimmerman - Reinhardt solution which is the mixture of  $\text{MnSO}_4$ ,  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$  is used in permanganometric estimation of  $\text{Fe}^{2+}$ .  $\text{MnSO}_4$  lowers the formal potential of  $\text{MnO}_4^-/\text{Mn}^{2+}$  redox couple, so that  $\text{MnO}_4^-$  oxidized only  $\text{Fe}^{2+}$  not  $\text{Cl}^-$ .  $\text{H}_3\text{PO}_4$  form complex with  $\text{Fe}^{3+}$  and thus lowers the formal potential  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and also masking the yellow colour of  $\text{Fe}^{3+}$ .  $\text{H}_2\text{SO}_4$  maintains the acidity.

### Chemistry of Mn(VI):

The stable Mn(VI) species is manganate ion,  $\text{MnO}_4^{2-}$  which is formed as a green mass on fusing pyrolusite with alkali in excess air or in presence of an oxidizing agent like  $\text{KNO}_3$ .



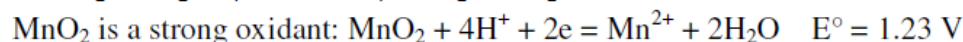
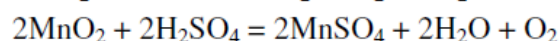
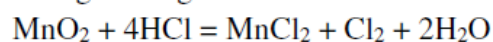
The green solution containing  $\text{MnO}_4^{2-}$  ion is stable only in alkali medium. In acidic condition it readily disproportionates to permanganate and  $\text{MnO}_2$ .



### Chemistry of Mn(IV):

The stable compounds of manganese(IV) are the dioxide  $\text{MnO}_2$ , halides  $\text{MnF}_4$  and the complexes  $\text{MnX}_6^{2-}$  where  $\text{X} = \text{F}, \text{Cl}, \text{CN}, \text{IO}_3$ .

$\text{MnO}_2$  is a slightly brownish black solid, mostly insoluble in water and inert to cold acid. It oxidizes hydrochloric acid and decomposes in concentrated sulphuric acid and nitric acid on strong heating.

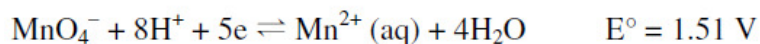
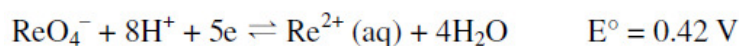
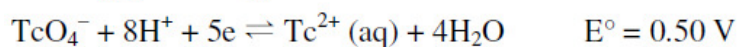


### Chemistry of Mn(II):

This is the most stable oxidation state of manganese. The greyish-green oxide,  $\text{MnO}$ , has the rock salt structure but its composition is variable. It shows antiferromagnetic behaviour through superexchange mechanism.  $\text{MnO}$  is insoluble in water. Its basic character is shown by ready dissolution in acids forming Mn(II) salts.  $\text{MnO} + 2\text{H}_3\text{O}^+ + 3\text{H}_2\text{O} = [\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

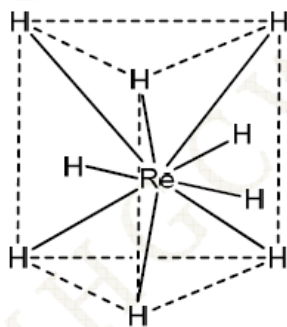
**Technetium(Tc): [Kr]4d<sup>6</sup>5s<sup>1</sup> and Rhenium(Re): [Xe]4f<sup>14</sup>5d<sup>5</sup>6s<sup>2</sup>**

+VII is the most stable oxidation state, being only weakly oxidizing in acid medium, while Mn(VII) is strongly oxidizing. Among the lower oxidation states, +V and +VI states are less common and tend to disproportionate. Tc(III) and Re(III, IV) are quite stable where as II state is strongly reducing for Tc and Re.



The  $\text{TcO}_4^-$  and  $\text{ReO}_4^-$  ions appear colourless as their charge transfer bands lie in the UV region. The red colour of crystalline  $\text{HTcO}_4$  may arise due to distortion of the tetrahedral structure giving some absorption in the blue end of the visible region.

Treatment of perrhenate with potassium in ethylenediamine or alcoholic solution gives a water soluble rhenium species which contains  $\text{ReH}_9^{2-}$  ion. The structure of  $\text{ReH}_9^{2-}$  is tri-capped trigonal prism. The Re atom is at the centre of a trigonal prism of six H atoms. Three more H atoms are linked along rectangular face centre.



**Group 8: Iron (Fe)[Ar]3d<sup>6</sup>4s<sup>2</sup>, Ruthenium(Ru)[Kr]4d<sup>7</sup>5s<sup>1</sup> and Osmium(Os)[Xe]4f<sup>14</sup>5d<sup>6</sup>6s<sup>2</sup>**

❖ In moving across the transition series, iron is the first element which fails to attain its group oxidation state of +8. The highest oxidation state known (so far) is +6 in [FeO<sub>4</sub>]<sup>2-</sup>. It is highly oxidizing and easily reduced to Fe<sup>2+</sup>.

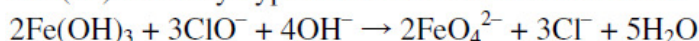
❖ On the other hand, ruthenium and osmium do attain group oxidation state (+8), and this is the highest oxidation state for any element. Ruthenium(VIII) is significantly less stable than Os<sup>VIII</sup>. The reaction of the metals with oxygen produces respectively, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>, Ru<sup>IV</sup>O<sub>2</sub> and Os<sup>VIII</sup>O<sub>4</sub>.

**Iron (Fe): Electron configuration: [Ar] 3d<sup>6</sup>4s<sup>2</sup>**

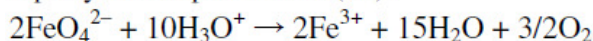
The +II oxidation state is most stable while the +III state is slightly oxidizing. Higher oxidation state is not common. The highest oxidation state shown is +VI.

**Higher oxidation state:**

A red purple solution containing Fe(VI) as FeO<sub>4</sub><sup>2-</sup> ions is obtained by oxidation of hydrated iron(III) oxide by hypochlorite in concentrated alkali.



The ferrate ion is stable only in a strongly alkaline medium. In neutral and acid medium it rapidly decomposes to Fe(III).



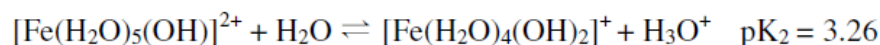
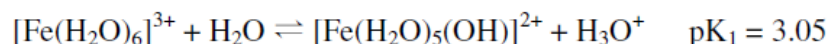
Notably, ferrate ion is stronger oxidizing agent than permanganates, chromates.

**Chemistry of iron(III):**

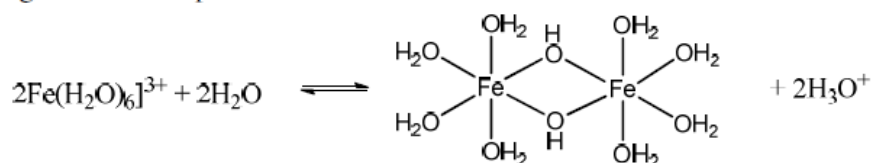
Fe<sub>2</sub>O<sub>3</sub> is insoluble in water but dissolves in acid to form salts of iron(III). Fe<sub>3</sub>O<sub>4</sub> is a mixed oxide of iron(II) and iron(III). The brown precipitates obtained from iron(III) solution are actually hydrous oxide FeO(OH) having different chain structure involving FeO<sub>6</sub> octahedra. FeF<sub>3</sub>, FeCl<sub>3</sub>, FeBr<sub>3</sub> are known but FeI<sub>3</sub> can't be prepared because iron(III) oxidizes iodide to iodine. 2Fe<sup>3+</sup> + 2I<sup>-</sup> = 2Fe<sup>2+</sup> + I<sub>2</sub>

**Aqueous solution chemistry:**

The pale violet hexa-aqua ion, [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> is known in solution as well as in crystal. The ion undergoes further hydrolysis producing acids.



The hydroxo species are brown due to charge transfer absorption in UV region having a tail into the visible region. Above pH ~ 2, the reaction proceed further to right, precipitating the hydroxide, which may be [Fe(H<sub>2</sub>O)<sub>3</sub>(OH)<sub>3</sub>] or FeO(OH). The hexa-aqua ion also forms hydroxo-bridge dinuclear species.

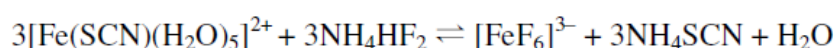
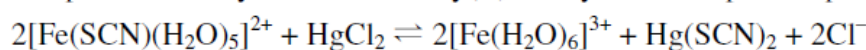




### Complex compounds of Fe(III):

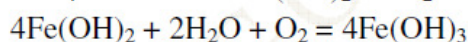
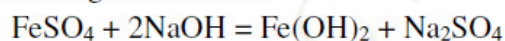
Addition of aqueous ammonia to aqueous Fe(III) precipitates the hydrous oxide and no simple ammine complex exists in water. Chelating ligands like 2,2'-dipyridyl and o-phenanthroline produces water soluble low spin complexes,  $[\text{Fe}(\text{dipy})_3]^{3+}$  and  $[\text{Fe}(\text{o-phen})_3]^{3+}$ . Iron(III) forms hexacyanoferrate(III),  $[\text{Fe}(\text{CN})_6]^{3-}$ . It is low spin complex. These  $\text{CN}^-$  ion are not generally ionisable that's why not poisonous.

The intense blood-red colour is developed on adding thiocyanate to Fe(III) solution is due to the  $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$ . This reaction is used to detect the presence of iron(III) in solution. Fluorides or mercuric chloride discharge this red colour due to the formation of fluoro complex or weakly ionized mercury(II) thiocyanate complex respectively.



### Chemistry of iron(II):

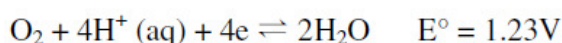
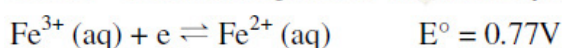
Addition of sodium hydroxide solution to aqueous iron(II) in complete absence of air produces white precipitate of iron(II) hydroxide,  $\text{Fe}(\text{OH})_2$ . It readily turns green and then brown on exposure to air when it gets oxidized.



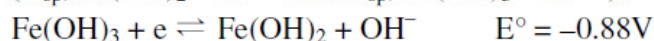
### Aqueous chemistry of Fe(II):

The pale green  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  ion is present in aqueous solution and also in crystalline salt like  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and Mohr's salt,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ . The hexa aqua ion is barely acidic due to lower charge of metal ion, enabling precipitation of  $\text{FeCO}_3$  and  $\text{Fe}(\text{OH})_2$ .

The  $\text{Fe}^{2+}$  ion is susceptible to oxidation by air according to the potentials.



The oxidation is slow in acidic solution in comparison to oxidation by other strong oxidizing agents like  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{MnO}_4^-$ ,  $\text{H}_2\text{O}_2$ . For this reason volumetric estimation of iron is possible. Oxidation of iron(II) becomes rapid in alkaline medium due to lower solubility of  $\text{Fe}(\text{OH})_3$  ( $K_{\text{sp}}, \text{Fe}(\text{OH})_2 \sim 10^{-14}$  and  $K_{\text{sp}}, \text{Fe}(\text{OH})_3 \sim 10^{-36}$ ).

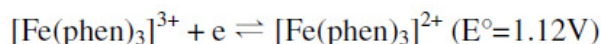
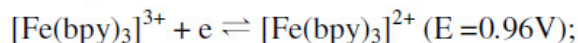


This is why precipitates of  $\text{Fe}(\text{OH})_2$ , initially white, rapidly turns brown on exposure to air.

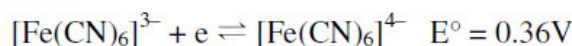
### Complex compounds of Fe(II):

The  $\text{Fe}^{2+}$  ion forms a variety of complexes most of which are octahedral and high spin except with very strong field ligands like 2,2'-dipyridyl, 1,10-phenanthroline. Though anhydrous iron(II) halides absorb ammonia gas to give the hexa ammine,  $[\text{Fe}(\text{NH}_3)_6]^{2+}$ , this is readily decomposed in water.  $[\text{Fe}(\text{NH}_3)_6]\text{Cl}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2 + 2\text{NH}_4\text{Cl} + 4\text{NH}_3$

The  $\text{Fe}^{3+}/\text{Fe}^{2+}$  potential is affected by chelation. The  $\text{Fe}^{2+}$  ion is a good  $\pi$  donor in comparison to  $\text{Fe}^{3+}$  which bears higher charge. Accordingly,  $\pi$ -acceptor ligands like 2,2'-dipyridyl (bpy), and 1,10-phenanthroline (phen) greatly stabilizes iron(II). Both oxidation states give rise to low spin complexes where the potential is modified as:



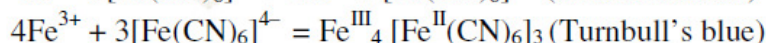
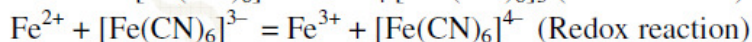
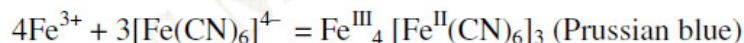
Iron(II) readily form anionic cyano complex,  $[\text{Fe}(\text{CN})_6]^{4-}$ , a low spin complex, substantially lowers the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  potential.



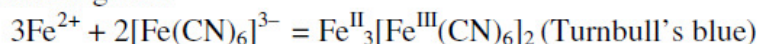
The lower value of  $E^\circ$  suggests that Fe(III) forms a more stable complex with  $\text{CN}^-$  than Fe(II) because the negative charge on  $\text{CN}^-$  disfavors metal ligand back bonding. But, thermochemical data and temperature variable  $E^\circ$  study show that the enthalpy term ( $\Delta H^\circ$ ) for oxidation of  $[\text{Fe}(\text{CN})_6]^{4-}$  is actually more positive than that for the oxidation of  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  ion. Therefore other some factor may plays role. Actually, the higher charge on the  $[\text{Fe}(\text{CN})_6]^{4-}$  ion results in a very large negative entropy of hydration which may alter the ultimate value of  $E^\circ$  for the cyanide system.

#### Prussian blue and Turnbull's blue:

The  $[\text{Fe}(\text{CN})_6]^{4-}$  ion reacts with aqueous solution of iron(III) in excess producing a deep blue precipitate called Prussian blue. Similarly, the  $[\text{Fe}(\text{CN})_6]^{3-}$  ion produces a blue precipitate with aqueous solution of iron(II), known as Turnbull's blue. It has now been established that both blue substances are same and have formula  $\text{Fe}^{\text{III}}_4 [\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$  ( $x = 14-16$ ) Actually, in air  $[\text{Fe}(\text{CN})_6]^{3-}$  is reduced to  $[\text{Fe}(\text{CN})_6]^{4-}$  with concomitant oxidation of Fe(II) to Fe(III).



At earlier, it was suggested that the composition of Turnbull's blue is  $\text{Fe}^{\text{II}}_3[\text{Fe}^{\text{III}}(\text{CN})_6]_2$  and hence different name is given.

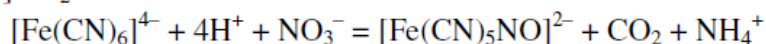


The colour of Turnbull's blue is less intense compared to Prussian blue because after a redox conversation Turnbull's blue is formed. That's why concentration of the reacting species i.e.,  $\text{Fe}^{3+}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  always less than the concentration of initial reactant i.e.,  $\text{Fe}^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$ .

The basic structural motif of the solid consists of a cubic lattice with low spin Fe(II) and high spin Fe(III) joined by CN bridges lying along the edges. The cyanide coordinate strongly to Fe(II), giving an  $\text{Fe}^{\text{II}}\text{C}_6$  octahedral unit. The nitrogen of the cyanide and some of the interstitial water molecules present in the lattice interact with Fe(III). The intense blue colour of the compound arises from intra valence charge transfer from Fe(II) to Fe(III).

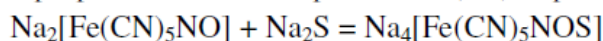


**Sodium nitroprusside:** It is prepared by heating  $K_4[Fe(CN)_6]$  with 30%  $HNO_3$ . On cooling the solution becomes brown and neutralising by  $Na_2CO_3$  yielding ruby-red crystals of  $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ .

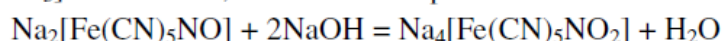


It is diamagnetic and contain low spin Fe(II) and  $NO^+$  rather than Fe(III) and NO. This is consistent with N–O distance of 113 pm and stretching frequency at  $1947\text{ cm}^{-1}$ , which is considerably higher than that for NO.

The ion forms an intense purple colour with sulphide ions ( $S^{2-}$ ) in presence of alkali.

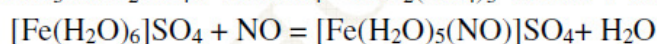
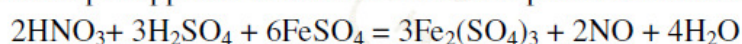


It also gives a rose red colouration with sulphites, due to formation of  $Na_4[Fe(CN)_5(NO)SO_3]$ . With alkali, a red nitro complex is formed.

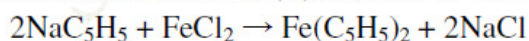


### Brown ring complex:

A dark brown ring is formed at the junction when freshly prepared ferrous sulphate is added to the nitrate solution acidified with conc. of  $H_2SO_4$ . The brown ring compound is formulated as  $[Fe(H_2O)_5(NO)]^{2+}$ . The recent studies on kinetics and mechanism of the reaction of NO with aqueous Fe(II) solution and EPR, Mossbauer spectra suggests that the complex is best described by the presence of high spin Fe(III) coordinated by  $NO^-$ . The observed spin state  $S = 3/2$ , is explained by the antiferromagnetic coupling of Fe(III) with  $NO^-$  i.e. two unpaired electrons on  $NO^-$  have spin opposite to those of the five unpaired d–electrons in iron(III).



**Ferrocene or bis-( $\eta^5$ -cyclopentadienyl)iron(II):** It is very interesting organometallic compound of iron. The reaction of cyclopentadienyl magnesium bromide with  $FeCl_3$  produces an orange compound,  $C_{10}H_{10}Fe$ , of iron(II). It is also readily prepared by the reaction of sodium cyclopentadienide with iron(II) chloride in THF.



### Ruthenium(Ru): $[Kr]4d^75s^1$ and Osmium(Os): $[Xe]4f^{14}5d^66s^2$

The observed highest oxidation state is VIII however VI and IV being the most stable state. Oxidation state ranges to –II, Ru being most stable in III state and Os in IV state.

❖ Addition of aqueous ammonia to a solution of  $RuCl_3$  in air slowly forms an intense red solution from which a diamagnetic solid can be isolated. This can be represented as a mixed valence compound,  $[(NH_3)_5Ru^{III}-O-Ru^{IV}(NH_3)_4-O-Ru^{III}(NH_3)_5]^{6+}$ . The diamagnetism has been explained by assuming  $\pi$ -overlap forming polycentric M.O.s

❖ Reduction of  $RuCl_3$  with hydrazine or zinc amalgam in presence of ammonia gives the dinitrogen complex  $[Ru(NH_3)_5(N_2)]^{2+}$ , the first reported coordinated dinitrogen complex.

❖ Some complex containing two Ru atoms in different formal oxidation state capable to transfer electron across the ligands. These mixed valence complexes generally  $Ru^{II}$  and  $Ru^{III}$  are called Creutz-Taube complex.





**Group 9: Cobalt(Co) [Ar]3d<sup>7</sup>4s<sup>2</sup>, Rhodium(Rh) [Kr]4d<sup>8</sup>5s<sup>1</sup> and Iridium(Ir) [Xe]4f<sup>14</sup>5d<sup>7</sup>6s<sup>2</sup>**

❖ The variation of oxidation states as compared to the previous groups has diminished because of the increasing stability of the (n – 1)d electrons, that results stronger attraction of nucleus towards electron preventing the elements to attain the highest oxidation states.

❖ The most common oxidation states of cobalt are +2 and +3. Virtually all of Co<sup>3+</sup> complexes are low-spin, producing a particularly high CFSE. Because of the high CFSE the heavier elements, Rh and Ir, shown the stable +3 oxidation state.

**Cobalt (Co): Electron configuration: [Ar]3d<sup>7</sup>4s<sup>2</sup>**

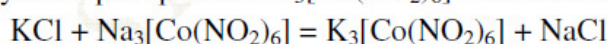
The important oxidation state of cobalt is +2 and +3. +3 oxidation state is strongly oxidizing in aqueous acid medium and as such there is no aqueous chemistry in this oxidation state. But a wide range of coordination compounds and simple compound like oxide, fluoride, sulphate, and nitrate are also known.

**Complex of Co(III):**

Co(III) forms coordination complex with various ligands for example, [CoF<sub>6</sub>]<sup>3-</sup>, [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>, [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, [Co(CN)<sub>6</sub>]<sup>3-</sup>, [Co(en)<sub>3</sub>]<sup>3+</sup>, [Co(ox)<sub>3</sub>]<sup>3-</sup> etc. Most of the Co(III) complex is low spin except [CoF<sub>6</sub>]<sup>3-</sup>, [CoF<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>].

Cobalt(II)–ammonia solution can uptake oxygen producing peroxo–bridge complexes. The red or brown [(NH<sub>3</sub>)<sub>5</sub>Co–O–O–Co(NH<sub>3</sub>)<sub>5</sub>]<sup>4+</sup> complexes are diamagnetic while the green complex [NH<sub>3</sub>)<sub>5</sub>Co(O<sub>2</sub>)Co(NH<sub>3</sub>)<sub>5</sub>]<sup>5+</sup> is paramagnetic with superoxide ion (O<sub>2</sub><sup>-</sup>) and contains both Co(III) in octahedral coordination.

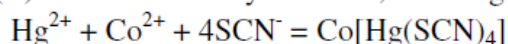
**Sodium cobaltinitrite, Na<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>]:** It is used to detect potassium ion which forms the very sparingly soluble yellow precipitate of K<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>] from acetic acid solution.



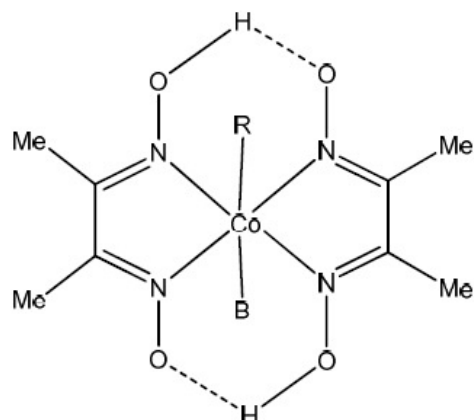
**Complex compounds of Co(II):**

Aqueous solution of cobalt(II) contain the pink hexa aqua ion, [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>. The addition of conc. HCl it turns to deep blue colour due to formation of [CoCl<sub>4</sub>]<sup>2-</sup> complex. [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> is a octahedral complex of cobalt(II), a d<sup>7</sup> system. The pink colour arises due to d-d transition which is LaPorte forbidden but spin allowed. It absorbs green region of visible light. On the other hand, [CoCl<sub>4</sub>]<sup>2-</sup> is tetrahedral complex of cobalt(II). The blue colour arises due d-d transition absorbing low energy orange light of visible region. The d-d transition is both LaPorte and spin allowed that's why give intense colour.

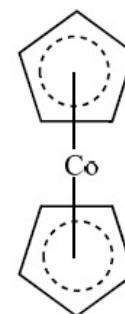
The addition of Hg(II) salt to a solution of cobalt(II) in excess thiocyanates quantitatively precipitates blue [HgCo(NCS)<sub>4</sub>]. It contains Co(II) tetrahedrally coordinated by N–atoms of thiocyanates while the Hg(II) is coordinated by S–atoms, resulting a polymeric structure.



**Cobaloximes:** It is a model complex formed by dimethylglyoxime with cobalt. It mimics the reaction of vitamin B<sub>12</sub>. The metal centre can be reduced to blue or green Co(I) state which can act as a strong nucleophile and powerful reducing agent.



R = alkyl, aryl, or acid anion  
B = base e.g. pyridine



Cobaltocene

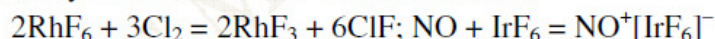
Cobaltocene,  $\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2$ , is one electron paramagnetic. It is a 19e species and acts as a reducing agent.

**Rhodium (Rh):**  $[\text{Kr}]4d^85s^1$  and **Iridium (Ir):**  $[\text{Xe}]4f^{14}5d^76s^2$

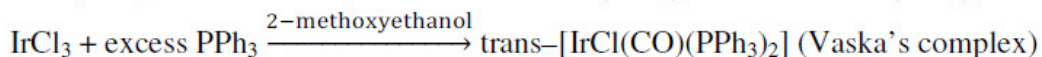
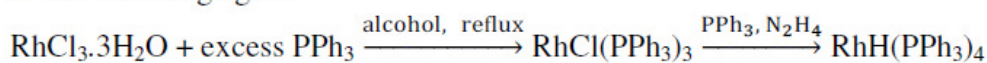
Rh and Ir show less tendency to attain higher oxidation state. Though the highest oxidation state found is VI, the most stable states for Ir are IV and III, and for Rh only III. The oxidation state VI is found in hexafluoride  $\text{MF}_6$ .  $\text{RhF}_6$  and  $\text{IrF}_6$  are unstable and oxidize water vigorously.



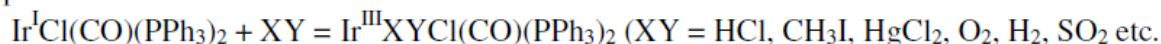
In absence of water, they even oxidize free chlorine and NO.



Lower oxidation state: +I oxidation state is stabilized by  $\pi$ -acid ligands like CO,  $\text{PPh}_3$ ,  $\text{PR}_3$ , alkenes, arenes. The complexes are mainly square planar, though tetrahedral and five coordinate species are also known. These complexes are readily prepared by the reduction of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{K}_2\text{IrCl}_6$  in presence of ligand. The ligand itself or alcoholic solvent are often acts as reducing agent.



Both  $[\text{Rh}^{\text{I}}\text{Cl}(\text{PPh}_3)_3]$  (Wilkinson's catalyst) and  $[\text{Ir}^{\text{I}}\text{Cl}(\text{CO})(\text{PPh}_3)_2]$  are square planar, undergo oxidative addition reaction with neutral molecules to give octahedral complexes with metal is present in +III oxidation state.



**Group 10: Nickel (Ni) [Ar]3d<sup>8</sup>4s<sup>2</sup>, Palladium(Pd) [Kr]4d<sup>10</sup>5s<sup>0</sup> and Platinum(Pt) [Xe]4f<sup>14</sup>5d<sup>9</sup>6s<sup>1</sup>**

The highest oxidation state is +6 but this is attained only by platinum, in PtF<sub>6</sub>. Nickel and palladium only reach +4. At the other extreme, palladium and platinum provide no oxidation state below zero. All the three elements shows +2 oxidation state extensively. The palladium and platinum have a strong preference for the square planar geometry.

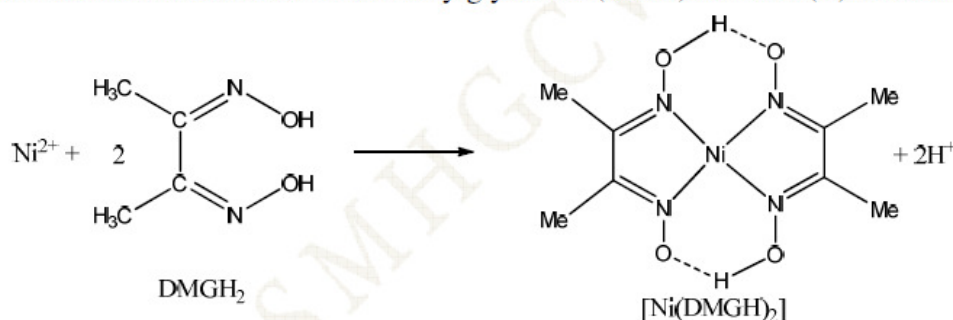
**Nickel (Ni):Electron configuration: [Ar]3d<sup>8</sup>4s<sup>2</sup>**

Nickel has only one important oxidation state, +II. Few compounds of Ni(III) and Ni(IV) are also known.

**Complex compounds:**

Complexes of nickel(II) adopted variety of geometry like octahedral, square planar, tetrahedral, square pyramidal as well as trigonal bipyramidal. The energy difference between square planar, octahedral and tetrahedral geometry is not large and so one complex may exist in more than one geometry, sometimes in an equilibrium mixture.

[Ni(CN)<sub>4</sub>]<sup>2-</sup> and [Ni(DMG)<sub>2</sub>] are square planar complex and diamagnetic. [Ni(DMG)<sub>2</sub>] complex is formed as a rose red precipitate in ammoniacal or acetate buffer medium by the addition of 1% alcoholic solution of dimethylglyoxime (DMG) to nickel(II) solution.



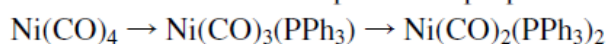
The [Ni(CN)<sub>4</sub>]<sup>2-</sup> ion may add one more CN<sup>-</sup> ion to form [Ni(CN)<sub>5</sub>]<sup>3-</sup> which may exist in both square pyramid and trigonal bipyramid structure.

The green octahedral complex [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> ion turns violet on addition of excess concentrated ammonia due to formation of [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>.

**Lower oxidation state:**

Reduction of the [Ni(CN)<sub>4</sub>]<sup>2-</sup> ion with potassium in liquid ammonia results red diamagnetic Ni(I) complex with Ni-Ni of type K<sub>4</sub>[Ni<sub>2</sub>(CN)<sub>6</sub>] (Bellucci's salt) and finally it converts to yellow compound, K<sub>4</sub>[Ni(CN)<sub>4</sub>]. K<sub>4</sub>[Ni(CN)<sub>4</sub>] is isoelectronic with Ni(CO)<sub>4</sub> and is believed to be tetrahedral. It may undergo substitution reaction with other neutral ligands to give other nickel(0) compounds, e.g. K<sub>4</sub>[Ni(CN)<sub>4</sub>] → K<sub>2</sub>[Ni(CO)<sub>2</sub>(CN)<sub>2</sub>]; K<sub>4</sub>[Ni(CN)<sub>4</sub>] → [Ni(SbPh<sub>3</sub>)<sub>4</sub>]

Nickel carbonyl, Ni(CO)<sub>4</sub> was the first metal carbonyl prepared and it is volatile. It was used in the isolation and purification of nickel by Mond process. It undergoes substitution reaction with phosphine, arsines which are stable with respect to disproportionation.





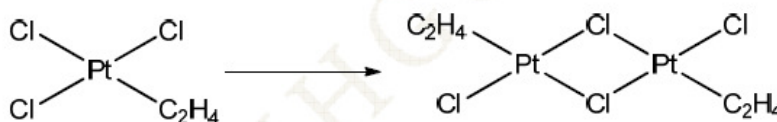
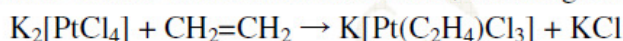
**Palladium(Pd): [Kr]4d<sup>10</sup>5s<sup>0</sup> and Platinum(Pt): [Xe]4f<sup>14</sup>5d<sup>9</sup>6s<sup>1</sup>**

Pd and Pt are reluctant to attain high oxidation state. The states of VI and V have only a few compounds of platinum. The oxidation state IV and II are common to both elements.

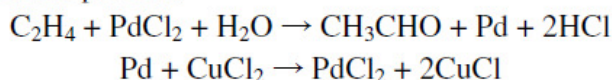
PtF<sub>6</sub> is dark red, volatile unstable solid. It is a powerful oxidizing agent, oxidize dioxygen to O<sub>2</sub><sup>+</sup>PtF<sub>6</sub><sup>-</sup> and Xenon to Xe(PtF<sub>6</sub>)<sub>n</sub>.

Both Pd(II) and Pt(II) form numerous complexes which are diamagnetic and mostly square planar. Due to soft nature, they show little affinity for F and O (hard) donor ligands but soft donors like P, S, CN, alkenes, alkynes forms large no. of complexes. Complexes of the type MX<sub>4</sub><sup>2-</sup> are formed by both metals with X = Cl, Br, SCN, CN. The stability of the halo complexes increases from Cl<sup>-</sup> < Br<sup>-</sup> < I<sup>-</sup>, because with increase of size of halogens the M-halogen dative π-bonding increases. The stability also increases from Pd(II) to Pt(II). The thiocyanate ion normally coordinates through the soft S-end but in presence of strong π-acceptor ligands (e.g. PR<sub>3</sub>), coordination occurs through the N-end.

The first organometallic compound synthesized was [Pt(C<sub>2</sub>H<sub>4</sub>)Cl<sub>2</sub>]<sub>2</sub>, by Zeise. He also synthesise the salt K[Pt(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>].H<sub>2</sub>O is named as Zeise salt. It is prepared by the action of C<sub>2</sub>H<sub>4</sub> on K<sub>2</sub>PtCl<sub>4</sub> in dilute HCl often speeded up by small amount of SnCl<sub>2</sub>. When an alcoholic solution of this is treated with concentrated HCl, an orange dimer is formed.



The coordinated alkenes are very susceptible to attack by nucleophiles like OH<sup>-</sup>, OMe<sup>-</sup>, Cl<sup>-</sup> etc. The dimeric (C<sub>2</sub>H<sub>4</sub>PdCl<sub>2</sub>)<sub>2</sub> gives CH<sub>3</sub>CHO and Pd with water. The palladium may be re-oxidised by CuCl<sub>2</sub>. The mixture of PdCl<sub>2</sub> and CuCl<sub>2</sub> converts ethylene to acetaldehyde, the process is known as Wacker process.





**Group 11: Copper (Cu)[Ar]3d<sup>10</sup>4s<sup>1</sup>, Silver (Ag) [Kr]4d<sup>10</sup>5s<sup>1</sup> and Gold (Au) [Xe]4f<sup>14</sup>5d<sup>10</sup>6s<sup>1</sup>**

The common oxidation states, particularly in aqueous solution, are +2 for Cu, +I for Ag, and +3 for Au. Ag has the lowest first ionization energy, while the sum of first and second is lowest for Cu and the sum of first, second, and third is lowest for Au. This illustrates the triad have different chemical behaviour.

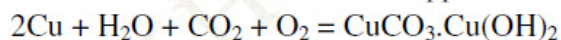
The size factor plays an important for this behaviour. The Cu<sup>II</sup> ion is smaller than Cu<sup>I</sup> and, having twice the charge, interacts much more strongly with solvent water (heats of hydration are -2100 and -580 kJ mol<sup>-1</sup> respectively). The difference is evidently sufficient to outweigh the second ionization energy of copper and to render Cu<sup>II</sup> more stable in aqueous solution (and in ionic solids) than Cu<sup>I</sup>, in spite of the stable d<sup>10</sup> configuration of the latter.

For silver, the ionic radii are both much larger and so the difference in hydration energies will be much smaller; in addition the second ionization energy is even greater than for copper. The +I ion with its d<sup>10</sup> configuration is therefore the more stable.

For gold, the stability of the 6s orbital and instability of the 5d as compared to silver, and leading respectively to the possibility of Au<sup>-</sup> and enhanced stability of Au<sup>III</sup>, have been convincingly ascribed to relativistic effects operating on s and p electrons. The high CFSE associated with square planar d<sup>8</sup> ions is a further factor favouring the +3 oxidation state.

**Copper (Cu): Electron configuration [Ar]3d<sup>10</sup>4s<sup>1</sup>**

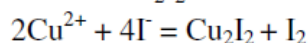
Copper slowly tarnishes in air owing to the formation of a thin film of oxide and sulphide. On long exposure to air, copper utensils get covered with a green basic sulphate CuSO<sub>4</sub>.3Cu(OH)<sub>2</sub>. In presence of carbon dioxide, basic copper carbonate is formed.



**Chemistry of copper(II):**

+2 is the main oxidation state of copper. Cu(OH)<sub>2</sub> is obtained as blue precipitate by adding alkali to aqueous copper(II). It is soluble in concentrated alkali, forming [Cu(OH)<sub>4</sub>]<sup>2-</sup> anion. and in ammonia solution forming a deep blue [Cu(NH<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>]<sup>2+</sup> ion. This deep blue solution known as Schweizers reagent dissolves cellulose (cotton).

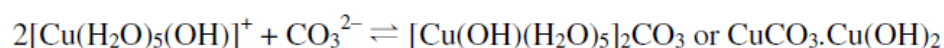
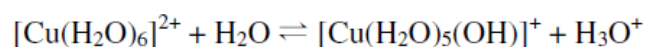
Fluoride, chloride, bromide of Cu(II) are known but CuI<sub>2</sub> is not formed because iodide reduces copper(II) with the precipitation of Cu<sub>2</sub>I<sub>2</sub>.



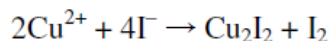
Copper(II) acetate is dimeric and hydrated, [Cu<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub>].2H<sub>2</sub>O having same structure of chromium acetate. This type of carboxylate compound has weak Cu-Cu interaction resulting partial quenching of the spin magnetic moments. That's why it shows spin only magnetic moment 1.4 B.M. at room temperature.

**Aqueous chemistry of Cu(II):**

The tetragonally distorted blue hexa aqua ion [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> is present in solution of copper(II) in water. The ion is mildly acidic, often causing precipitation of basic salts.



The Cu(II)–Cu(I) potential,  $\text{Cu}^{2+} + e \rightleftharpoons \text{Cu}^+ \quad E^\circ = 0.15\text{V}$ , suggests that Cu(II) should be a mild oxidizing agent. But, insolubility of  $\text{Cu}_2\text{I}_2$ , thermodynamically drives the reaction to completion. The Cu(II)–Cu(I) potential is also changed significantly in presence of  $\text{CN}^-$  when the Cu(I) becomes more stabilized.



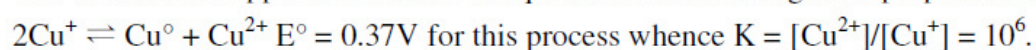
### Complex compound of Cu(II):

The yellow  $[\text{CuCl}_4]^{2-}$  ion is planar in  $(\text{NH}_4)_2[\text{CuCl}_4]$  but with larger cation such as  $\text{Cs}^+$ , the complex is flattened tetrahedron.

Addition of KCN to aqueous Cu(II) solution at room temperature causes reduction to colourless  $[\text{Cu}^{\text{I}}(\text{CN})_4]^{3-}$  with evolution of  $(\text{CN})_2$ , but in aqueous methanol at low temperature it is possible to characterize the violet  $[\text{Cu}(\text{CN})_4]^{2-}$  ion which has square planar structure.

### Aqueous chemistry of Cu(I):

The +I state for copper is not stable in aqueous solution owing to disproportionation.



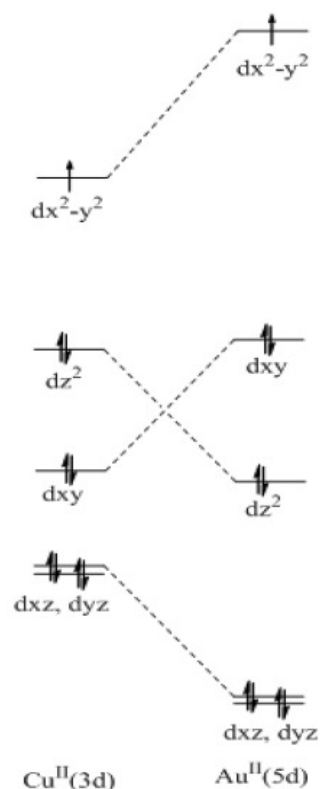
This suggests that the concentration of  $[\text{Cu}^{2+}]$  will be very large in comparison to  $[\text{Cu}^+]$ . The marked instability of  $\text{Cu}^+$  ion in water, in spite of  $d^{10}$  configuration with high exchange energy, may be due to higher hydration energy of  $\text{Cu}^{2+}$  ion than  $\text{Cu}^+$  because of smaller size and higher charge density of  $\text{Cu}^{2+}$ .

### Varying stability of different oxidation state: +II for Cu, +I for Ag and +III for Au

Firstly, the ionisation energy of these elements differs to each other. It is observed that  $I_1$  is lowest for silver, the sum of  $(I_1 + I_2)$  is lowest for copper and  $(I_1 + I_2 + I_3)$  is lowest for gold.

	Cu	Ag	Au
$I_1$	745	731	890
$I_1 + I_2$	2703	2804	2863
$I_1 + I_2 + I_3$	6281	6164	5758

On the other side, by comparing the sizes of the ions and the consequent hydration enthalpies it is observed that  $\text{Cu}^{2+}$  ion has much higher hydration enthalpy compare to  $\text{Cu}^+$  ion ( $-2100$  and  $-580 \text{ kJ mol}^{-1}$  respectively) and this is high enough to overcome the second ionisation energy of Cu resulting  $\text{Cu}^{2+}$  (aq) ion is more stable than  $\text{Cu}^+$  (aq) ion. But in case of Ag, because of the larger size of silver ions, the hydration energy cannot stabilize the Ag(II) ion over Ag(I). For Au, enthalpy of atomization, ionisation and hydration energy must be in favour of Au(III), though the  $\text{Au}^{3+}$  (aq) ion is not known. Actually for gold, the CFSE energy for the  $d^8$  configuration of Au(III) is much higher than Au(II). The last electron in  $dx^2-y^2$  orbital is so destabilized that it is easily removed.



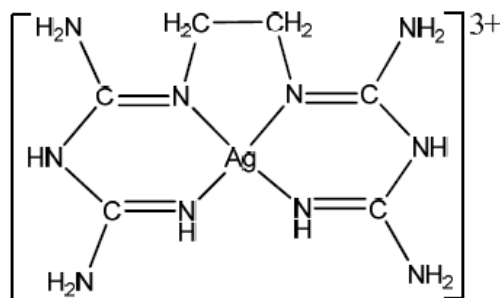
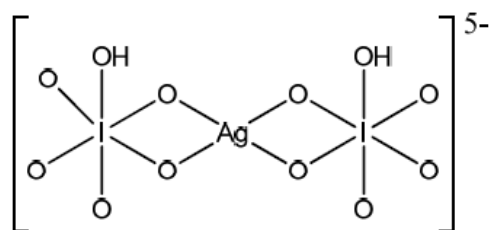


## Silver (Ag) [Kr]4d<sup>10</sup>5s<sup>1</sup> and Gold (Au) [Xe]4f<sup>14</sup>5d<sup>10</sup>6s<sup>1</sup>

The stable oxidation state for silver is Ag(I). +2 and higher are known, but are strongly oxidizing. For gold, the most stable state is Au(III). Au(I) being unstable with respect to disproportionation.  $3\text{Au}^+(\text{aq}) = \text{Au}^{3+}(\text{aq}) + 2\text{Au}(\text{s})$

### Oxidation state III:

Direct oxidation of Ag(I) in alkaline solution by  $\text{K}_2\text{S}_2\text{O}_8$  in presence of periodate or tellurate gives  $\text{Ag}^{\text{III}}$  complexes like  $\{\text{Ag}[\text{IO}_3(\text{OH})_2]_2\}^{5-}$  and  $\{\text{Ag}[\text{TeO}_4(\text{OH}_2)_2]_2\}^{5-}$ . Stable complex of  $\text{Ag}(\text{III})$  are formed by ethylene bis-biguanide by oxidation of  $\text{Ag}_2\text{SO}_4$  with  $\text{K}_2\text{S}_2\text{O}_8$ .



Gold(III) is the most common oxidation state of gold.  $\text{AuI}_3$  has not been isolated. The chloride and the bromide are red-brown solids have a planar dimeric structure  $\text{Au}_2\text{Cl}_6$ ,  $\text{Au}_2\text{Br}_6$  in both the solid and vapour phases. On being heated, both compounds lose halogen to form first the monohalide and finally metallic gold.

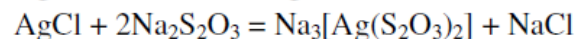
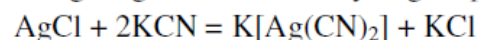
### Oxidation state II:

Silver only forms the difluoride,  $\text{AgF}_2$ . The  $[\text{Ag}(\text{H}_2\text{O})_4]^{2+}$  ion is obtained by dissolving  $\text{AgO}$  in aqueous  $\text{HClO}_4$  or by ozone-oxidation of  $\text{Ag}^+$ .  $E^\circ$  for  $\text{Ag}^{2+}-\text{Ag}^+$  couple is 2.0 V in 4M  $\text{HClO}_4$ , making  $\text{Ag}^{2+}$  a strong oxidizing agent.

$\text{Au}(\text{II})$  is strongly unfavourable in comparison to  $\text{Au}(\text{I})$  and  $\text{Au}(\text{III})$ . A rare example is maleonitriledithiolato complex,  $[\text{Au}(\text{mnt})_2]^{2-}$ .

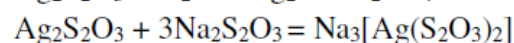
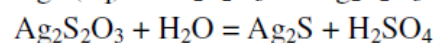
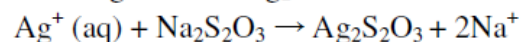
### Oxidation state I:

$\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$  are prepared by precipitating of  $\text{Ag}^+$  with appropriate halide ions. They dissolve in thiosulfate and cyanide solution.  $\text{AgCl}$  and  $\text{AgBr}$  soluble in aqueous ammonia though  $\text{AgBr}$  with difficulty.  $\text{AgI}$  is polymeric.  $\text{AgCl} + 2\text{NH}_3 = [\text{Ag}(\text{NH}_3)_2]\text{Cl}$



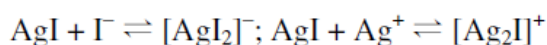
$\text{Ag}_2\text{O}$  also dissolves in ammonia, producing  $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ . In air the solution deposits the black explosive silver nitride  $\text{Ag}_3\text{N}$ , also called fulminating silver.

By addition of sodium thiosulphate to silver(I) solution, the white precipitate of silver thiosulphate,  $\text{Ag}_2\text{S}_2\text{O}_3$ , is formed. The precipitate decomposes on standing and rapidly on warming to black  $\text{Ag}_2\text{S}$  but dissolve in excess of sodium thiosulfate solution.





**Complexes:** Both Ag(I) and Au(I) form mainly two coordinate complexes. With increasing  $Z_{\text{eff}}$ , the differences between s and  $dz^2$  orbitals on the metals become sufficiently small to allow  $s-dz^2$  hybridization. Few two-coordinate complexes are  $[\text{Ag}(\text{NH}_3)_2]^+$ ,  $[\text{Ag}(\text{CN})_2]^-$ ,  $\text{AgX}_2^-$ . Silver iodide dissolves in solutions containing excess iodide and  $\text{Ag}^+$  due to complex formation.



Au(I) forms mainly symmetrical linear complex of type  $(\text{AuX}_2)^-$  where X = halogen, cyanide. These are stable in solid or in solution with excess halide ions, otherwise disproportionate into Au and Au(III) complex.  $3[\text{AuX}_2]^- = [\text{AuX}_4]^- + 2\text{Au} + 2\text{X}^-$

Au(-I) is present in  $\text{CsAu}$ . Because of inner  $4f^{14}5d^{10}$  shell the  $Z_{\text{eff}}$  on 6s orbital is so large that 6s orbital is stabilized. It is known as lanthanide contraction. Due to such effect 6s orbital can accept one more electron to attain the stable noble liquid  $6s^2$  configuration.

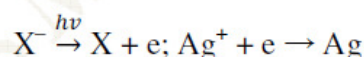
### Photography:

The halides are light sensitive, used in photography.

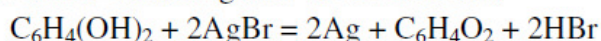
Photography is based on the light sensitivity of silver halides. The photographic plate/file consists of an emulsion of fine grain silver halide on a transparent medium like glass or celluloid. The silver halide is usually AgBr with some AgCl and organic dyes. AgI is used for very fast films. The organic dye acts as a photosensitizer helping light absorption over the entire visible band.

The following steps are to be done to producing a photograph.

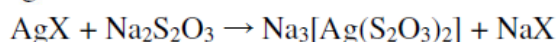
(i) Exposure to the object, forming a latent image on the film. A halide ion is excited by a photon loses its electron which subsequently reduces a silver ion to silver atom. A greater intensity of photon deposits more grains of silver and thus a latent image of fine layer of silver atoms is formed.



(ii) Developing intensifies the latent image by depositing more silver atoms on the latent image. A mild reducing agent (e.g. hydroquinone) is used which reduces only the exposed parts of the AgX, that is which contains grains of silver atoms.



(iii) Fixing is done by dissolving out the unchanged silver halide by washing with sodium thiosulphate (hypo). A 'negative' is thus formed.



(iv) Finally, printing is done from the negative on a photosensitive printing paper by repeating steps i and iii.

### Previous Year Questions

Q. The second and third row transition elements have almost similar radii — explain.

Hints: Due to lanthanide contraction of third row transition elements because of filled 4f orbital as well as relativistic effect. For example, Nb and Ta has similar size, because Nb is 4d element having electron configuration  $[\text{Xe}]4d^45s^1$  whereas Ta is 5d transition element having  $[\text{Xe}]4f^{14}5d^36s^2$ . In Ta, due to improper screening capacity of filled 4f<sup>14</sup> orbital and relativistic stabilization of 6s<sup>2</sup> orbital is causing strong attraction of nucleus towards outermost 6s electron popularly known as lanthanide contraction. As a result, size of Ta is decreased appreciable extent. But, this type contraction is not observed in Nb. That's why Nb and Ta have almost similar covalent radii.

Q. Write down the chemical equation involved when H<sub>2</sub>O<sub>2</sub> is added to a solution of titanium(IV) sulphate in presence of H<sub>2</sub>SO<sub>4</sub>.

Hints: Titanium peroxo species,  $[\text{Ti}(\text{O}_2)(\text{SO}_4)_2]^{2-}$  is generated.

Q. State with equation what happens when an acidic solution of Ti<sup>4+</sup> is treated with dilute solution of H<sub>2</sub>O<sub>2</sub> followed by addition of few drops of NH<sub>4</sub>HF<sub>2</sub> solution.

Hints: First, titanium peroxo species,  $[\text{Ti}(\text{O}_2)(\text{SO}_4)_2]^{2-}$  is generated and then  $[\text{TiF}_6]^{2-}$  is formed due to addition of NH<sub>4</sub>HF<sub>2</sub>.

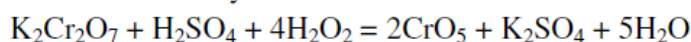
Q. Magnetic moment of VO(acac)<sub>2</sub> is 1.7 BM – Discuss.

Q. VO(acac)<sub>2</sub> has magnetic moment of 1.7 BM but V(acac)<sub>3</sub> is 2.8 BM – Explain.

Hints: Vanadium is present +IV oxidation state in VO(acac)<sub>2</sub>. Therefore, it has d<sup>1</sup> configuration containing only one unpaired electron. So,  $\mu = \sqrt{1(1+2)} = 1.73$  B.M. While in V(acac)<sub>3</sub>, vanadium exist in +III oxidation. So, it has d<sup>2</sup> configuration with two unpaired electron. So,  $\mu = \sqrt{2(2+2)} = 2.83$  B.M. Notably, orbital magnetic moment is also present.

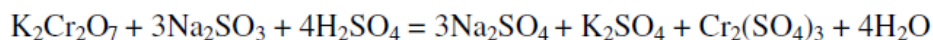
Q. What happens when an aqueous solution of K<sub>2</sub>CrO<sub>4</sub> is acidified with H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> is added in cold condition? The resulting solution is finally shaken with diethyl ether. Give equations.

Hints: Solution becomes blue due to formation of peroxo species, CrO<sub>5</sub>. Colour disappears gradually due to decomposition of CrO<sub>5</sub> to Cr<sup>3+</sup>(aq) and O<sub>2</sub> in aqueous solution. If the solution is shaken in ether, CrO<sub>5</sub> is goes to ether medium where it is more stable that's why the colour concentrates in the ether layer.



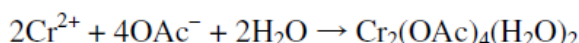
Q. Acidified  $K_2Cr_2O_7$  solution turns green when sodium sulphite solution is added to it — explains.

Hints: Due to formation of  $Cr_2(SO_4)_3$ .



Q. Addition of sodium ethanoate to aqueous solution of Cr(II) gives a red diamagnetic product. Draw the structure of the product noting any features of interest.

Hints: Hydrated Chromium(II) acetate which is also known as chromous acetate is formed. It exists as dimer. Cr-Cr quadruple bond is present that's why it is diamagnetic in nature.



Q. Cr(II) acetate complex is diamagnetic yet it is a  $d^4$  system — Explain.

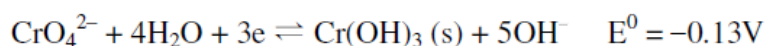
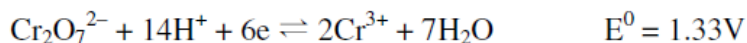
Hints: Cr(II)-Cr(II) quadruple bond is formed. All eight electron, four from each Cr(II), are paired to form  $(\sigma + 2\pi + \delta)$  bonds.

Q. Justify the trend in LMCT energies:  $CrO_4^{2-} < MoO_4^{2-} < WO_4^{2-}$

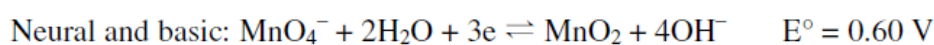
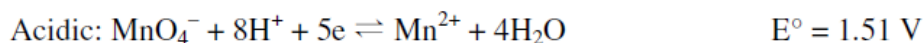
Hints: All the elements belong to Gr. 6 and metal ions are present in +VI oxidation state. So, all the metal ions have  $d^0$  configuration. Therefore, d-d transition is not possible but, ligand to metal charge transfer transition occur. These charge transfer band arises due to promotion lone pair electron of oxygen into the low lying vacant metal orbitals. Since, the energy sequence of d-orbital increases in the order  $3d < 4d < 5d$ . So, the energy gap between oxygen orbital with metal d-orbital is highest for  $WO_4^{2-}$  and lowest for  $CrO_4^{2-}$ . Therefore, the energy sequence of the LMCT band will be  $CrO_4^{2-} < MoO_4^{2-} < WO_4^{2-}$ .

Q.  $K_2Cr_2O_7$  is an oxidant in acidic medium but  $KMnO_4$  is an oxidant in both acidic and alkaline medium – explain.

Hints:  $Cr_2O_7^{2-}$  and  $CrO_4^{2-}$  exist in equilibrium. In acidic medium  $Cr_2O_7^{2-}$  is the main species, so only in acidic medium it is act as oxidizing agent. But, in alkaline medium  $CrO_4^{2-}$  is the main species present in solution only acts as mild oxidizing agent.



While,  $MnO_4^-$  exists in acid as well as in alkali medium.





Q.  $\text{Mn}^{3+}$  and  $\text{Cr}^{2+}$  are isoelectronic but  $\text{Mn}^{3+}$  is an oxidant and  $\text{Cr}^{2+}$  is reductant —

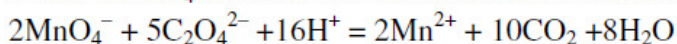
Explain.

Hints:  $\text{Cr}^{2+}$  is reducing as its configuration changes from  $d^4$  to  $d^3$ , the later having a half-filled  $t_{2g}$  level. So,  $\text{Cr}^{3+}$  ion, a  $d^3$  system, has higher CFSE than the  $\text{Cr}^{2+}$  ion, a  $d^4$  system. That's why,  $\text{Cr}^{2+}$  is oxidized to  $\text{Cr}^{3+}$  ion by losing one electron and reduced other species.

On the other hand,  $\text{Mn}^{3+}$  ion has one electron short to attain stable half filled configuration. So, transform from  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$  results attaining of the half-filled ( $d^5$ ) configuration which has extra stability. That's why  $\text{Mn}^{3+}$  reduced to  $\text{Mn}^{2+}$  ion by accepting one electron and oxidized other species. Therefore,  $\text{Mn}^{3+}$  acts as oxidant and  $\text{Cr}^{2+}$  acts as reducing agent.

Q. Write down an example of reaction where  $\text{KMnO}_4$  acts as an oxidising agent.

Hints:  $\text{KMnO}_4$  oxidizes oxalic acid to carbon dioxide.



Q.  $\text{Mn}^{2+}(\text{aq})$  is faintly coloured whereas aqueous solution of  $\text{KMnO}_4$  is highly coloured – Explain.

Hints:  $\text{Mn}^{2+}$  is a  $d^5$  system, all d orbitals are singly occupied ( $t_{2g}^3 e_g^2$ ). So, no spin allowed d-d transition is expected. But, few forbidden transitions from ground state ( ${}^6\text{A}_{1g}$ ) to excited states ( ${}^4\text{T}_{1g}$ ,  ${}^4\text{T}_{2g}$ ,  ${}^4\text{A}_{1g}$ ,  ${}^4\text{E}_g$ ,  ${}^4\text{A}_{2g}$  etc. originates from  ${}^4\text{G}$ ,  ${}^4\text{P}$ ,  ${}^4\text{D}$ ,  ${}^4\text{F}$  free ion states arises involving only one spin reversal) is falling in visible region. That's why in absence of any charge transfer transition,  $\text{Mn}(\text{II})$  complexes are expected to be either colourless or very faint colour.

While, Mn is present in +VII oxidation state in permanganate ion, it is a  $d^0$  system. So, d-d transition is not expected. The pink colour of permanganate ion arises due to LMCT transition from filled oxygen orbital to vacant d-orbital of manganese absorbing green region of visible light. Since, CT transition is both spin and LaPorte allowed, colour is intense.

Q. Discuss the quadruple bonding in  $[\text{ReCl}_8]^{2-}$ .

Hints: Similar to  $\text{Cr}_2(\text{OAc})_4(\text{H}_2\text{O})_2$ . Here,  $\text{Re}(\text{III})$  is also a  $d^4$  system. .

Q.  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple has less positive electrode potential than  $\text{Mn}^{3+}/\text{Mn}^{2+}$  — give the reason.

Hints:  $\text{Fe}^{3+}$  ion has stable half filled,  $d^5$  configuration. Therefore, it has less affinity to accept one electron to form  $\text{Fe}^{2+}$ , a  $d^4$  system. Whereas,  $\text{Mn}^{3+}$  is a  $d^4$  system and it has one electron short to attain stable half filled,  $d^5$  configuration. That's why,  $\text{Mn}^{3+}$  has high affinity to form  $\text{Mn}^{2+}$  by accepting one electron.

Q. Room temperature magnetic moment of  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  is 3.9 BM — Comment on the oxidation state of Fe atom in this complex ion.

Hints: Fe and NO is present as Fe(III) and  $\text{NO}^-$  respectively. Fe(III), a  $d^5$  system, has five unpaired electron and  $\text{NO}^-$  has two unpaired electron. The anti-ferromagnetic coupling between Fe(III) and  $\text{NO}^-$  centre resulting three unpaired electrons. So,  $\mu = \sqrt{3(3 + 2)} = 3.87$  B.M.

Q. Comment on the oxidation state of iron in  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ .

Hints: Fe and NO is present as Fe(II) and  $\text{NO}^+$  respectively.

Q. Why prior to titration of  $\text{Fe}^{2+}$  by standard  $\text{KMnO}_4$  solution in HCl medium a small volume of Zimmermann – Reinhardt solution is added?

Hints: The reduction potential of  $\text{MnO}_4^-/\text{Mn}^{2+}$  (1.51 V) couple is higher than the  $\text{Cl}_2/\text{Cl}^-$  (1.36 V) redox couple. Therefore,  $\text{MnO}_4^-$  oxidizes  $\text{Cl}^-$  to  $\text{Cl}_2$  instead of  $\text{Fe}^{2+}$ . That's why, Z-R (mixture of  $\text{MnSO}_4$ ,  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$ ) solution is used which lower down the reduction potential of  $\text{MnO}_4^-/\text{Mn}^{2+}$  below 1.36 V and also reduction potential of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple is also decreased that facilitates the redox process.

Q. Blue colour of Turnbells blue is less intense than that of Prussian blue — why?

Hints: See chemistry of iron. (Gr. 8)

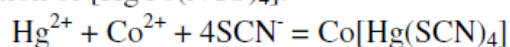
Q. Give one example of high spin Co(III) complex and calculate its spin only magnetic moment.

Hints:  $\text{K}_3[\text{CoF}_6]$ ,  $[\text{CoF}_3(\text{H}_2\text{O})_3]$  these are high spin complex of Co(III).

Co(III),  $d^6$ , high spin configuration in Oh field is ( $t_{2g}^4 e_g^2$ ). It has four unpaired electron resulting spin magnetic moment will be  $\sqrt{4(4 + 2)} = 4.90$  B.M.

Q. What happens when Co(II) acetate is treated with ammonium thiocyanate in presence of mercuric chloride in aqueous solution.

Hints: The addition of Hg(II) salt to a solution of cobalt(II) in excess thiocyanates produces a blue solution due to formation of  $[\text{HgCo}(\text{NCS})_4]$ .



Q.  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$  is pale pink but turns into deep blue when excess conc. HCl is added—why?

Q. A deep blue solution containing Co(II) in concentrated HCl gradually turns pale pink on addition of excess water – Explain.

Hints:  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is a high spin octahedral complex with electron distribution  $t_{2g}^5 e_g^2$ . The pink colour arise due to absorption of a tail of green light causing d-d transition,  $t_{2g}^5 e_g^2 \rightarrow t_{2g}^4 e_g^3$ , which is spin allowed but Laporte forbidden. But, with addition of Conc. HCl, it converts to  $\text{CoCl}_4^{2-}$ , a tetrahedral complex. Now, the d-d transition,  $e^4 t_2^3 \rightarrow e^3 t_2^4$ , is both spin and LaPorte allowed gives intense blue colour due to absorption of orange light.



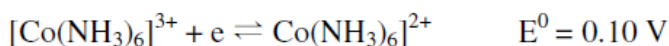
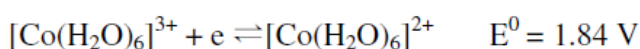
Q. Normally  $\text{Co}^{3+}$  is powerful oxidizing agent in  $\text{Co}^{3+}/\text{Co}^{2+}$  system. However, if excess  $\text{CN}^-$  is added then  $\text{Co}^{2+}$  turns into powerful reducing agent – Comment.

Hints: Co(II) is the stable oxidation state. Due to many d-electrons, the 3d orbital becomes stabilized and it has less affinity to show higher oxidation state. That's why,  $\text{Co}^{3+}$  is reduced to  $\text{Co}^{2+}$  and oxidizes other species.  $\text{Co}^{3+} + e = \text{Co}^{2+}$

But, in presence of  $\text{CN}^-$ ,  $\text{Co}^{3+}$  forms a stable low spin complex,  $[\text{Co}(\text{CN})_6]^{3-}$  which has high CFSE energy. That's why,  $\text{Co}^{2+}$  ion is oxidized to  $\text{Co}^{3+}$  by losing one electron. Therefore,  $\text{Co}^{2+}$  acts as reducing agent in presence of  $\text{CN}^-$ .  $\text{Co}^{3+} + 6\text{CN}^- = [\text{Co}(\text{CN})_6]^{3-}$

Q. Of the redox couples  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}/[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}/[\text{Co}(\text{NH}_3)_6]^{2+}$  which one is more oxidizing and why?

Hints:  $\text{NH}_3$  is stronger field ligand than  $\text{H}_2\text{O}$ . So,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  has higher CFSE than  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ . Since, the oxidized form of ammine complex is more stable than aqueous complex, the reduction potential is decreased for  $[\text{Co}(\text{NH}_3)_6]^{3+}/[\text{Co}(\text{NH}_3)_6]^{2+}$  redox couple. Therefore,  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  is more oxidizing than  $[\text{Co}(\text{NH}_3)_6]^{3+}$ .





Q. Co(II) complex with high spin state shows magnetic moment 4.8 – 5.2 B.M. in Oh field, while in Td field it is 4.0 – 4.4 B.M. Explain.

Hints: Co(II),  $d^7$  system, has configuration  $t_{2g}^5 e_g^2$  in octahedral and  $e^4 t_2^3$  in tetrahedral. The configuration indicates that in octahedral field, the total magnetic will be sum of spin moment of three unpaired electron and orbital contribution, whereas there is only spin magnetic moment in tetrahedral field.

Q. The N–O distance in  $[\text{Co}(\text{diars})_2\text{NO}]^{2+}$  is 168 pm and the  $\angle \text{Co-N-O}$  bond angle is  $180^\circ$ . Reaction of the complex with  $\text{SCN}^-$  forms  $[\text{Co}(\text{diars})_2(\text{NCS})\text{NO}]^{2+}$  in which N–O distance is 185 and  $\angle \text{Co-N-O}$  bond angle is  $135^\circ$  – Explain.

Hints: In  $[\text{Co}(\text{diars})_2\text{NO}]^{2+}$ , NO exists as  $\text{NO}^+$  and so, coordinated in linear fashion. Whereas, in  $[\text{Co}(\text{diars})_2(\text{NCS})\text{NO}]^{2+}$ , NO exists as  $\text{NO}^-$  and so, coordinated in bent fashion. The change of bonding fashion is take place due to maintain 18e rule for metal ion.



Q. Explain why and how the structure of  $[\text{MCl}_4]^{2-}$  ion change from  $\text{M} = \text{Ni}$  to  $\text{Pt}$ .

Q.  $[\text{NiCl}_4]^{2-}$  is tetrahedral while  $[\text{PdCl}_4]^{2-}$  and  $[\text{PtCl}_4]^{2-}$  are square planar – Explain.

Hints:  $[\text{NiCl}_4]^{2-}$  is tetrahedral while  $[\text{PdCl}_4]^{2-}$  and  $[\text{PtCl}_4]^{2-}$  are square planar. This is happen because  $[\text{NiCl}_4]^{2-}$  is high spin complex where Ni is  $sp^3$  hybridised whereas,  $[\text{PdCl}_4]^{2-}$  and  $[\text{PtCl}_4]^{2-}$  are low spin complexes where Pd and Pt is  $dsp^2$  hybridized. Pd and Pt form low spin complex because: (i) Due to large and more diffuse nature of 4d and 5d orbitals, metal electrons strongly interacts with ligand resulting large splitting of d-orbital. (ii) At the same time, pairing energy is also less in 4d and 5d orbitals compared to 3d orbital. (iii) The heavier transition metal ions have always a higher tendency to accommodate more electron density than the lighter elements that results electron pairing in inner d-orbital.

Q. The  $[\text{Ni}(\text{CN})_4]^{2-}$  ion is square planar whereas  $[\text{NiCl}_4]^{2-}$  is tetrahedral – Explain.

Hints:  $\text{CN}^-$  is strong field ligand causing large crystal field splitting of d-orbitals of metal. That's why nickel(II) forms low spin complex where nickel is  $dsp^2$  hybridized. Therefore, the structure of  $[\text{Ni}(\text{CN})_4]^{2-}$  ion is square planar. Whereas,  $[\text{NiCl}_4]^{2-}$  is high spin complex of nickel(II) with  $sp^3$  hybridization of nickel. So, it is tetrahedral.

Q.  $[\text{NiCl}_4]^{2-}$  is paramagnetic while  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic – Explain.

Hints:  $\text{CN}^-$  is stronger field ligand than  $\text{Cl}^-$ . That's why, nickel(II), a  $d^8$  system, forms low spin square planar complex with  $\text{CN}^-$  where nickel is  $dsp^2$  hybridized. Since, all eight electrons of nickel(II) in  $[\text{Ni}(\text{CN})_4]^{2-}$  are paired, it is diamagnetic. On the other hand, nickel(II) forms high spin tetrahedral complex with  $\text{Cl}^-$  where nickel is  $sp^3$  hybridized. Since, nickel(II) contains two unpaired electron,  $[\text{NiCl}_4]^{2-}$  is paramagnetic.

Q. Both  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Ni}(\text{CO})_4]$  are diamagnetic but they have different geometries. Explain.

Hints:  $[\text{Ni}(\text{CN})_4]^{2-}$  is a low spin complex of nickel(II), a  $d^8$  system where all electron are paired. So, it is diamagnetic. But, nickel is  $dsp^2$  hybridized. That's why, it is square planar. Whereas,  $[\text{Ni}(\text{CO})_4]$  is low spin complex of nickel(0), a  $d^{10}$  system, having no unpaired electron. So, it is diamagnetic. But, nickel is  $sp^3$  hybridized. That's why, it is tetrahedral.

Q. Octahedral Ni(II) complexes have magnetic moments in the range 2.9 – 3. B.M. whereas tetrahedral Ni(II) complexes have moments upto 4.1 BM and square planar Ni(II) complexes are diamagnetic – Explain.

Hints: Octahedral nickel(II) complexes have only spin magnetic moment whereas, tetrahedral nickel(II) complexes have both spin and orbital moment as nickel(II) has partially filled  $t_2$ -orbital in  $T_d$  ligand field.

Q. Starting from hydrated nickel(II) chloride how will you prepare  $\text{K}_2[\text{Ni}(\text{CN})_4]$ ?

Hints: Initially, aqueous solution of nickel(II) produces pale blue precipitate due to addition of KCN solution. But, the precipitate is dissolved in excess of  $\text{CN}^-$  due to formation of stable  $[\text{Ni}(\text{CN})_4]^{2-}$ .

Q. Explain the abnormal magnetic moment of  $\text{Cu}_2(\text{acac})_4 \cdot (\text{H}_2\text{O})_2$  complex.

Q. Cu(II) acetate monohydrate shows subnormal magnetic moment — Discuss.

Q. Copper(II) formate tetrahydrate have a magnetic moment value of 1.67 BM – Explain.

Hints: In spite of  $d^9$  configuration of copper(II), these complexes are dimeric. Due to dimeric nature, the unpaired electron of each copper(II) ion interacts antiferromagnetically to some extent that results lowering of spin magnetic moment.

Q. Cu, Ag and Au have the stable oxidation states +2, +1 and +3 respectively – Why?

Hints: See the chemistry of Gr. 11.

Q. Simple Cu (I) salts are not stable in aqueous solutions – why?

Hints: See the chemistry of Gr. 11.

Q. Explain the composition of the following complexes –  $[\text{CuF}_6]^{3-}$  and  $[\text{AuF}_4]^-$ .

Hints: The large crystal field splitting of 5d orbital of Au(III) results the formation of low spin square planar complex of type  $[\text{AuF}_4]^-$  whereas, crystal field of 3d orbital of Cu(III) is not so large that's why Cu(III) form octahedral complex of type  $[\text{CuF}_6]^{3-}$ .

Q. Why  $\text{K}_3[\text{CuF}_6]$  is paramagnetic while  $\text{K}[\text{AgF}_4]$  is diamagnetic.

Hints: Both Cu(III) and Ag(III) are  $d^8$  electron system. But,  $\text{K}_3[\text{CuF}_6]$  is a octahedral complex of Cu(III) whereas,  $\text{K}[\text{AgF}_4]$  is low spin square planar complex. Since, all electrons are paired in  $\text{K}[\text{AgF}_4]$ , it is diamagnetic. But,  $\text{K}_3[\text{CuF}_6]$  contains two unpaired electron, therefore, it is paramagnetic.

Q. What do you mean by masking agent? Give an example.

Hints: A masking agent is a reagent that reacts with some chemical species that might interfere in the chemical analysis whereas demasking is the process where the masked substance regains its ability to response the particular reaction. For example, KCN is used as masking agent to detect  $\text{Cd}^{2+}$  in presence of  $\text{Cu}^{2+}$  ion.

Q. What do you mean by 'Mischmetal'?

Hints: Mischmetal means mixed metal. Generally, alloy of rare-earth elements is known as Mischmetal. It is also called cerium mischmetal, or rare-earth mischmetal. A typical composition is approximately 55% cerium, 25% lanthanum, and 15~18% neodymium, with traces of other rare earth metals.



Q. Do you expect  $Zn^{2+}$  to form stable octahedral complexes with  $\pi$ -acceptor ligands? Give reasons for your answer.

Hints: The  $\pi$ -acidic ligand bonded with metal ion through synergistic fashion. For this type of bonding, metal ion should have low lying vacant orbital for  $\sigma$ -acceptance as well as suitable filled orbital for  $\pi$ -back donation. But,  $Zn^{2+}$  does not have suitable orbital for synergistic bonding because all 3d-orbitals are filled and are lower in energy. At the same time, the central metal atom has to be used  $sp^3d^2$  hybridized orbital to form octahedral complex. But, the energy 4d orbital of  $Zn^{2+}$  is very high that demands requirement of high hybridization energy for  $sp^3d^2$  hybridization. It is notable that,  $d^2sp^3$  hybridization is not possible for zinc as inner 3d orbital is completely filled. That's why,  $Zn^{2+}$  does not form stable octahedral complexes with  $\pi$ -acceptor ligands.

Q. To remove  $Pb^{2+}$  from human body it is better to use  $Na_2Ca(EDTA)$  than  $Na_2H_2(EDTA)$  – Explain.

Hints: The Pb-EDTA complex has high stability constant than Ca-EDTA. Therefore, the use of  $CaNa_2EDTA$  results formation of Pb-EDTA with displacing calcium from the Ca-EDTA complex. That's why,  $CaNa_2EDTA$  is used for the treatment of  $Pb^{2+}$  poisoning.

But, if we use EDTA as  $Na_2H_2EDTA$ , then Pb-EDTA complex as well as Ca-EDTA complex is formed as  $Ca^{2+}$  ion is present in biological environment that results urinary excretion of calcium leading to hypocalcaemia. To overcome this hazard,  $CaNa_2EDTA$  is used for the treatment of lead poisoning. Due to high stability constant of Pb-EDTA complex,  $CaNa_2EDTA$  is reacted with  $Pb^{2+}$  present in the body fluids, excreting lead as  $PbNa_2EDTA$  leaving  $Ca^{2+}$  behind.