ch-1

Transition Series (D-Block elements)

[→ पीछे रहना / बिमारी

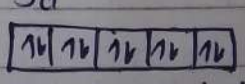
The elements last e⁻ enters in d-subshell. such elements are known as d-block elements.
d-block elements are generally considered as transition metals due to following reasons-

(i) In electronic configuration last electron enters in penultimate shell (n-1)
For Eg- $_{21}Sc$ - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$
$n=4$, $(n-1=3)$

(ii) d-block elements are present between s & p block in periodic table (iii) d-block elements have similarity with s-block as well as p-block.

(iv) In d-block oxidation state or valency are variable

→ "All transition metals ~~bring~~ belongs to d-block of periodic table but all d-block elements are not transition metals."
Because for transition d-subshell should have vacant space. Generally Zn, Cd, Hg are not considered as transition metal because their d-subshell is full-filled. So, they don't represent variable valency in their properties.
For Eg- $_{30}Zn$ - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$



No. of unpaired e⁻ = 0

First Transition series - $_{21}Sc$, $_{22}Ti$ ⟶ $_{30}Zn$ (3d)
Second Transition series - $_{39}Y$ ⟶ $_{48}Cd$ (4d)
Third Transition series - $_{57}La$, $_{72}Hf$ ⟶ $_{80}Hg$ (5d)
Fourth Transition series - $_{89}Ac$, $_{104}Unq$ ⟶ $_{112}Uub$ (6d)

* Hg is in liquid state
* Zn, Cd also have low MP & BP.

* Electronic configuration of first transition series.

→ ns^{1-2} $(n-1)d^{1-10}$ ← Penultimate shell

Metallic bonding ↑

*	21 Sc	– $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$	↑ MP & BP
	22 Ti	– $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$	
	23 V	– $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$	
	24 Cr	– $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^4$ (Aufbau)	
		$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$ (stability)	
	25 Mn	– $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$ → (MP & BP ↓)	
	26 Fe	– $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$	↓ MP & BP
	27 Co	– $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$	
	28 Ni	– $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$	
*	29 Cu	– $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^9$ (Aufbau)	
		$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$ (stability)	
	30 Zn	– $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$ → (MP & BP ↓↓)	

↳ Volatile metal (low MP & BP)

→ No. of unpaired electrons

→ Penultimate shell represents metallic bond & last shell represents covalent bond. ←

No. of unpaired e^- ↑ → High melting & boiling point

→ General Properties

(1) Metallic Nature- All elements are metallic nature of d-block.

(2) Physical state- In d-block Zn and Cd are volatile as metal with low M.P. and B.P. and Hg is present in liquid state. Rest elements are present in solid state with high MP & BP.

(3) Melting and Boiling point - In d-block element MP & BP are generally high because in these elements the e^- of outer shell will participate in covalent bonding & e^- of (n-1)d subshell participate in metallic bonding

The magnitude of covalent bond is nearly same in all elements because external shell has only two electron but the magnitude of metallic bond is variable because it depends on no. of unpaired e^- in d- subshell

On the basis of these facts it is clear that in d- block the order of M.P & BP should be abnormal

In a given series MP & BP will increase upto 4th member of series due to increase in the no. of unpaired e^-. The 5th element has slightly lower M.P & BP. because it exists in halffilled state. So, it is ~~not~~ extra stable and it has poor tendency to form metallic bond.

From 6 to 9 the no. unpaired e^- and the magnitude of metallic bonding will decrease. So M.P & B.P. will reduce in same order.

In last member of series d- subshell is fullfilled So, metallic bonding is not possible in it ~~is~~ only weak covalent bond is responsible for their melting and boiling points. So, last element of the series has minimum M.P & B.P.

(4) Magnetic Behaviour - The elements having unpaired e^- in their valence shell or $(n-1)d$ subshell will attract towards magnetic field. These elements are known as Paramagnetic elements.

The elements which have only paired e^- are repelled by magnetic fuild. Such elements are Diamagnetic elements

Generally, d- block have paramagnetic charater due to presence of unpaired e^- in their valence shell or s or d - subshell. Only Zn, Cd, Hg are diamagnetic because they have fullfilled configuration or they don't have any unpaired e^-

The magnitude of attraction force is different in these elements. It is measured by terms of Magneton. And it was given by Bohr Magneton so, the unit of attraction force towards magnetic field is also known as Bohr Magneton. It is calculated as follows:-

(Bohr Magneton) $BM = \sqrt{n(n+2)}$

where, n = no. of unpaired e^- (attracted towards M.f. and are Paramagnetic)

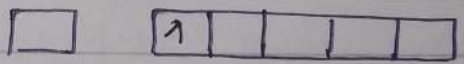
* "p" e^- repelled towards M.f. are diamagnetic)
* Zn, Cd, Hg show diamagnetic behaviour)

→ Bohr Magneton of $_{21}Sc^{+2}$

$BM = \sqrt{n(n+2)}$

$_{21}Sc = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$

$_{21}Sc^{+2} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^1$



no. of unpaired $e^- = 1$

$BM = \sqrt{n(n+2)}$

$= \sqrt{1(1+2)}$

$= \sqrt{1(3)}$

$= \sqrt{3}$

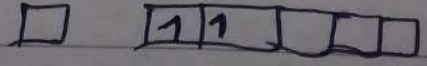
(Paramagnetic)

$BM = 1.73$ magneton

→ Bohr Magneton of $_{22}Ti^{+2}$

$_{22}Ti = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$

$_{22}Ti^{+2} = 1s^2\ 2s^2\ 2p\ 3s^2\ 3p^6\ 4s^0\ 3d^2$



No. of unpaired $e^- = 2$

$BM = \sqrt{n(n+2)}$

$BM = \sqrt{2(2+2)}$

$BM = \sqrt{2(4)}$

$= \sqrt{8}$

$= 2\sqrt{2}$ (Paramagnetic)

$= 2 \times 1.414$

BM = 2828 magneton

→ **Bohr Magneton of 25^{Mn+3}**

$25^{Mn} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$

$25^{Mn^{13}} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^4$

□ | ↑ | ↑ | ↑ | ↑↓ |

$BM = \sqrt{n(n+2)}$ No. of unpaired $e^- = 4$

$= \sqrt{4(4+2)}$

$= \sqrt{4(6)}$

$= \sqrt{24}$

$= 2\sqrt{6} = 2\sqrt{2 \times 3}$ (Paramagnetic)

$= 2 \times 1.414 \times 1.73$

$= 2.828 \times 1.73$

BM = 4.89244 magneton

→ **Bohr Magneton of 28^{Ni+2}**

$28^{Ni} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$

$28^{Ni^{+2}} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^8$

□ | ↑↓ | ↑↓ | ↑↓ | ↑ | ↑ |

$BM = \sqrt{n(n+2)}$ No. of unpaired $e^- = 2$.

$= \sqrt{2(2+2)}$ (Paramagnetic)

$= \sqrt{2 \times 4}$

$= 2\sqrt{2}$

$= 2 \times 1.414$

BM = 2.828 Magneton

→ **Bohr Magneton of 27^{Co}**

$27^{Co} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$

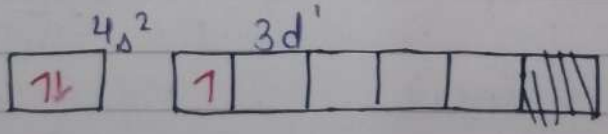
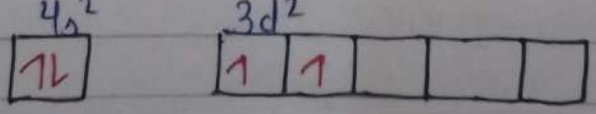
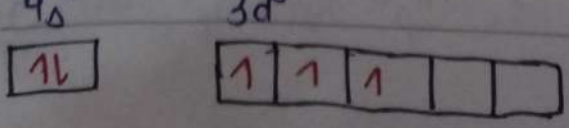
| ↑↓ | ↑↓ | ↑ | ↑ | ↑ |

$BM = \sqrt{n(n+2)}$
$= \sqrt{3(3+2)}$
$= \sqrt{3(5)}$
$BM = \sqrt{15} = 3.87$ magneton

No. of unpaired $e^- = 3$
(Paramagnetic)

5- Variable valency / oxidation state- In d-block elements will represent more than one valency or oxidation state. It is due to the ~~e-ic~~ electronic configuration of d-block metals. In d-block e^- will enter in outermost shell as well as penultimate shell The energy difference between these shells is minimum. So e^- of 'n' as well as (n-1) can easily used in bond formation. So, these elements will represent more than one valency or oxidation state.

But Zn, Cd, Hg have fullfilled d-subshell. So, only s-e^- will participate in bonding. Due to this fact, these elements don't represents variation in valency or oxidation state.

S.No.	Elements	Electronic configuration	valency or Oxi. state
1-	21^{Sc}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$ 	+2, +3 $21^{Sc^{+2}}$, $21^{Sc^{+3}}$
2-	22^{Ti}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$ 	+2, +3, +4 $21^{Ti^{+2}}$, $21^{Ti^{+3}}$, $21^{Ti^{+4}}$
3-	23^{V}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$ 	+2, +3, +4, +5 $23^{V^{+2}}$, $23^{V^{+3}}$, $23^{V^{+4}}$, $23^{V^{+5}}$

S.No.	Elements	Electronic configuration	Valency or Oxi state
4-	$_{24}Cr$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^4$	+2, +3, +4, +5, +6
		$4s^2$ $3d^4$ (Aufbau)	$_{24}Cr^{+1}$
		→ stability	$_{24}Cr^{+2}$, $_{24}Cr^{+3}$, $_{24}Cr^{+4}$, $_{24}Cr^{+5}$, $_{24}Cr^{+6}$
		$4s^1$ $3d^5$	
5-	$_{25}Mn$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$	+2, +3, +4, +5, +6, +7
		$4s^2$ $3d^5$	$_{25}Mn^{+2}$, $_{25}Mn^{+3}$, $_{25}Mn^{+4}$, $_{25}Mn^{+5}$, $_{25}Mn^{+6}$, $_{25}Mn^{+7}$
6-	$_{26}Fe$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$	+2, +3, +4, +5, +6
		$4s^2$ $3d^6$	$_{26}Fe^{+2}$, $_{26}Fe^{+3}$, $_{26}Fe^{+4}$, $_{26}Fe^{+5}$, $_{26}Fe^{+6}$
7-	$_{27}Co$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$	+2, +3, +4, +5
		$4s^2$ $3d^7$	$_{27}Fe^{+2}$, $_{27}Fe^{+3}$, $_{27}Fe^{+4}$, $_{27}Fe^{+5}$, 2[illegible]
8-	$_{28}Ni$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$	+2, +3, +4
		$4s^2$ $3d^8$	$_{28}Ni^{+2}$, $_{28}Ni^{+3}$, $_{28}Ni^{+4}$
9-	$_{29}Cu$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^9$	+1, +2, +3
		$4s^2$ $3d^9$ (Aufbau)	$_{29}Cu^{+1}$, $_{29}Cu^{+2}$, $_{29}Cu^{+3}$
		→ stability	

S No.	Elements	Electronic configuration	Valency or Oxi. state
10-	30^{Zn}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$ $4s^2$ $3d^{10}$ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂	+2 $30^{Zn^{+2}}$

* It means that the middle element of each series can represent the highest value of Oxidation state.

i.e. 25^{Mn} = +2, +3, +4, +5, +6, +7

(6) Catalytic properties - Generally d-block metals are good catalyst because these elements will represent more than one valency or oxidation state, So, they can increase their valency upto maximum when they partipate in reaction and provide effective surface area for the collision of reactant molecules. After the formation of product they return to their normal state and easily removed from the reaction

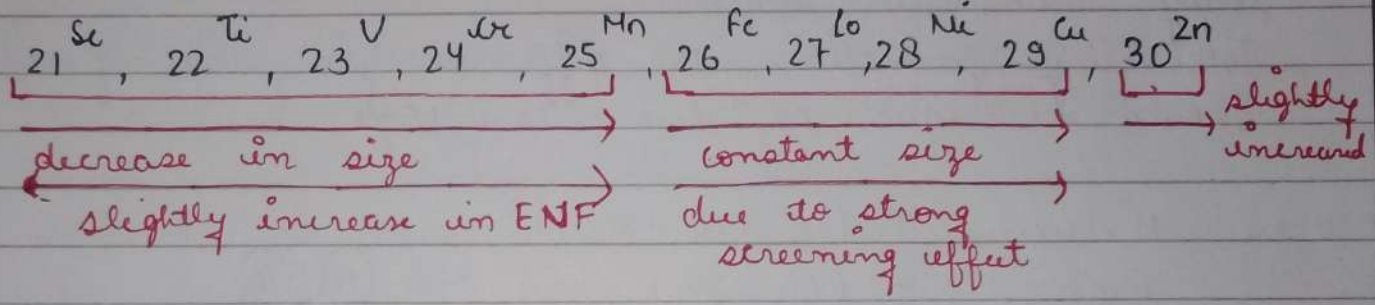
Good reducing agent - Fe, Ni, Zn

Good oxidising agent - Cu, Ag, Au, Pt, $K_2Cr_2O_7$ (Potassium dichromate), $KMnO_4$ (Potassium permagnate)

* Catalyst are a thing or a substance that causes change *

(7) Atomic radius - Generally the size of d-block metals are nearly same because in these elements last e⁻ does not enter in valence shell but it enters in penultimate shell. So, the outermost shell is nearly constant and it is not influenced by the no. of e⁻ but it is observed that in a given series the atomic

size will slightly decrease upto middle of the series because as the atomic no. increases, the Effective nuclear attraction force will slightly increase. So, the e^- of valence shell will attract towards nucleus. So, the size of atom will reduce. But after middle of the series pairing of e^- starts and it creates a strong screening effect. Both of these factors will counter balance each other. So, the radius of elements after middle is nearly constant.



In last member of the series the atomic size will slightly increase because in last element d- subshell is full-filled and the screening effect and repulsion b/w e^- will be maximum and it will donate the effective nuclear charge So, the size of the last element will be slightly increased / larger than its nearly elements.

Ex- Atomic radius [parameter (pm)]

decrease in A.R. ↓

- 21 Sc → 144
- 22 Ti → 132
- 23 V → 127
- 24 Cr → 118
- 25 Mn → 117

constant

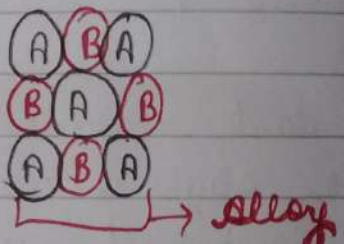
- 26 Fe → 117
- 27 Co → 116
- 28 Ni → 195
- 29 Cu → 114

[30 Zn → 130 slightly large

~~(8)~~ * The decreasement ~~b/w~~ the in attraction force b/w the e^- and nucleus is called Screening / Shielding effect *

(8) Alloy formation - The homogeneous mixture of two or more metals is known as alloy.
For alloy formation the size of metal should be same or nearly same. so, that their atoms can easily adjust in the crystal structure of other metals.
For alloy formation d-block is most suitable because their valence e⁻ enters in penultimate shell. So, the outershell is unaffected and the size of metal in a given series is nearly same. so, d-block metals can easily form alloy with each other.
For alloy formation the difference in size of metal should be equal or less than 15%.

Ex- Nichrome - (Ni + Cr + Mn)
Brass - (Cu + Zn)
Bronze - (Cu + Sn)
Gun Metal - (Cu + Sn + Zn)
Rold Gold - (Al + Cr + Zn)



(9) Formation of Interstitial compound - The d-block metals interact with small sized atom of 1st and 2nd period like Halogen, Carbon, Nitrogen and Oxygen and form the compound which is known as Interstitial compound.
In these compounds small sized atom does not enter in the crystal structure of metal but it will easily adjust in the free space or void or intraspace present in crystal. For interstitial compounds the difference in size of element should be more than 15%.

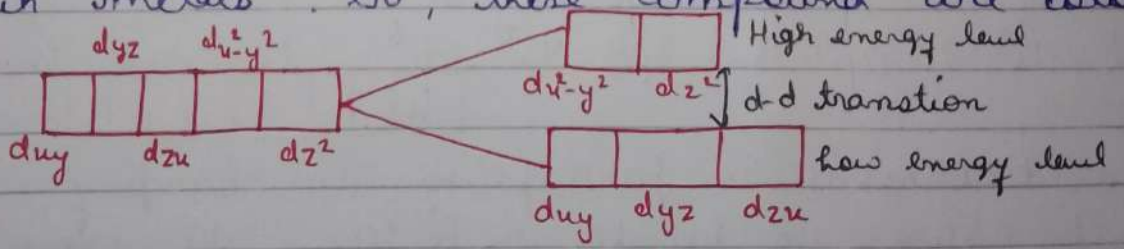
→ void / free space / interstitial space

Interstitial compound

(10) Formation of coloured compound – Crystal field theory can explain the coloured nature of d-block metals or ions in their solid states and solution form. CFT was given by Bethe and Vleck. Acc. to it -

Orbitals of d-subshell have slightly difference in energy, so, that d-subshell exists in degenerate or spliting form. In d-subshell 3 orbitals show low level energy and 2 other orbitals show high level energy. The energy gap b/w these orbital is very low. so, that e⁻ can easily be excited ~~to~~ from low to high level energy. The transition of e⁻ b/w these orbitals is known as d-d transition. The energy gap is responsible for the particular colour of metals.

The metals in which d-subshell is fullfilled, d-d transition is not possible in such metals. So, these compound are colourless.



Q- Why Zn^{+2}, Cd^{+2}, Hg^{+2} are colourless

Ans- $_{30}Zn$ – $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$ (ground state)

$_{30}Zn^{+2}$ = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^{10}$ (excited state)

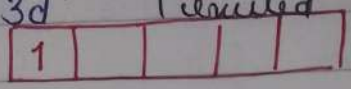
↑↓	↑↓	↑↓	↑↓	↑↓	Fullfilled

Because Zn^{+2}, Cd^{+d}, Hg^{+2} have fullfilled d-subshell. So, d-d transition is not possible in these metal. So, energy gap cannot create in these metals. So, these metals are colourless or white.

Q- Why $[Sc(H_2O)_2]^{+3}$ is colourless but $[Ti(H_2O)_2]^{+3}$ is a coloured compound.

Ans- $_{21}Sc$ – $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$ (ground stage)
$_{21}Sc^{+3}$ – $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^0$ (excited stage)

$_{22}Ti$ – $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$ (ground stage)
$_{22}Ti^{+3}$ – $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^1$ (excited stage)

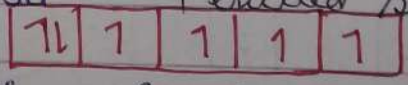


In $[Sc(H_2O)_2]^{+3}$ d-subshell is not taking part in e.c because it has 0 e^-. So, there is no energy gap b/w high energy level and low energy level. i.e. why $[Sc(H_2O)_2]^{+3}$ is colourless
where as, in $[Ti(H_2O)_2]^{+3}$ d-subshell has one unpaired e^-. So- d-d transition exist and energy gap can be created. i.e. why they are coloured compound.

Q- Why $FeSO_4$ is a green coloured compound.

⇒ $FeSO_4 \rightleftharpoons Fe^{+2} + SO_4^{-2}$

$_{26}Fe = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$ (ground stage)
$_{26}Fe^{+2} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^6$ (excited stage)



Because d-subshell is participating in bonding. The d-d transition is possible in $FeSO_4$. So, energy gap has been created. i.e. why $FeSO_4$ is a green coloured compound.

(11) Formation of complex compound - d-block metals are present b/w s and p block, So, the size of d-block metal is smaller than s-block and larger than p-block i.e. s > d > p. d-block metals increase their valency upto manganese because of

variation in valency. Due to this fact, the charge density $\left(\frac{\text{charge}}{\text{size}}\right)$ is very high and they can easily interact with ligands and form complex compounds

Among different series of d-block metals as the no. of shell increases the size of metal increases from 3d to 5d i.e. why charge density of metal and capacity of complex formation decreases from 3d to 5d.

s-block metals don't participate in complex formation ~~decreases from 3d to 5d~~. because they have largest ~~s-block metals don't participate~~ size and low charge among metals. So, the charge density and affinity towards ligands is very low.

Ex- $K_4[Fe(CN)_5]$, $[Ni(CO)_4]$, $[Zn(NH_3)_4]^{+2}$, $[Ni(CN)_4]^{-2}$

(12) Ionization Potential / Ionization Energy / I.P. value -

I.P. is the minimum energy required to remove loosely bounded e^-

The I.P. of d-block elements is more than s-block and less than p-block elements. i.e. $s < d < p$

The order of I.P. in a given series is not uniform, As the atomic no. increases the I.P. value increases because the no. of shells are constant But effective nuclear attraction force increases regularly. After middle of the series pairing of e^- starts and electronic repulsion force and screening effect will counter balance the E.N.C i.e. why the IP value is nearly constant.

The elements which have half-filled and fullfilled configuration, will have exceptionally high value of I.P. because of stable configuration

From 3d ⟶ 5d the no. of shells increases then I.P. value decreases.

$$I.P. \propto \frac{1}{\text{atomic radius}}$$

(13) Reactivity - Reactivity of d-block is less than s-block and larger than p-block. i.e. s > d > p
Because reactivity depends ~~on~~ inversely on their IP value. The IP value of these elements is more than s-block, so, removal of e^- in d-block is difficult compare to s-block IP value of these elements is less than p-block. So, e^- in d-block can easily removed in compare to p-block.
So, in a given series the reactivity decreases and after middle of the series reactivity will be nearly same.
From 3d ⟶ 5d the IP value decreases. So, the reactivity increases.

$$\text{Reactivity} \propto \frac{1}{I.P.}$$

(14) Electropositivity - d-block elements are less electropositive in compare to s-block and more electropositive in compare to p-block. i.e. s > d > p. Because the I.P. value of d-block is more than s-block and less than p-block.
In a given series the electropositivity will decrease due to increase in I.P. value. But after middle of the series electropositivity will be nearly same.
Among different series the electropositivity increases due to decrease in their I.P. value from 3d to 5d series

$$\text{Electropositivity} \propto \frac{1}{I.P.}$$

and **Elektronegativity & I.P**

* Potassium permagnate ($KMnO_4$)

→ Methods of preparation

→ From pyrolusite (MnO_2) -

It is a natural ore of $KMnO_4$ and extracted from earth crust. It has been oxidised with air in basic medium and form K_2MnO_4 (potassium magnate).

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

Reaction with Halogen -

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

(Cl_2 = Halogen)

Oxidising agents: halogen, H_2O_2, aqueous sol^n of Ozone

Reaction with H_2O_2

$$2K_2MnO_4 + H_2O_2 \longrightarrow 2KMnO_4 + 2KOH$$

Reaction with aqueous soln. of ozone (O_3)

$$2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$$

→ Physical properties -

It is a purple coloured solid compound and soluble in water and the aqueous soln is red and its melting point 200°C

→ Chemical properties

Oxidising nature - It is an oxidising agent because on its decomposition it gives nascent oxygen. But oxidising nature is different in different medium.

(a) Acidic medium -

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5(O) + 3H_2O$$
(nascent O_2)

Ex - $NaNO_2$ - sodium nitrite

$$2KMnO_4 + 3H_2SO_4 + 5NaNO_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 5NaNO_3 + 3H_2O$$
(Sodium Nitrate)

Na_2SO_3 - Sodium Sulphide

$$2KMnO_4 + 3H_2SO_4 + 5Na_2SO_3 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 3H_2O$$
(sodium sulphate)

- **Equivalent weight of $KMnO_4$.**

$$2\overset{+1,+7}{K}\overset{-2}{Mn}O_4 + 3H_2SO_4 \longrightarrow \overset{+1}{K_2}SO_4^{-2} + 2\overset{+2}{Mn}SO_4^{-2} + 3H_2O + 5(O)$$

$$E = \frac{m \quad (mass)}{n \quad (change\ in\ oxidation\ state)}$$

mass of $KMnO_4$ = $39 + 55 + 16 \times 4$

= 158

$$E = \frac{158}{5}$$

$$\boxed{E = 31.6}$$

(b) Neutral medium -

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3(O)$$
(Nascent O_2)

Ex - Na_2SO_3

$$2KMnO_4 + H_2O + 3Na_2SO_3 \longrightarrow 2KOH + 2MnO_2 + 3Na_2SO_4$$

Na_2SO_3

$$2KMnO_4 + H_2O + 3Na_2SO_3 \longrightarrow 2KOH + 2MnO_2 + 3Na_2SO_4$$

- **Equivalent weight of $KMnO_4$**

$$2\overset{+1}{K}\overset{+7}{Mn}O_4^{-2} + H_2O \longrightarrow 2KOH + 2\overset{+4}{Mn}O_2^{-2} + 3(O)$$

$$E = \frac{158}{3}$$

$$\boxed{E = 52.66}$$

(c) **Basic / Alkaline medium –**

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + (O)$$
(Nascent O_2)

Ex - Alkenes.

$$2KMnO_4 + 2KOH + CH_2=CH_2 \longrightarrow 2K_2MnO_4 + \underset{\underset{\text{ethylene glycol}}{|\quad|}}{\overset{OH\quad OH}{CH_2 - CH_2}}$$

- **Equivalent weight of $KMnO_4$**

$$2\overset{+1}{K}\overset{+7}{Mn}O_4^{-2} + 2KOH \longrightarrow \overset{+1}{2K_2}\overset{+6}{Mn}O_4^{-2} + H_2O + O$$

$$E = \frac{158}{1}$$

$$\boxed{E = 158}$$

→ **Uses Of $KMnO_4$**

(1) $KMnO_4$ is used as oxidising agent but oxidising power depends upon the nature of medium
(2) $KMnO_4$ is used as an antiseptic.
(3) $KMnO_4$ is used in printing Machine.

* Chromyl chloride (CrO_2Cl_2)

→ Method of preparation.

1) It can be prepared by the reaction of chromic anhydride (CrO_3) with HCl in the presence of concentrated H_2SO_4

$$CrO_3 + 2HCl \xrightarrow[H_2SO_4\ \Delta]{\text{Concentrated}} CrO_2Cl_2 + H_2O$$

2) By dissolving chromic acid (H_2CrO_4) with concentrated HCl and form chromyl chloride.

$$H_2CrO_4 + 2HCl\ (\text{conc.}) \longrightarrow CrO_2Cl_2 + 2H_2O$$

→ Physical properties.

(1) It is a dark red coloured compound which is in a liquid form.
(2) It is miscible in carbondisulphide and tetrachloroethane.
(3) Its melting point 117°C, freezing point 96.5°C

→ Chemical properties.

(1) Hydrolysis - On its hydrolysis it will give chromic acid (H_2CrO_4)

$$CrO_2Cl_2 + 2H_2O \longrightarrow H_2CrO_4 + 2HCl$$

2) Reaction with NaOH -

$$CrO_2Cl_2 + 4NaOH \longrightarrow \underset{\text{(sodium chromate)}}{Na_2CrO_4} + 2NaCl + 2H_2O$$

* amphoteric compound – equally reacts with acids & bases

3- Oxidising property = CrO_2Cl_2 is a moderate oxidising agent and it will oxidised toluene into benzaldehyde by Etard reaction.

$$C_6H_5CH_3 + 2[O] \xrightarrow[\Delta]{CrO_2Cl_2} C_6H_5CHO + H_2O$$

OR

$$C_6H_5CH_3 + [O] \xrightarrow[\Delta]{CrO_2Cl_2} C_6H_5CH_2-OH \xrightarrow[-H_2O]{+HOH} C_6H_5CHO + H_2O$$

Benzylalcohol — Benzaldehyde

→ Uses -

(1) It is used as an oxidising agent.
(2) It is used as amphoteric compound because it reacts with acid and base equally. Due to this property, it is used in the analysis of acidic and basic radical.

* Titanium Dioxide (TiO_2)

→ Method of preparation -

1) When we react titanium tetra-chloride with ammonium hydroxide then it will form Titanium tetra hydroxide and Ammonium chloride.
On heating titanium tetra hydroxide it will form Titanium dioxide and two molecules of water.

$$TiCl_4 + 4NH_4OH \longrightarrow Ti(OH)_4 + 4NH_4Cl$$

(Titanium tetra chloride) + (ammonium hydroxide) → (Titanium tetra hydroxide) + Ammonium tetra chloride

$$Ti(OH)_4 \xrightarrow{\Delta} TiO_2 + 2H_2O$$

(Titanium tetra hydroxide) → (Titanium dioxide) + water

(2) On hydrolysis

$TiCl_4 + 4H_2O \longrightarrow Ti(OH)_4 + 4HCl$

$Ti(OH)_4 \xrightarrow{\Delta} TiO_2 + 2H_2O$

→ Physical properties.

(1) Titanium dioxide is a colourless solid compound
(2) It is water resistant
(3) It it will melt above 300 °C

→ chemical properties :-

(1) Reaction with coke powder :-
Coke powder will reduce TiO_2 and form pure titanium and carbon monoxide.

$TiO_2 + 2C \longrightarrow Ti + 2CO\uparrow$
(Titanium dioxide) (coke powder) (pure Titanium) (carbon mono oxide)

(2) Reaction with coke powder and Halogen -
when we react titanium dioxide with coke powder and Halogen it forms titanium tetrachloride and carbon monoxide.

$TiO_2 + 2C + 2Cl_2 \longrightarrow TiCl_4 + 2CO\uparrow$
(Titanium dioxide) (coke powder) (Halogen/ chloride) (Titanium tetra chloride) (carbon mono oxide)

(3) Amphoteric nature -
TiO_2 is amphoteric compound because it reacts with acid and base equally and form their salt

$TiO_2 + H_2SO_4 \longrightarrow TiOSO_4 + H_2O$
Titanium dioxide — Sulphuric acid — Titanly sulphate

TiO_2 + NaOH ⟶ Na_2TiO_3 + H_2O

(TiO_2 (Titanium dioxide), NaOH (sodium hydroxide), Na_2TiO_3 (sodium Titanate), H_2O (Water))

→ Uses -

(1) It is a water resistant and it is used in coating of electronic devices
In oil paints TiO_2 is used as white pigment
(2) It is preffered over basic lead acetate $[Pb(OH)_2.Pb(CH_3COO)_2]$ because the compounds of lead are poisonous

* Vanadium pentaoxide (V_2O_5)

→ Method of preparation.

(1) It can be prepared by the direct oxidation of Vanadium

$4V + 5O_2 \longrightarrow 2V_2O_5$
Vanadium Pentaoxide

(2) It can be prepared by the oxidation of vanadium trioxide.

$V_2O_3 + O_2 \longrightarrow V_2O_5$
Vanadium trioxide — Vanadium pentaoxide

→ Physical properties.

(1) It is a yellowish red coloured solid compound
(2) It is partially soluble in water.
(3) It will melt 276°C

→ Chemical properties.

(1) Reduction

→ Reduction with a non-metal SO_3

$$V_2O_5 + SO_3 \longrightarrow V_2O_4 + SO_2 + O_2$$

Vanadium pentaoxide — sulphur trioxide — Vanadium tetra oxide — Sulphur dioxide — Oxygen

→ Reduction with a non-metal SO_2

$$V_2O_5 + SO_2 \longrightarrow V_2O_3 + S + 2O_2$$

Vanadium pentaoxide — sulphur dioxide — Vanadium tri oxide — Sulphur — Oxygen.

(2) Oxidation

→ Oxidation with Sulphur with high temperature

$$V_2O_5 + S \xrightarrow{\Delta} V_2O_3 + SO_2$$

→ Oxidation with H_2 with high temperature

$$V_2O_5 + H_2 \xrightarrow{\Delta} V_2O_4 + H_2O$$

→ Oxidation with H_2S with high temperature

$$V_2O_5 + H_2S \xrightarrow{\Delta} V_2O_4 + H_2O + S$$

(3) Catalytic property

In contact-chamber method it is used as a catalyst to convert SO_2 into SO_3

$$2SO_2 + O_2 \overset{V_2O_5}{\rightleftharpoons} 2SO_3$$

(4) Reaction with HCl

$$V_2O_5 + 10HCl \longrightarrow 2VCl_5 + 5H_2O$$

→ Uses.

(1) It can be used as a oxidising as well as reducing agent
(3) It is used as a catalyst in formation of SO_3

* Chromium oxide (Cr_2O_3)

→ Method of preparation.

(1) In lab -, It can be prepared by the decomposition of $(NH_4)_2Cr_2O_7$ ammonium dichromate. at high temperature.

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} Cr_2O_3 + N_2 + 4H_2O$$

ammonium dichromate → chromium oxide, Nitrogen, Water.

(2) By the dehydration of chromium hydroxide

$$2Cr(OH)_3 \xrightarrow{\Delta} Cr_2O_3 + 3H_2O$$

chromium hydroxide → chromium oxide, Water

→ Physical properties

(1) It is a green coloured solid compound
(2) It is soluble in water and in other polar solvents
(3) It will ~~dis~~ dissociate at very high temperature

→ Chemical properties

(1) Dissociation -
It is a stable compound and will not dissociate directly but it will can be reduced to chromium by using coke powder at high temperature.

$Cr_2O_3 + 3C \longrightarrow 2Cr + 3CO\uparrow$
(chromium oxide) (coke powder) (chromium) (carbon mono oxide)

(2) Alumino thermic process -
In this method Al is used for the reduction of Cr_2O_3

$Cr_2O_3 + 2Al \xrightarrow[Mg\ wire]{\Delta} 2Cr + Al_2O_3$
chromium oxide Aluminium chromium

3) Oxidation
when we oxidise Cr_2O_3 by air it forms chromium pentaoxide.

$Cr_2O_3 + O_2 \xrightarrow{\Delta} Cr_2O_5$
chromium oxide (air) chromium pentaoxide

Reaction with NaOH

$Cr_2O_3 + 2NaOH \longrightarrow Na_2Cr_2O_7 + 2H_2O$
chromium oxide sodium hydroxide sodium di-chromate water

→ Uses

(1) It is used in metallurgy of chromium
(2) In preparation of sodium or potassium salt of chromate and dichromate

Q- Why in d-Block 4d and 5d series have similar properties?

Ans- This is because 4d and 5d series elements have virtually the same atomic and ionic radii due to lanthanoid contraction.

→ Lanthanoid contraction is the steady decrease in the size of the atoms and ions of the rare-Earth elements with increasing atomic number from lanthanum (atomic No. 57) through lutetium (atomic No. 71).