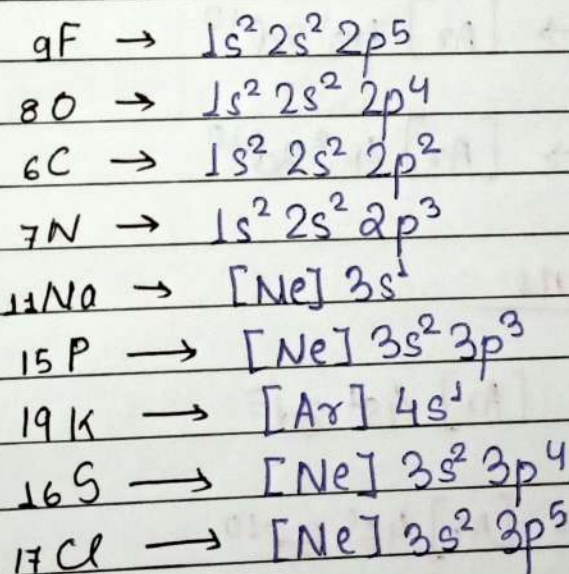
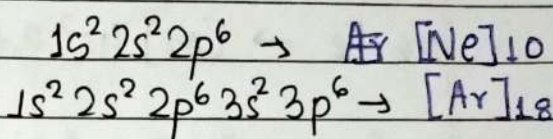
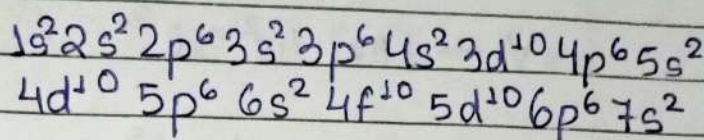
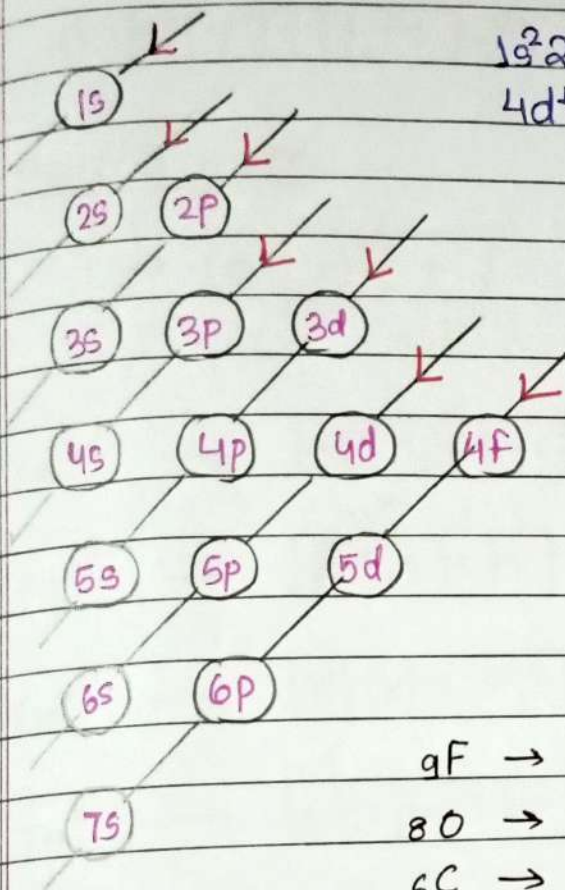
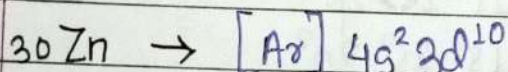
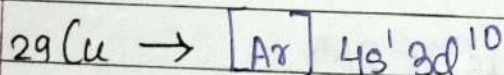
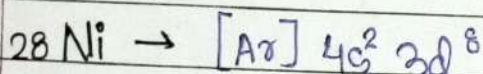
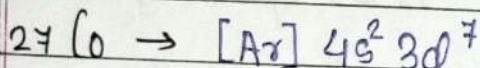
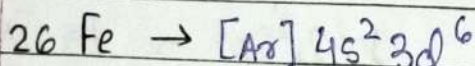
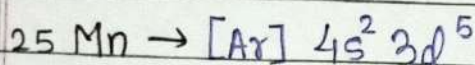
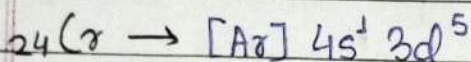
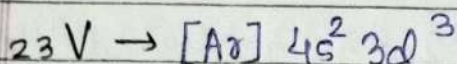
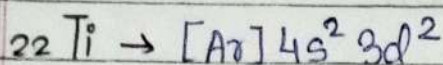
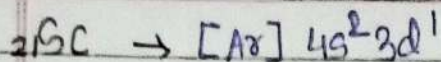


D & F Block Elements

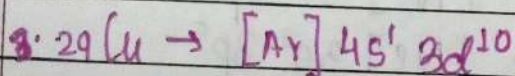
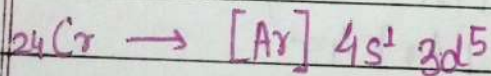
• Periodicity

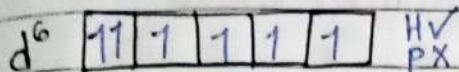
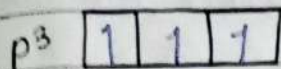
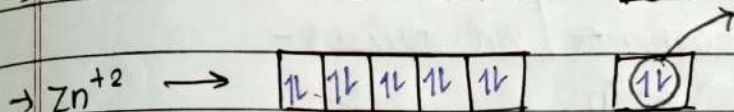
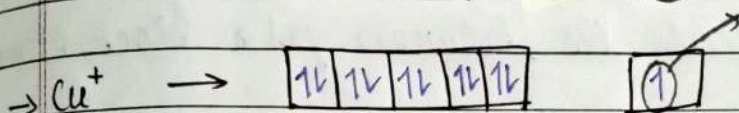
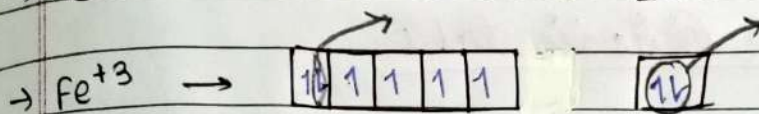
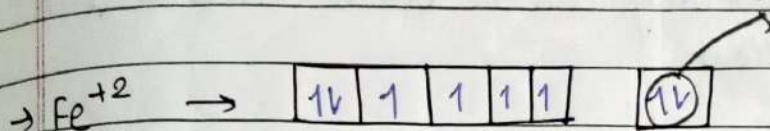
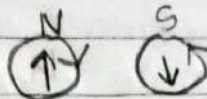
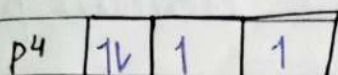
- Basic electron filling rule
- Aufbau rule





exceptions



Hund's rulePauli's rule

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→ d block:-

The elements in which the elements are enter in $(n-1)d$ orbitals.

$(n-1)d \rightarrow$ penultimate shell

→ Transition element:-

- d block element are called transition elements because their properties are between p & s blocks.
- $[Zn, Cd, Hg] \rightarrow$ They are d block elements but not transition.

⇒ Position in Periodic table

d block elements lie between p & s block elements

→ 1st transition elements / 3d series:-
 $21Sc \rightarrow 30Zn$

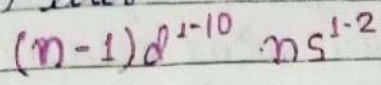
→ 2nd transition elements / 4d series:-
 $39Y \rightarrow 48Cd$

→ 3rd transition elements / 5d series:-
 $57La, 72Hf \rightarrow 80Hg$

→ 4th transition elements / 6d series:-
 $89Ac, 109Rf \rightarrow 112Uub$

Electronic configuration

In the d block elements the electronic configuration are:-



Exceptional configuration of Cu, Cr:-

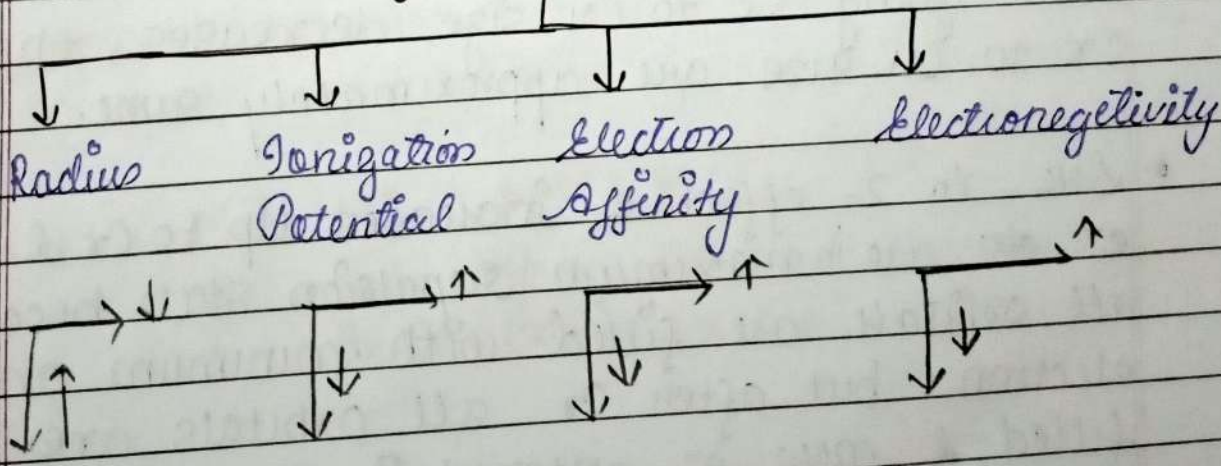
The exception in 1st series is $Z=24$ & $Z=29$.

It may be observed/noticed that unlike other elements, Cr & Cu have single electron in 4s orbital this is due to the gain of additional stability by the atom either they have half filled or fulfilled.

In chromium orbital are filled with $5e^-$ & in copper orbital filled with $10e^-$ which is fulfilled.

Properties:-

Physical Properties



⇒ Radius:-

The atomic radius of transition metal lies between s & p orbitals. From going left to right size decreases rapidly after some element size is approximately same & at the end size again is slightly increases.

1. Atomic radius:-

- - The size of d block elements lies between s & p block element.

Explanation:-

D block elements are lie between s & p block. So their size are slightly smaller than s & large than p.

- - From going left to right size decreases upto Cr than size all approximately same.

Explanation:-

From going Sc to Cr size decreases, then Cr to Cu size are approximately same.

- Due to 2- effective increases up to Cr & e^- & e^- are in maximum repulsion state because all orbitals are filled with minimum one electron, but after Cr all orbitals are filled & new e^- entered in penultimate $(n-1)$ shell.

o At the end the size are slightly increases -

Explanation

All electrons (orbitals) are filled with 2 electrons. The repulsion force are greater than the attraction from nucleus force that's why size slightly increases.

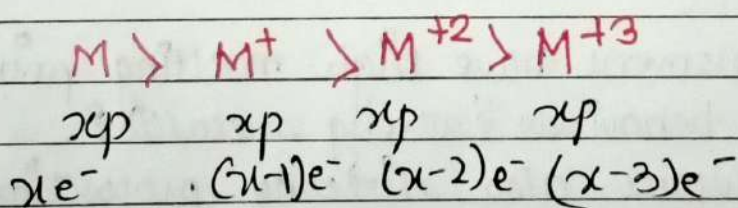
o From going top to bottom size increases but 5d & 6d series, 6th & 7th period have approx. same size.

Explanation Due to lanthanoids contraction & actinoids contraction.

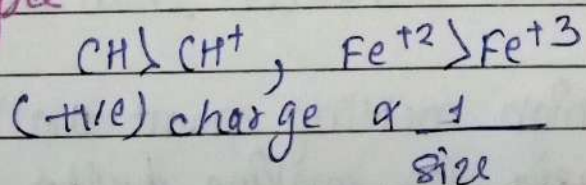
2. Ionic Radius:-

o They all are metal so, they easily remove electrons so, they only make cation when electrons remove from an element their size always decreases.

Explanation: when electron removed Z -effective increases due to no. of proton increased.



Example



→ Metallic behaviour:-

- Electricity conductor
- heat conductor
- hard
- ductile
- malleable
- Tensile

All transition element are metallic they are ductile, tensile, malleable, hard, heat, conductor, high melting point good conductor of electricity & heat.

→ Trends

- from getting left to right metallic behaviour increases upto manganese then decreases due to.
unpaired electron $\times$ metallic behaviour
- more unpaired electron more metallic more paired electron less metallic.
- That's why (Zn), (Cd), (Hg) are least metallic. [except]
- one & only ~~one~~ metal which is formed in liquid state is Hg.

→ point

- Transition element have high melting point due to the metallic behaviour [strong metallic].
- Metallic behaviour also directly proportional to unpaired electron.
- Melting point increases (Sc) to (Cr) then decreases Mn to Zn
- Tungsten have a high melting point that's why it is used in filament for making bulbs.

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- Hg, have least melting & boiling point that's why it is used to making thermometer & barometer.

- In 3d series (Cr) & (Mn) have max. melting point and Zn have min. melting point.

→ Ionization potential

- These ionization enthalpies are greater than s but lesser than p.

$s < d < p$, This is due to their size.

- There are lots of irregularities in I-P of d block elements.

- Their IPs are increases from going left to right but they show always IInd ionization enthalpy due to the extra electrons available in 4s, (ns). But,

- But, Exceptionally Cu & Cr shows the 1st ionization enthalpy. Due to exceptional configuration (ns¹).

⇒ Oxidation number

The net numerical charge or no. of electrons transferred in any element or metal of d-block are called as oxidation no.

1. D block element show variable oxidation no. except Zn, Cd, Hg (only one oxidation no.) why they are called non transition elements.

2. Common electronic configuration are +2 except Cr, Cu they show +1 oxidation no.

Cr Cu
+1 +1

3 - After removing ns electron they are kernel

4 - Kernel are unstable they loose more electron.

5. Maximum oxidation no. $\geq ns e^- + \text{no. of } e^- \text{ in d orbital.}$

6. Min. oxidation no. = $ns e^-$

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^9 4s^1$	$3d^{10} 4s^2$
+2	+2	+2	+1	+2	+2	+2	+2	+1	+2
+3	+3	+3	+2	+3	+3	+3	+3	+2	
	+4	+4	+3	+4		+4	+4		
		+5	+4	+5			+5		
			+5	+6					
				+7					

The highest oxidation no. of d-block in Ru & Os

Ru
Os] +8

In 3d series maximum oxidation no. is Mn. ~~+7~~
Mn = +7

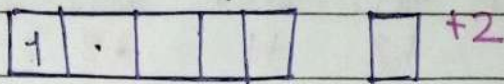
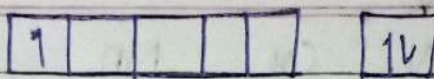
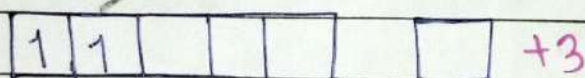
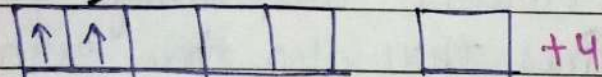
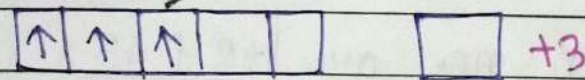
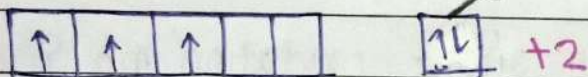
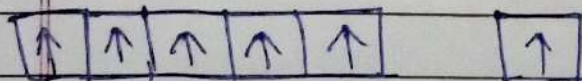
Trends

from going left to right oxidation no. increases then decreases.

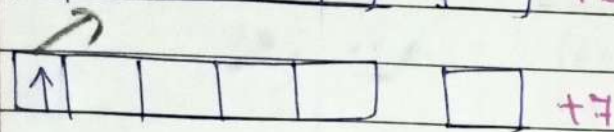
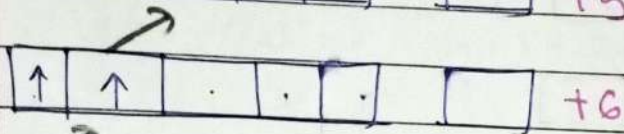
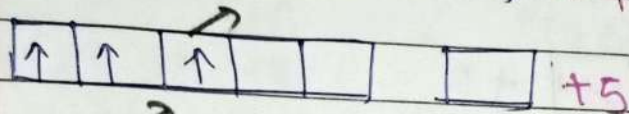
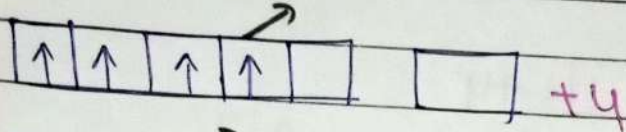
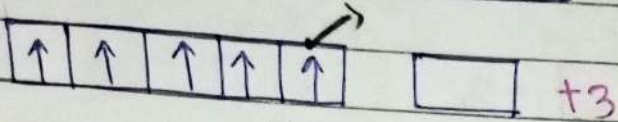
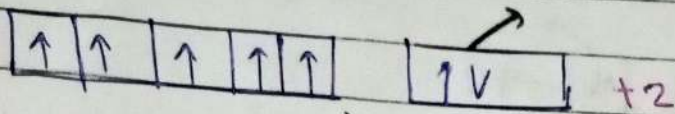
Most common oxidation no. are +2 & +3

Max. oxidation no. elements are always from mid range. Sometimes they also show zero oxidation no. example [Ni(CO)₄]

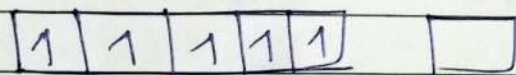
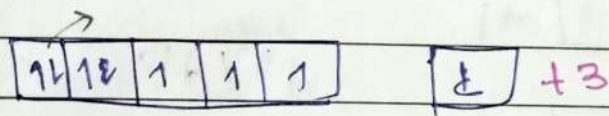
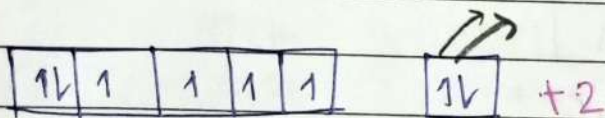
Most of the elements oxidation no. depend upon unpaired e^- d^0 d^5 $d^{10} \rightarrow$ stable configuration

0-21 Sc - $3d^1 4s^2$  $d^0 \rightarrow$ configuration0-22 Ti - $3d^2 4s^2$ 0-23 V - $3d^3 4s^2$ 0-24 Cr - $3d^5 4s^1$ 

o- $25 \text{ Mn} - 3d^5 4s^2$

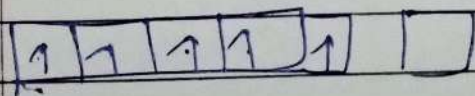
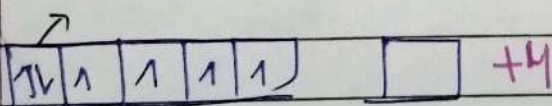
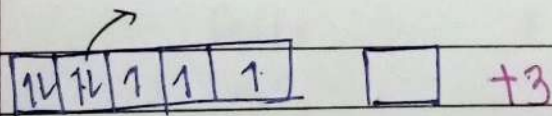
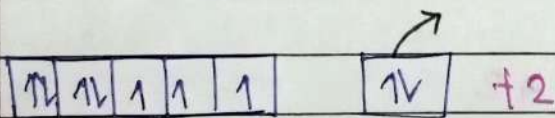


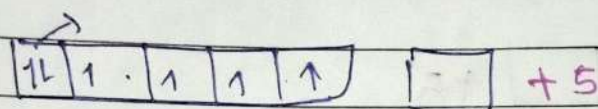
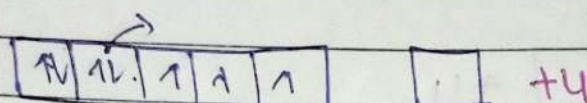
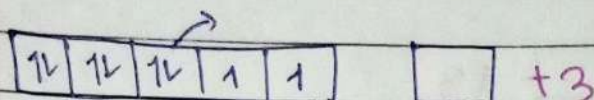
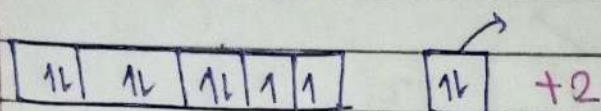
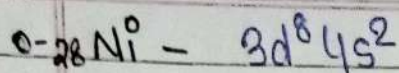
o- $26 \text{ Fe} - 3d^6 4s^2$



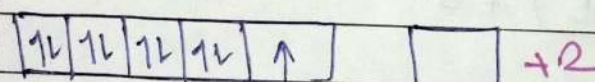
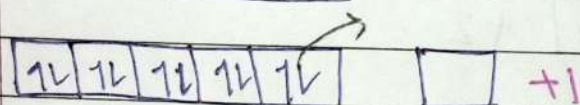
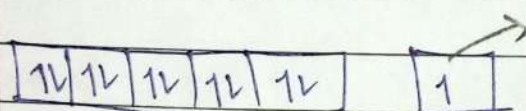
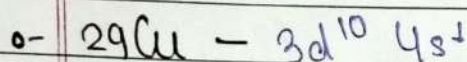
$d^5 \rightarrow \text{stable}$

o- $27 \text{ Co} - 3d^7 4s^2$

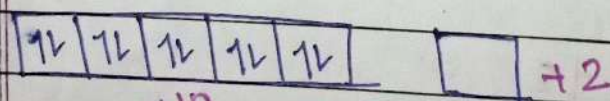
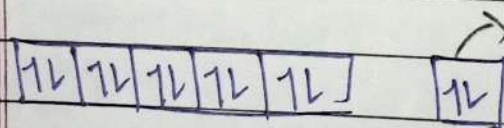




$d^5 \rightarrow \text{stable}$

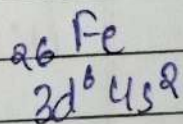
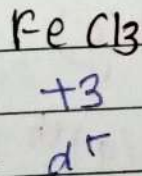
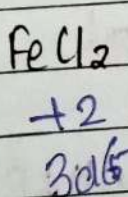
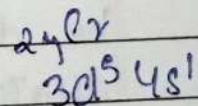
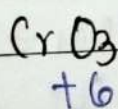
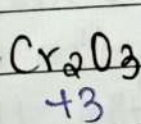
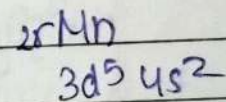
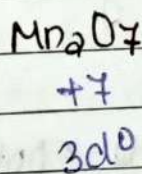
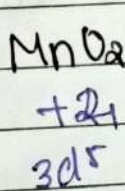
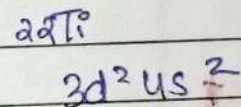
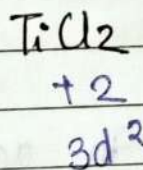
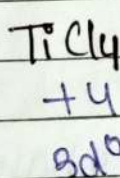
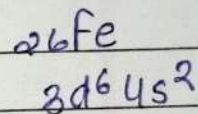
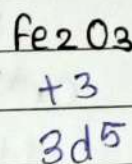
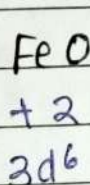
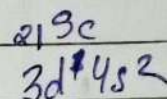
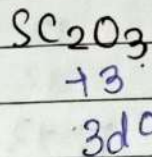
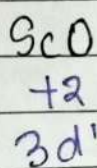
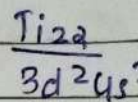
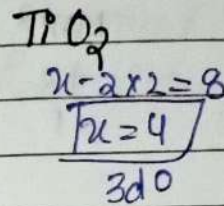
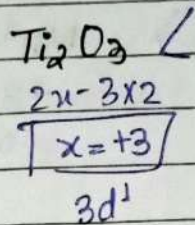
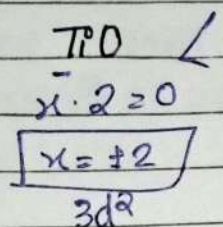


$d^5 \angle d^{10}$

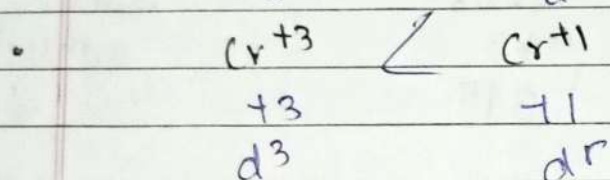
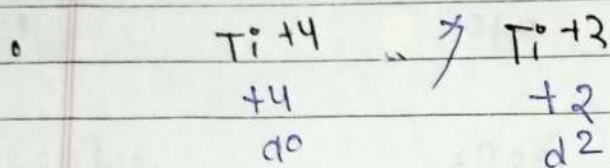
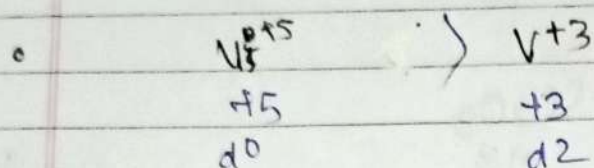
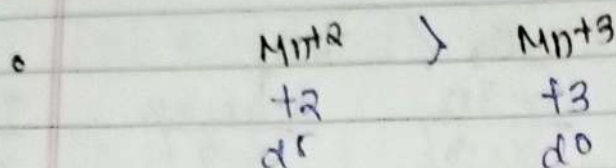


$d^{10} - \text{stable}$

⇒ Stable Configuration.



⇒ Ionic form

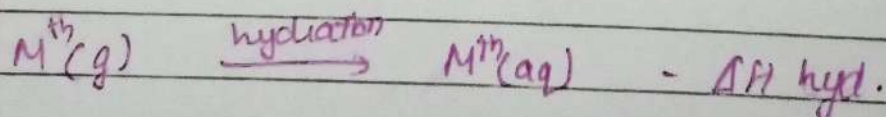
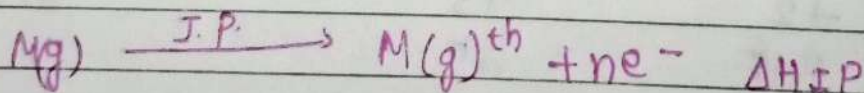
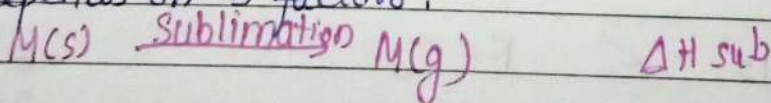


50*

• Cu^{+2} more stable in aqueous phase due to very high heat of hydration while Cu^{+1} have d^{10} configuration.

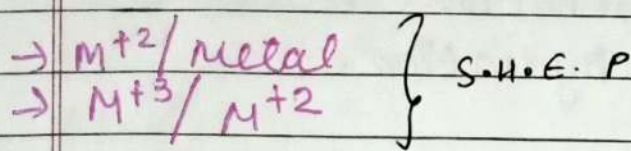
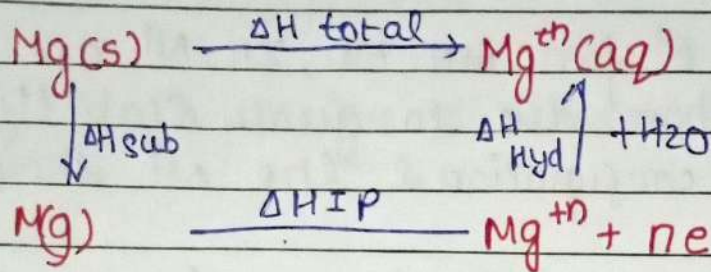
→ Standard electrode potential

Thermodynamically, the transition of element can be defined as smaller the ionization enthalpy greater the stability but in solution the stability depends on 3 factors.



• Total energy = $\Delta H_{\text{sub}} + \Delta H_{\text{IP}} + \Delta H_{\text{Hyd}}$.

So, If we want to change any metal into its aqueous solution so, we must have three stages to do that.

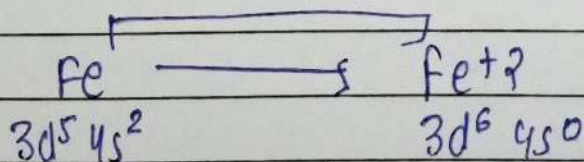
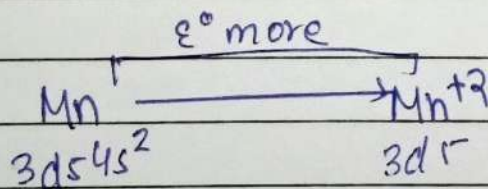
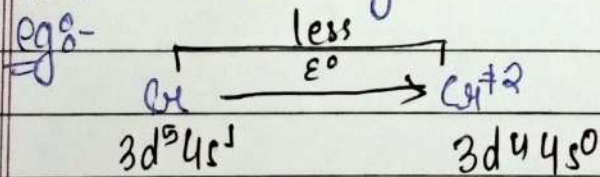


Hydration energy $\propto \frac{\text{cation charge}}{\text{cation size}}$

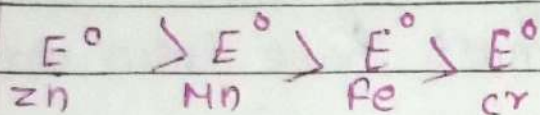
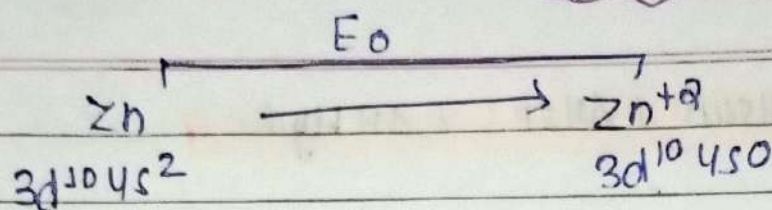
eg:- $\text{Cu}^+ < \text{Cu}^{+2}$

$\Rightarrow$ Trends in M^{+2}/M

There is no regular trend because IP 1st & IP second & Sublimation do not show any regular trend but there is some sufficient information about stability.



E° more - stability more
 E° less - stability less



The value of E° for ~~Mn~~ Mn, Zn, Ni are more -ve than due to greater stability of Mn^{+2} , ~~Ni~~, Zn^{+2} configuration & the Ni show exception unexpected behaviour because of high -ve enthalpy of hydration.

- Copper show unique behaviour in the series this only metal having +ve value of E° . That's why it do not liberate acid from H_2 only react with oxidizing acid $[\text{HNO}_3, \text{H}_2\text{SO}_4, \text{H}_2\text{SO}_5]$ the reason thats E° are positive. The total energy are not balanced by hydration energy

$$\Delta H_{\text{total}} = \Delta_{\text{sub}}H + \Delta_{\text{ion}}H + \Delta_{\text{hyd}}H$$

2) Trends in M^{+3}/M^{+2}

1. Very low value of $Sc^{+3}/Sc^{+2} \rightarrow Sc^{+3}$ more stable due to d^0 configuration.

2. The highest value of $Zn \cdot Zn^{+2}/Zn^{+3} \rightarrow Zn^{+2}$ more stable d^{10} configuration.

3. It is not possible to create Zn^{+3} due to its stability.

4. High value of $Mn^{+3}/Mn^{+2} \rightarrow Mn^{+2}$ more stable d^5 configuration. It is not possible to make Mn^{+3} easily.

5. Very low value of E° in Fe.

$Fe^{+3}/Fe^{+2} \rightarrow Fe^{+2}$ more stable d^6 configuration.

More negative E° values means more tendency to form that ion.

Note: d^{1-9} are also stable due to the half filled
t2g.

Brice

Page: / /

Date: / /

$\Rightarrow$ Oxidizing agent and reducing agent

- Compound that show high oxidation no. they are good oxid. agents because they want to take electrons from other.

eg: CrO_3 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$.

• Reducing agent

Compounds which are in the lower oxidation state show good red. agent they want to oxid. him self & Red. other.

eg: NO , Cr_2O , MnO_2 .

$\Rightarrow$ acid Oxide

$\Rightarrow$ Oxides

- higher oxidation oxides are acidic & covalent type.

Lower ox. no. oxides are basic ionic type.

Intermediate o. No. are amphoteric.

+1 ⇒				Cr_2O						Cu_2O
+2	FeO	TiO	VO	CrO	MnO	FeO	CoO	NiO	CuO	ZnO
+3	Ge_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_2O_3	Co_2O_3	Ni_2O_3	Cu_2O_3	Zn_2O_3
+4		TiO_2	V_2O_4	Cr_2O_4	MnO_2		CoO_2	NiO_2		
+5			V_2O_5	Cr_2O_5	Mn_2O_5					
+6				CrO_3	MnO_3			Ni_2O_5		
+7					Mn_2O_7					

⇒ Halides

The highest oxidation no. in halide are TiX_4 but fluoride show +5 & +6 also.

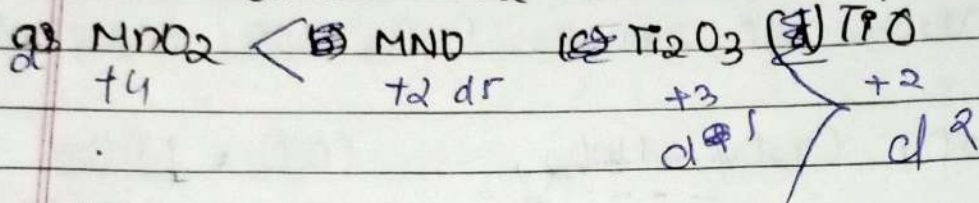
Some examples:

+6				CrF_6							
+5			VF_5	CrF_5							
+4	TiX_4	VX_4	CrX_4	MnF_4							
+3	TiX_3	VX_3	CrX_3	MnF_3	FeX_3	CoF_3					
+2	TiX_2	VX_2	CrX_2	MnX_2	FeX_2	CoX_2	NiX_2	CuX_2	ZnX_2		
+1								CuX^{II}			

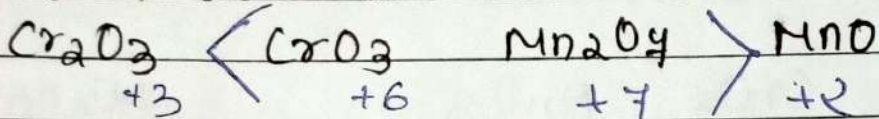
$\text{X} = \text{F}$ or I , $\text{I} = \text{X}^{\text{I}} = \text{F} \rightarrow \text{BF}_3, \text{X}^{\text{II}} = \text{F}, \text{ClO}_2, \text{X}^{\text{III}} = \text{Cl} - \text{I}$

⇒ Lower Oxidation no. are ionic. High. ox. no. are covalent.

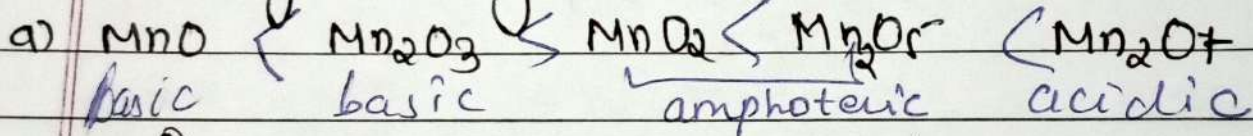
Que.1 Which oxides are more stable?



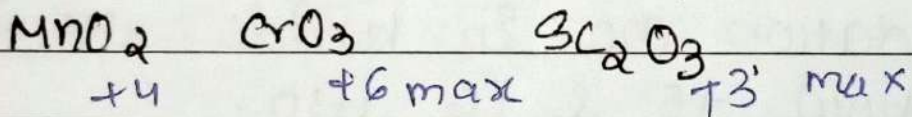
Ques 2 Which oxide are more acidic.



Ques. 3 Order of acidity in Mn Oxide.



(Q.4) Which oxide are amphoteric



और का
amphoteric.

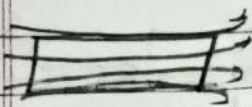
⇒ Magnetic Behaviour

paramagnetic

→ e unpaired

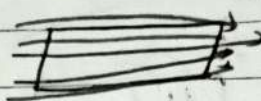
→ $\mu = \sqrt{n(n+2)} \text{ BM}$

magnetic moment $n = \text{no. of unpaired } e^-$

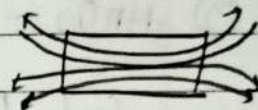


diamagnetic

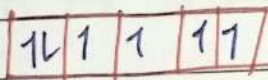
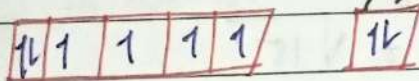
All ~~are~~ are paired



ferromagnetic
Fe, CO, Ni



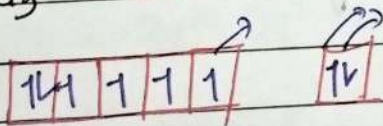
eg: $\text{FeO} = {}_{26}\text{Fe} \rightarrow 3d^6 4s^2$



- Paramagnetic

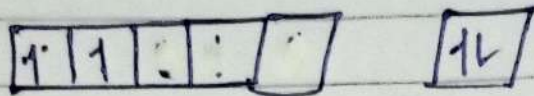
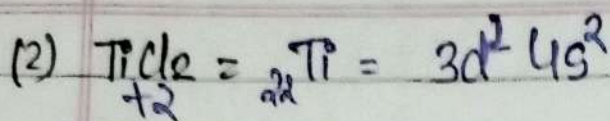
$$\begin{aligned} \mu &= \sqrt{n(n+2)} \text{ BM} \\ &= \sqrt{4(4+2)} \\ \mu &= \sqrt{24} \text{ BM} \end{aligned}$$

Ques: $\text{FeCl}_3 \rightarrow {}_{26}\text{Fe} \rightarrow 3d^6 4s^2$



• Paramagnetic

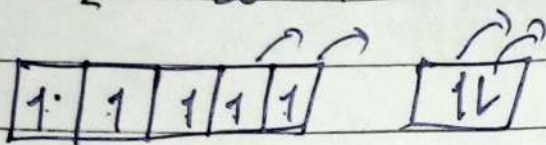
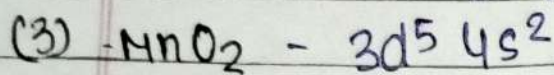
$$\mu = \sqrt{4(4+2)} = \sqrt{24} \text{ BM}$$



Paramagnetic

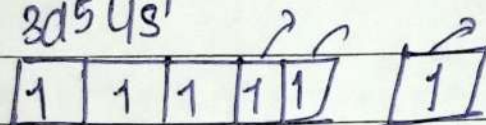
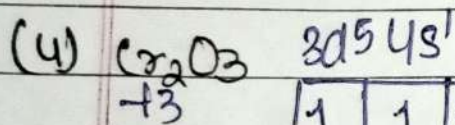
$$\mu_B = \sqrt{n(n+2)}$$

$$= \sqrt{2(2+2)} = \sqrt{8} \text{ BM}$$



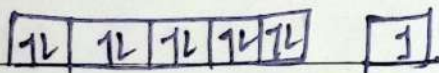
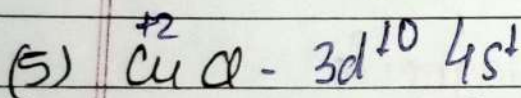
Paramagnetic

$$\mu = \sqrt{5(5+2)} = \sqrt{35} \text{ BM}$$



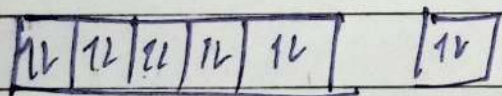
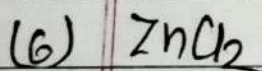
Para magnetic

$$\mu_B = \sqrt{15}$$



Diamagnetic

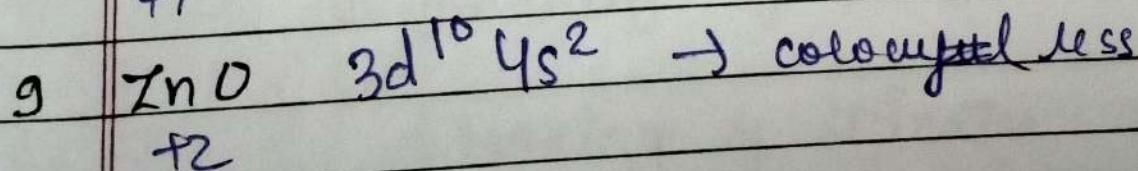
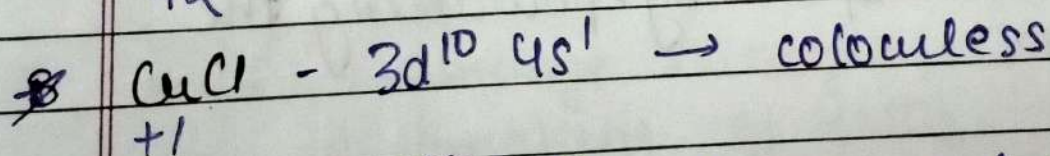
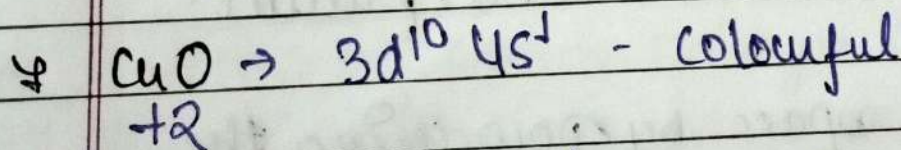
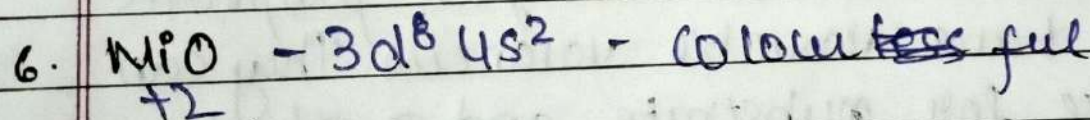
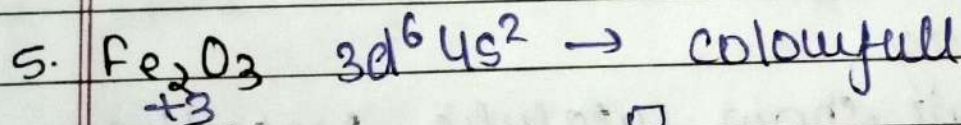
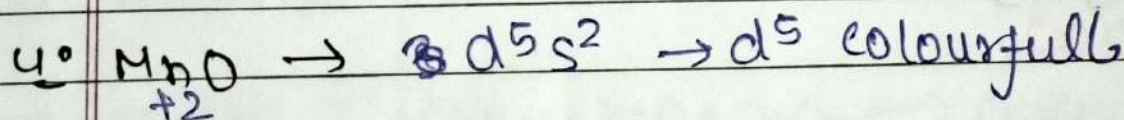
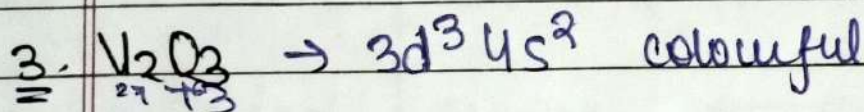
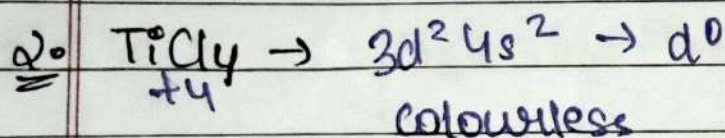
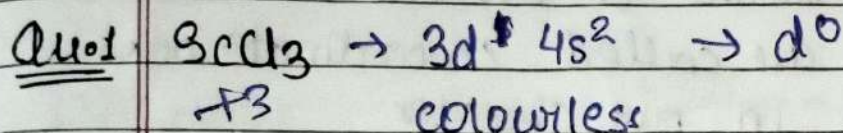
$$\mu_B = 0$$



Diamagnetic

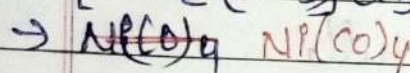
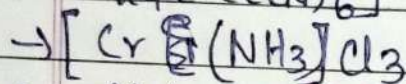
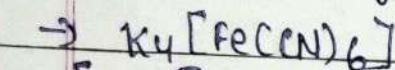
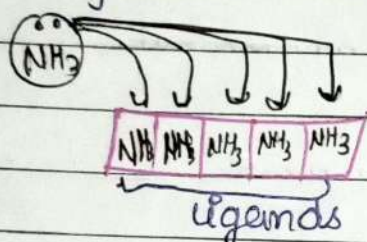
Colour property

- unpaired - colour ~~less~~ full
⇒ paired - colour ~~less~~ less



⇒ Making of coordinate compounds

d-block element easily make co-ordinate because they have lot of space in d orbitals. So, any compound which have extra lone pair can be put in this vacant d-orbital i.e. called ligands. & the bond are called 'co-ordinate bond'. We'll further discuss in next chapter.



→ Catalytic property

d-block element show catalytic properties because they have variable valencies. They can make space for substrate and product. [Exacient].

We can increase space by powdering the catalyst.

CatalystReaction / Uses

- | | |
|---------------------------------|---|
| (1) $TiCl_3$ | Ziegler-Natta catalyst making of polyethylene |
| (2) V_2O_5 | $SO_2 \xrightarrow{V_2O_5} SO_3$ contact process making of H_2SO_4 |
| (3) MnO_2 | $2KClO_3 \xrightarrow{MnO_2} 2KCl + O_2$ decomposition |
| (4) Fe | $N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$ Habber's process |
| (5) $FeCl_3$ | $CS_2 + 2Cl_2 \xrightarrow{FeCl_3} CCl_4 + 2S$ fire extinguisher |
| (6) $FeSO_4 + H_2O_2$ | Alcohol $\longrightarrow$ Aldehyde fenton's Reagent |
| (7) $PbCl_2$ | $C_2H_4 + H_2O + PbCl_2 \longrightarrow CH_3CHO + HCl + Pd$
Wacker's process |
| (8) Pd | Phenol $\longrightarrow$ cyclohexane (hydrogenation) |
| (9) Pt/PtO | Adam's Catalyst (reduction) |
| <u>10</u> $\frac{Pt/Rh}{Pt/Ir}$ | Gauche catalyst, Ostwald process, making of HNO_3 |
| (11) Cu | Making of silicates |
| (12) W/V | Making of Nylon 6,6 |
| (13) WCl_2 | Decons process making HCl |
| (14) Ni | Raney Nickel making Alkanes (Reduction)
(Hydrogenation) |

* Alloy formation

⇒ D block element can make easily alloy with other metals bcz their size are approx. same

examples:

- (1) Brass $\rightarrow$ Cu + Zn 2:1
- (2) Bronze $\rightarrow$ Cu + Tin (Sn) 3:1
- (3) Gun metal $\rightarrow$ Cu + Zn + Sn
- (4) German silver $\rightarrow$ Cu + Zn + Ni 2:1:1
- (5) Bell metal $\rightarrow$ Cu + Sn [48:1]
- (6) Nichrome $\rightarrow$ Ni + Cr + ~~Fe~~ Fe
- (7) Alnico $\rightarrow$ Al + Ni + Co
- (8) Type metal $\rightarrow$ Pb + Sn + Sb
- (9) Solder $\rightarrow$ Pb + Sn
- (10) Magnesium $\rightarrow$ Al + Mg [9:1]
- (11) Duralumin $\rightarrow$ Al + Mn + Cu
- (12) Artificial gold $\rightarrow$ Cu + Ag [9:1]
- (13) Constantan $\rightarrow$ Cu + Ni [38:2]

⇒ Iron alloy

- | | C% |
|----------------------------------|------------|
| a) wrought Iron (purest form) | 0.1 - 0.25 |
| b) steel (strongest form) | 0.25 - 2.0 |
| c) Cast Iron | 2.6 - 4.3 |
| d) Pig Iron (from blast furnace) | 2.3 - 4.6 |

⇒ Gold alloy:-

24 carat gold $\rightarrow$ 100% pure Au

22 carat gold $\rightarrow$ 91.6% Au

20 Carat gold $\rightarrow$ 83.3% Au

14 Carat gold $\rightarrow$ Au + Ag + Cu
5 : 3 : 2

⇒ Steel Alloy:-

(1) Vanadium Steel $\rightarrow$ Fe + V

(2) Chromium Steel $\rightarrow$ Fe + Cr

(3) Nickel steel Fe + Ni

(4) Magnese steel Fe + Mn

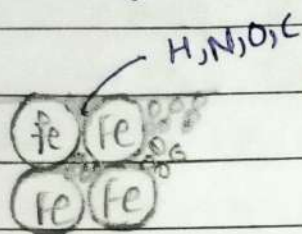
(5) Stainless steel Fe + Cr + Ni

(6) Tungsten steel Fe + W

(7) Invar Fe + 36% Ni

⇒ Interstitial Compounds

- The transitional element form large of interstitial compound. In which small atoms such as hydrogen, nitrogen, carbon, oxygen ~~are~~ found in interstitial sites or in voids. It is because of large size of d-block elements.



eg:- TiC , TiH_2 , Mn_4N , Fe_3H ,
 Fe_3C etc.

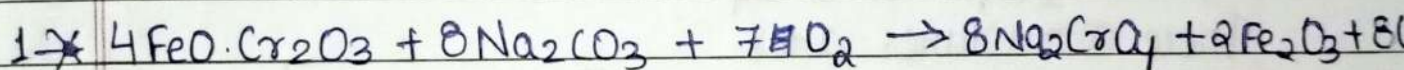
- The bond present in them neither covalent nor ionic.
- There some important characters are:-
 - They are very hard, rigid;
 example:- Steel, which is alloy of Fe & carbon. are very harder & its hardness is similar as diamond.
 - They have high melting point which are higher than pure metal.
- They show higher conductivity than metal (Electric and thermal).
- They are chemically inert, chemically they do not react with acid, base, salt.

⇒ Some compounds of D-block

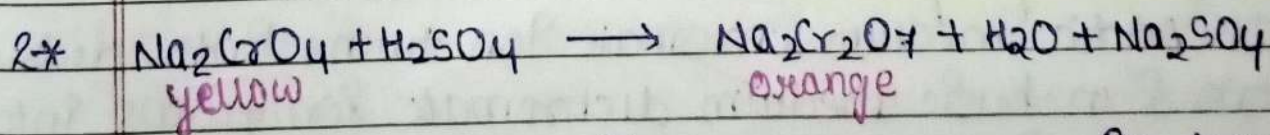
1 → $K_2Cr_2O_7$

- Potassium dichromate is a very imp. chemical substance which is used in leather industries, oxidant for many substance like Azo-compounds, peroxides etc.
- It is obtained by the chromate ore $[FeCr_2O_4] \rightarrow$ ferrous chromate.

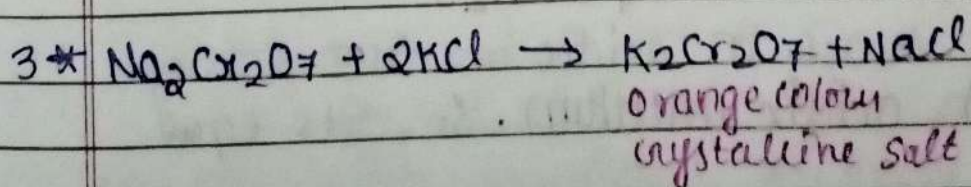
→ Preparation



- Iron chromate reacts with sodium carbonate and makes sodium chromate. In reverberatory furnace where roasting process takes place. The process ores directly react in presence of oxygen.
- And Now, This sodium chromate which is yellow in colour directly reacts with oxidized acids & make orange colour sodium dichromate

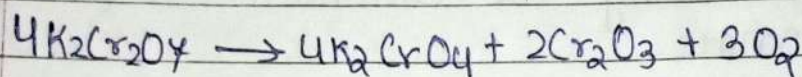


- Now this sodium di-chromate reacts with KCl & makes potassium dichromate

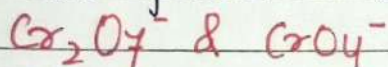


⇒ Physical Properties.

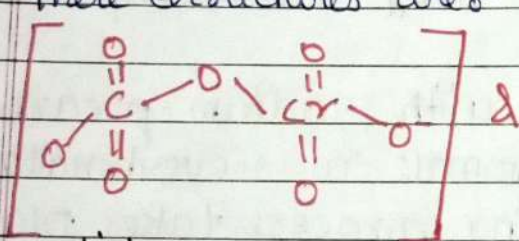
1. $K_2Cr_2O_7$ are orange in color whose melting point are 6,069 K.
2. They are moderate soluble in cold water & highly soluble in hot water.
3. When it is heated direct in air gives / evolve oxygen



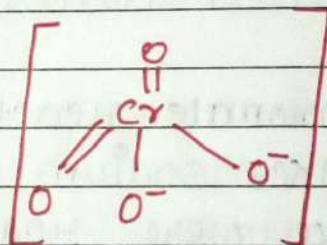
4. They are found in two ionic forms



These structures are:-



- dichromate



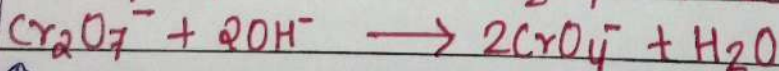
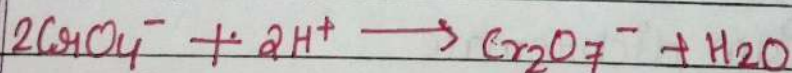
- chromate

- orange in colour

- yellow in colour

⇒ Chemical properties

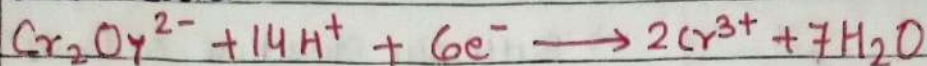
1. In Acidic medium chromate ion turns into dichromate ion & in basic medium dichromate ion turns into chromate ion.



They mostly react in acidic medium & they give 6 e⁻ in acidic medium. So, its equiv. weight is:-

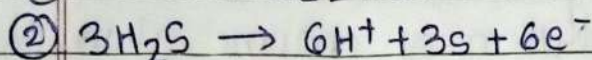
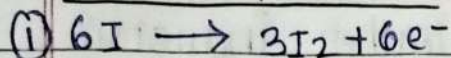
$$Eqwt = \frac{M.W. \text{ of } K_2Cr_2O_7}{6} = \frac{294}{6} = 49$$

They are good oxidizing agent because they give high electrode potential during reactions with acid.

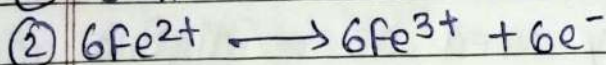
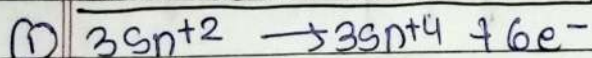


$$E^\circ = 1.33 \text{ Volt}$$

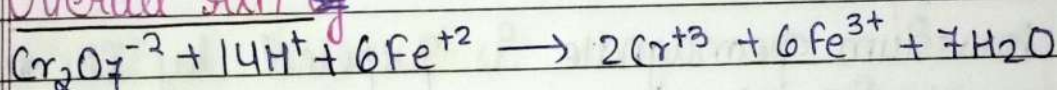
- Rxn with ^{non}metals:



- Rxn with ~~non~~metals:



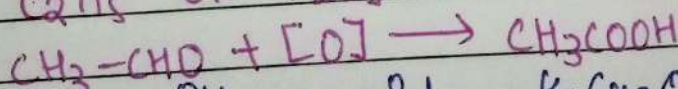
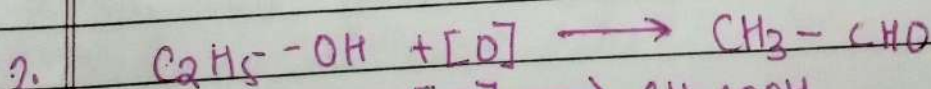
Overall rxn



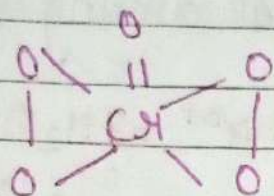
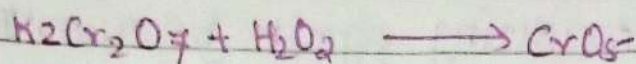
⇒ Uses of $\text{K}_2\text{Cr}_2\text{O}_7$

1. Test of drunken & drive. The above rxn helps to identify the drunk & driven & the amount of alcohol consumed by driver.

If she/he asked to breath into acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solⁿ. taken in test tube. Orange colour of $\text{K}_2\text{Cr}_2\text{O}_7$ solⁿ turns green that means driver are drunken.



Reaction with peroxide - $\text{K}_2\text{Cr}_2\text{O}_7$ reacts with peroxide and makes blue colour each of CrO_5



→ Butterfly structure of CrO_5

3. It is used in tanning in leather industries.
4. It is used in preparation of chrome alum, Cr_2O_3 , CrO_3 , CrO_2Cl_2 , K_2CrO_4 , $CrCl_3$.
5. It is used in the photography ~~hard~~ for hardening of gelatin film.
6. In Organic chemistry used as oxidizing agent.

⇒ $KMnO_4$

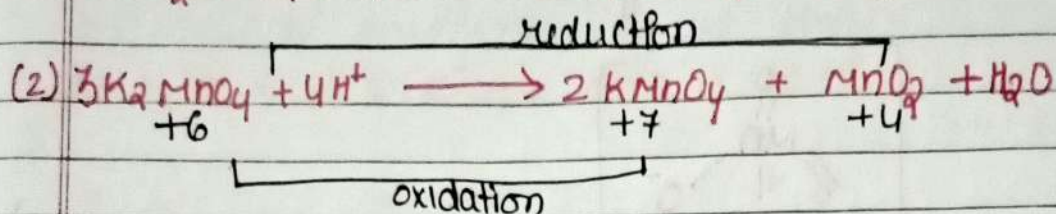
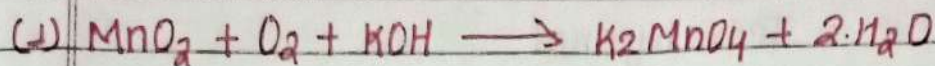
- Potassium permanganate is prepared by the mineral pyrolucite MnO_2 .

• Method of Preparation.

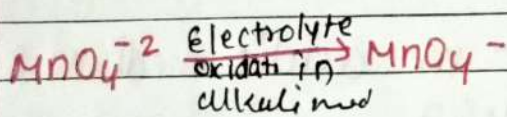
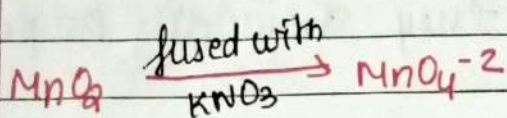
→ MnO_2 react with KOH and makes potassium ~~mag~~ manganet. this potassium manganet oxidized in the presence of acid & makes potassium permagnet and MnO_2 by disproportionation reaction.

• Disproportionation rxn:-

A compound which can oxidize & reduce himself that is called Disproportionation rxn

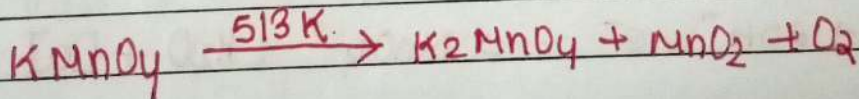


* In commercial purpose KMnO_4 makes by pyrolucite with rxn with fused KNO_3 & again electrolyte oxidation in alkaline medium



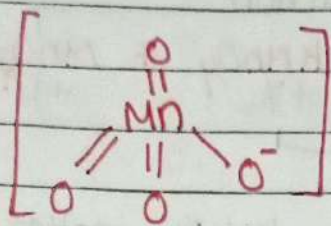
→ Physical Properties

1. It is deep purple colour cluster with greenish shine it has become unshiny in presence of air.
2. Solubility: slightly soluble in water & more soluble in hot water.
3. In presence of heat they break into.



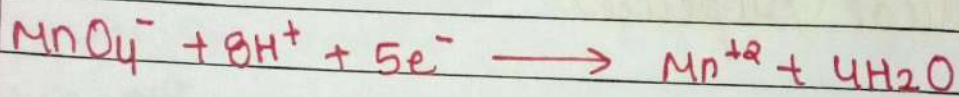
3. They are good oxidizing agent. Their chemical properties discussed later.

Structure - Tetrahydral



⇒ Chemical Properties

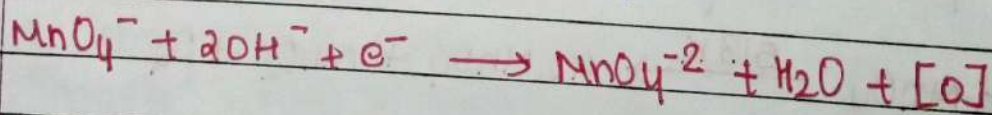
- In different medium they show diff. Properties
- In acidic medium:-
- It converts into Mn^{+2} in acidic medium & equivalent weight is 31.6 g



$$\text{eq. wt.} = \frac{\text{Mw}}{\text{Val}} = \frac{158}{5} = 31.6 \text{ g//}$$

→ In basic / alkali medium

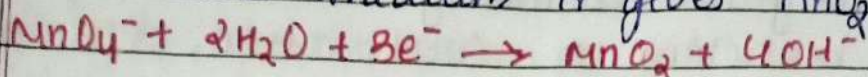
- In basic medium it converts into MnO_4^{2-} & eq. weight is 158 g.



$$\text{eq. wt} = \frac{\text{mw}}{\text{val}} = \frac{158}{1} = 158 \text{ g//}$$

- In neutral medium

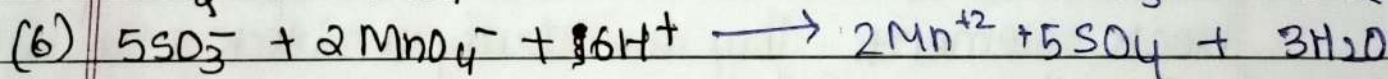
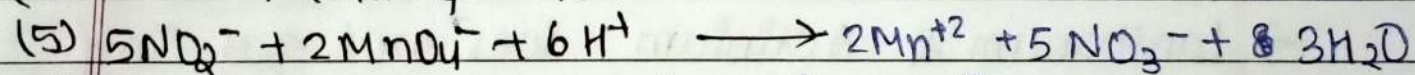
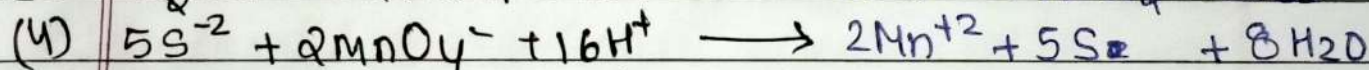
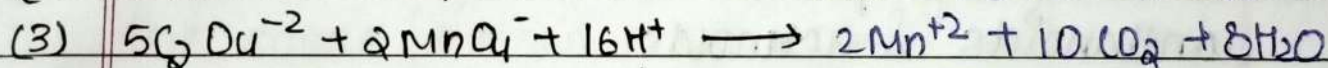
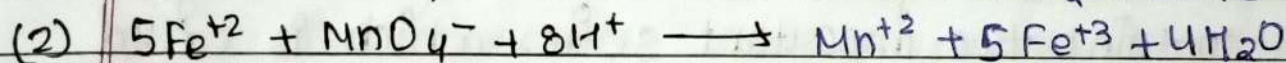
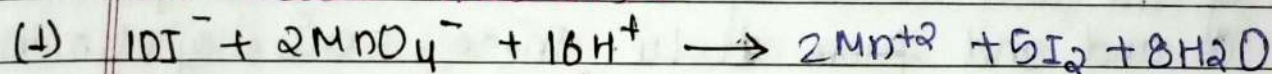
In neutral medium it gives MnO_2 .



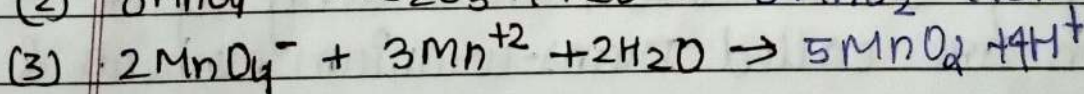
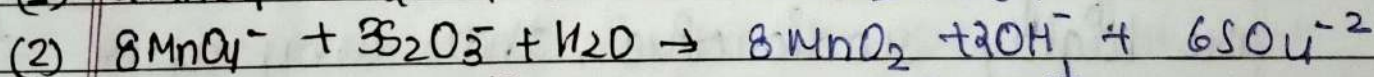
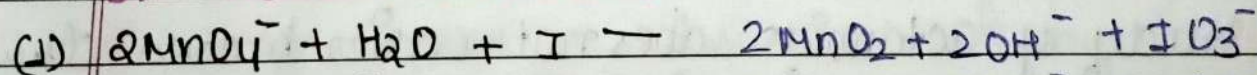
$$eq. \text{ weight} = \frac{mw}{valency} = \frac{158}{3} = 52.67 \text{ g}$$

Note: It is clarified by above rxn $KMnO_4$ are good in acidic & moderate in neutral medium. but in basic do not work with its 100% efficiency.

In acidic medium:



In neutral medium:-



→ Uses:-

- Used in analytical chemistry.
- Used as bleaching of wool, cotton, silk, textile
- decolorisation of oils etc.
- Used as germicides & disinfectant.
- A very dil. solⁿ of KMnO_4 used as gargling for ~~mouth~~ mouth sore
- Also used in purifying water of stinking wells
- In laboratory it is called as Baeyer's reagent.

→ f block elements

The inner transition elements, ~~f~~ f-block consist of the two series of 14-14 elements starts from Ce and end from Lu. These series of element contains two important series which is called lanthanoids & actanoids.

- Lanthanum & Actinium does not put in f-block elements. They are truly d-block element which is from 3rd ~~gr~~ group.
- Study of actanoids does not easier because they are highly radioactive, thats why after uranium are called Trans-uranium elements & used only in atomic bomb or nuclear energy ~~or~~ developing, fuel which is used in nuclear reactor, Breeder reactor.

• Lanthanoids

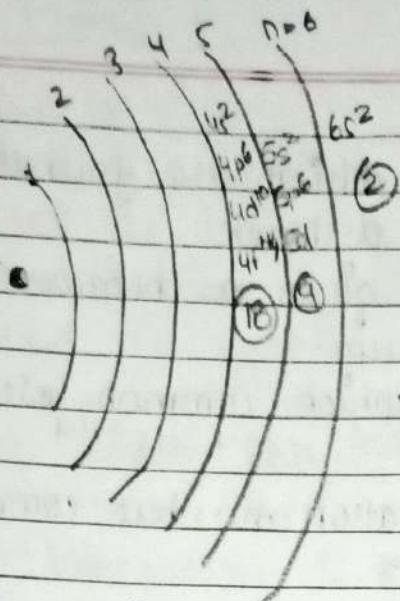
- Lanthanoids are elements which are found between third & fourth group of d-block.
- The name lanthanoids are given as because they are starting from lanthanum.
- They are the elements which common electronic configuration are $6s^0 6s^{0-2} 5d^{0-1} 4f^{1-14}$
- They show variable oxidation no. but common oxidation no. are +2 & +3.

→ Atomic & Ionic size

from going left to right in the series size are always decreases because from going left to right z -effective increases & net attraction force also increases that's why size decreases. One more reason the effect are called Lanthanoid contractions.

→ Lanthanoid contractions:-

- 1) It is a unique feature which only found in lanthanoid & actinoids. In this property when electrons enter in f subshell, there d subshell are completely filled ~~it~~ with $10e^-$ due to that reason there is a shield/screen of 18 electrons [extra 10 electrons of d -block are d subshell] due to that reason there a layer of electrons directly attracted by the nucleus & the size will shrink. and their effect in $6s$ & $5f$ are negligible.



$$Z_{\text{eff}} = Z - \sigma$$

↓

att. force by ~~nucleus~~ nucle.

rep. for big elec.

2) These size are shrink up to that very the size of Zr, Hf are approx. same

⇒ Oxidation state

They show $+2$ & $+3$ configuration but still some element show $+4$ configuration.

eg: Ce^{+4}

Some other element which is found in $+4$.

Tb, Pr, Nd, Dy.

Yb^{+2} have f^{14} but they show reducing property

⇒ General characteristic

⇒ All lanthanoid are silvery white, soft metal & tarnishing rapidly in air.

⇒ From going left to right hardness increases, samarium (62) are steel hard.

⇒ Boiling point Melting point $\rightarrow 1000 - 12,000\text{K}$
Sm has ~~1623~~ 1623K.

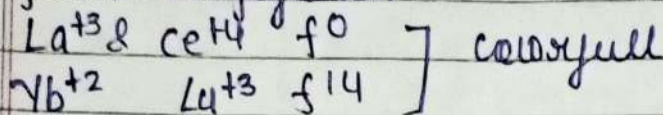
⇒ Good conductor of heat & electricity.

⇒ density increases from left to right

$\text{Lu} - \text{Yb} \uparrow$

$\text{Sm} - \text{Tm} \downarrow$

⇒ They are mostly colourless while they have f^0 & f^{14} configuration

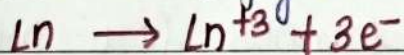


⇒ They all are paramagnetic.

⇒ The first Ionization enthalpy of Lanthanoid are around 600 kJ/mol & 2nd are around 1200 kJ/mol which is approximately equal to Calcium & 3rd ionization enthalpy is higher than other 2 because electrons remove from 4s orbital but exceptionally some element have higher 3rd I_p because of half filled and fulfilled f-orbital.

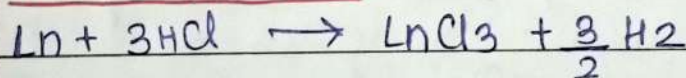
⇒ Oxidation no.

They show +3 configuration.

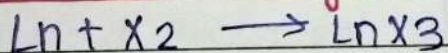


⇒ Chemical properties:-

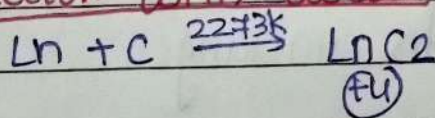
(1) React with acid:



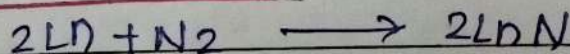
(2) React with halogen:



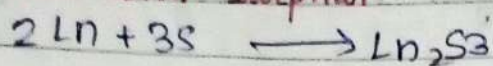
(3) Reaction with carbon: [Exception]



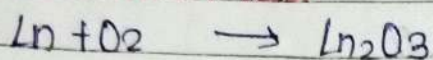
(4) React with N_2 :



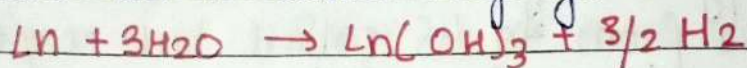
(5) React with sulphur



(6) React with air



* These oxides are basic in nature that's why if they react with water they give-



* Generally these all oxides are basic in nature

⇒ Alloy formation

Lanthanoid is very famous for production of alloy with steel for making of plates & pipes.

• Misch metal

95% La, 5% Iron, trace amount of Si, C, Ca, Al

- It is used as magnesium based alloy which is used for making bullets, shell and lighter flint

Mixed oxides of lanthanoid are used as catalyst in petroleum cracking

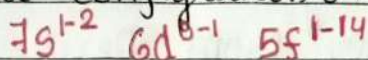
- Some (Ln) oxides are used as phosphors in television screen and in ~~fluor~~ fluorescent surface.

phosphors: - solid which emit emitted light
fluorescing: - surface which are brighter than other

⇒ Actinoids.

- They contain 14 elements Th-Lr.
- They all radioactive & their half life are approximately many years to 3 minutes.

→ electronic configuration: ~~5f~~



- The study of actinoids as compared to lanthanoid are more tougher because their members are found in only nano-gram quantity & all are radioactive.

- $5f^0, 5f^7, 5f^{14}$ are stable configuration.

ex:- Am & Cm both have f^7 configuration

⇒ Ionic and atomic size

from going left to right ionic size decreases due to actinoids contraction

- Reasons:- Screening effect of 5f

⇒ In lanthanoid & actinoid, lanthanoid contract more due to the poor shielding effect of 4f.

⇒ The ~~e~~ Ac contraction is more than La contraction
 ex. coz 5f e^- are more poorly shielding ^{than} 4f.

⇒ Uses / Application of f-d block

1. Iron & steel are most important for construction material.
2. Their main use are making of alloy with Cu, Mn, Ni.
3. TiO are used as pigmentation industries & MnO₂ used as dry cell.
4. Zn, Ni/Cd are also used in battery industries.
5. Group 11 Cu, Ag & Au used as making of coins by Taksar that's why they are called coinage metal.
6. V₂O₅, making of H₂SO₄ from SO₂.
7. TiCl₄ + Al(CH₃)₃ combine & called Ziegler-Natta catalyst which is used in making of polyethene.
8. Iron catalyst is used as conversion of ammonia from H₂ & N₂ that Haber's process.
9. PdCl₂ convert ethyne to ethanal called Wacker's process.
10. Nickel complex used as polymerization of alkynes & benzene.
11. AgBr used to in making films and light sensitive device in photography industries.

Questions

a. Match the catalyst with the process

CATALYST

PROCESS

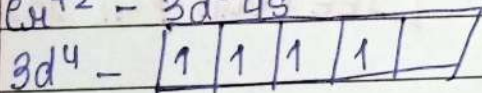
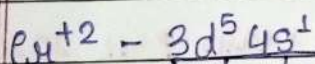
- | | |
|--------------------------|--|
| 1. V_2O_5 | i. The oxidation of ethyne to ethanal |
| 2. $TiCl_4 + Al(CH_3)_3$ | ii. Polymerisation of alkynes |
| 3. $PdCl_2$ | iii. Oxidation of SO_2 in the manufacture of H_2SO_4 |
| 4. Nickel complexes | iv. Polymerisation of ethylene |
- which of the following is the correct option:

anso 1-iii, 2-iv, 3-i, 4-ii

Q. The calculated spin only magnetic moment of Cr^{2+} ion is -

[NEET (Sep.) 2020]

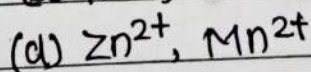
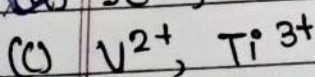
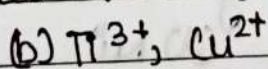
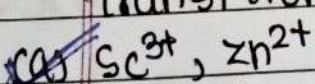
- (a) 4.90 BM (b) 5.92 BM (c) 2.84 BM (d) 3.87 BM.



$$n=4$$

$$\sqrt{4(4+2)} \text{ BM} = \sqrt{24} \text{ BM} = 5 \text{ BM} //$$

Q. In the following pair, the one in which both transition metal ions are colourless is:



[JEE Main P-11, 2022]

Ques. Which of the following 3d-metal ion will give the lowest enthalpy of hydration ($\Delta_{hyd} H$) when dissolved in water? [JEE main 2022]

- (a) Cr^{2+} d^4 - 40p (b) Mn^{2+} d^5 50p
(c) Fe^{2+} d^6 - 40p (d) Co^{2+} d^7 30p

Ques. Composition of gun metal is: [JEE main P-I, 2021]

- (a) Cu, Zn, Sn (b) Al, Mg, Mn, Cu
(c) Cu, Ni, Fe (d) Cu, Sn, Fe

Ques. Cast iron is used for the manufacture of: [JEE main P-II, 2020]

- (a) Wrought iron & steel
(b) Wrought iron, pig iron & steel.
(c) Wrought iron & pig iron
(d) pig iron, scrap iron & steel

Ques. The purest form of commercial iron is:

[JEE main P-II 2020]

- (a) Wrought iron
(b) scrap iron & pig iron
(c) pig iron
(d) Cast iron

Ques. Atomic radius of Ag is similar to: [JEE M (P-I) 2020]

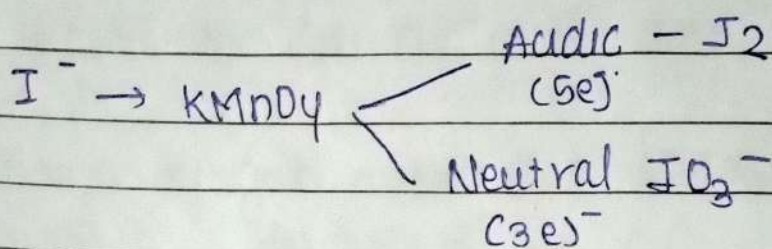
- (a) Cu (b) Hg (c) Au (d) Ni

Ques. Galvanization is applying a coating of: [JEE M 2016]

- (a) Pb (b) Cr (c) Cu (d) Zn

Que. When neutral or faintly alkaline KMnO_4 is treated with potassium iodide, iodide ion is converted into 'x.' x is:- [Neet 2019]

- a) I_2 (b) IO_4^- (c) IO_3^- (d) IO^-



Que. Match the columns metal ions given in column I with the spin magnetic moments of ion given in column II & assign the correct code [NEET 2018]

Column I	Column II
(1) $\text{Co}^{3+} \rightarrow d^6 - 4 \uparrow$	(i) $\sqrt{8} \text{ BM}$
(2) $\text{Cr}^{3+} \rightarrow d^3 - 3 \uparrow$	(ii) $\sqrt{35} \text{ BM}$
(3) $\text{Fe}^{3+} \rightarrow d^5 - 5 \uparrow$	(iii) $\sqrt{3} \text{ BM}$
(4) $\text{Ni}^{2+} \rightarrow d^8 - 2 \uparrow$	(iv) $\sqrt{24} \text{ BM}$
	(v) $\sqrt{15} \text{ BM}$

(a)

1	2	3	4
iv	i	ii	iii
iv	v	ii	i

(b)

1	2	3	4
i	ii	iii	iv
iii	v	i	ii

	U.P.
$\sqrt{3} \text{ BM}$	= 1
$\sqrt{8} \text{ BM}$	= 2
$\sqrt{15} \text{ BM}$	= 3
$\sqrt{24} \text{ BM}$	= 4
$\sqrt{35} \text{ BM}$	= 5

Ques. Which one of the following ions exhibits d-d transition & paramagnetism as well? [NEET 2018]

- (a) MnO_4^- (b) $\text{Cr}_2\text{O}_7^{2-}$ (c) CrO_4^{2-} (d) MnO_4^{2-}
- ↓ ↓ ↓ ↓
- $+7, d^0$ $+6, d^0$ $+6, d^0$ $+6, d^1$

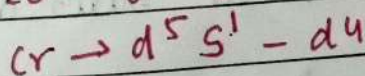
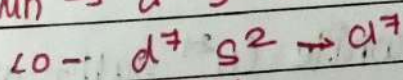
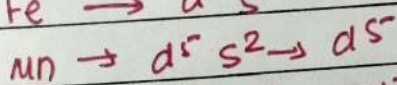
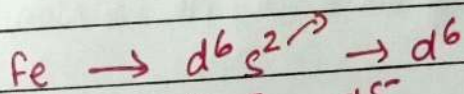
Ques. Magnetic moment 2.84 BM is given by [At. no. Ni = 28, Ti = 22, Cr = 24, Co = 27]. (AIPMT 2015, 14)

- (a) Ni^{2+} (b) Ti^{3+} (c) Cr^{3+} (d) Co^{2+}
- $d^8 s^2 \rightarrow 2 \text{ u.p.}$ $\sqrt{8} = 2 \text{ u.p.}$

Ques. for the 4 successive transition elements (Cr, Mn, Fe & Co) the stability of $+2$ oxidation state will be there in which of the following order? [AIPMT 2011]

(At. no. Cr = 24, Mn = 25, Fe = 26, Co = 27)

- (a) $\text{Fe} > \text{Mn} > \text{Co} > \text{Cr}$
- (b) $\text{Co} > \text{Mn} > \text{Fe} > \text{Cr}$
- (c) $\text{Cr} > \text{Mn} > \text{Co} > \text{Fe}$
- (d) $\text{Mn} > \text{Fe} > \text{Cr} > \text{Co}$



Ques. Which one of the following ions has e^- configuration $[Ar] 3d^6$?

[At no Mn = 25, Fe = 26, Co = 27, Ni = 28]

[AIPMT 2010]

- (a) Ni^{3+} $\downarrow$ $d^5 s^2 \rightarrow d^7$ (b) Mn^{3+} $\downarrow$ $d^5 s^2 \rightarrow d^4$ (c) Fe^{3+} $\downarrow$ $d^6 s^2 \rightarrow d^5$ (d) Co^{3+} $\downarrow$ $d^7 s^2 \rightarrow d^6$

Ques. Which of the following pairs both the ions coloured in aqueous solⁿ?

At no. - Sc = 21, Ti = 22, Ni = 28, Cu = 29, Co = 27

- (a) Ni^{2+}, Ti^{3+} (b) Sc^{3+}, Ti^{3+}
(c) Sc^{3+}, Co^{2+} (d) Ni^{2+}, Cu^{+}

Ques. On what ground can you say that Scandium ($Z = 21$) is transition element but zinc ($Z = 30$) is not.

$\{ Sc^{+2}, Sc^{+3} \}$ - multiple o. no. = Transition
 $Zn^{+2} \rightarrow$ only one o. no. = Non Transition

Zn^{2+} salts are white while Cu^{2+} salts are coloured why?

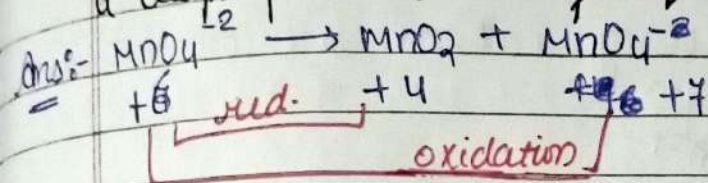
$Zn^{2+} \rightarrow d^{10} \rightarrow$ paired - colourless
 $Cu^{2+} \rightarrow d^9 \rightarrow$ unpaired - colourfull.

Ques. Explain giving reasons:

Transition metals & their compounds generally exhibit a paramagnetic behaviour.

Ans: $d^0 - d^{10}$ - only condition of diamagnetic rest all are paramagnetic.

Ques. What is meant by disproportion? Give example of a disproportion rxn in aqueous soln.



= when one element has 3 oxidation no. & the same element's oxidation & reduction will take place that is disproportion rxn.

Ques. Assign a reason for each of the following

(i) Transition metals (with the exception of Zn, Cd & Hg) are hard & high melting & boiling point.

Ans: due to lot of unpaired electrons in d-orbital

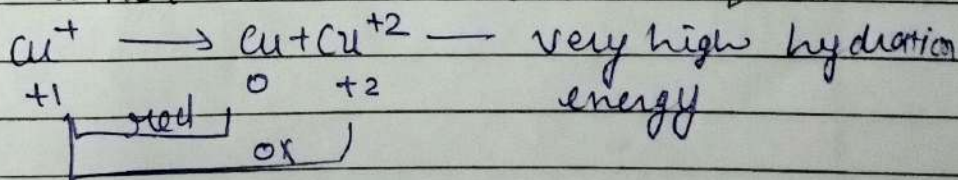
(ii) The ionization enthalpies (1st & 2nd) in the first series the transition elements are found to vary irregularly.

= d^5 & d^{10} configuration

size $\rightarrow \downarrow \text{Mn} \rightarrow \text{Fe} - \text{Ni same}, \text{Cu same Zn} \uparrow$

Ques. Assign the reasons

(i) CuCl is not known to exist in aqueous soln.



(2) Transition elements are much harder than the alkali metals.

volume ↓ density ↑

Que. (i) which metal in first transition series (3d-series) exhibits +1 oxidation state most frequently & why?

→ $\text{Cu}^+ \rightarrow d^{10}s^1 \rightarrow d^{10}$ - stable configuration.

(ii) which of the following cations are coloured in aqueous solⁿ & why?

$\text{Sc}^{3+}, \text{V}^{3+}, \text{Tl}^+, \text{Mn}^{2+}$

$d^0 \quad d^1 \quad d^0 \quad | \text{d-d trans. of}$
Al. Cr. Cl

Que. Give reason

(1) $\text{Sc}(21)$ is transition element but $\text{Ca}(20)$ is not.

(1) d^1 last electron / d end

(2) Ca d not present, $\text{Sc} \begin{matrix} +2 \\ +3 \end{matrix}$
 Ti^{+2}

(ii) The Fe^{2+} is much more easily oxidised to Fe^{3+} than Mn^{2+} to Mn^{3+}

d^5 stable

Que compare the chemistry of the actinoids with that of lanthanoids with reference to

- (1) electronic configuration
- (2) oxidation states
- (3) chemical reactivity

Ans: (1) $\text{La} \rightarrow 6s^{0-2} 5d^{0-1} 4f^{1-14} \rightarrow 4f^{1-14}, 5d^{0-1}, 6s^{0-2}$
 $\text{Ac} \rightarrow 7s^{0-2} 6d^{0-1} 5f^{1-14} \rightarrow 5f^{1-14}, 6d^{0-1}, 7s^{0-2}$

(2) $\text{La}^{+2}, +3, +4$

$\text{Ac}^{+3}, +4$

(3) Both are highly reactive.

Que Why do actinoids show wide range of oxidation states? Write one similarity between the chemistry of lanthanoids and actinoids.

Ans: - The actinoid contraction is more than lanthanoid contraction coz 5f electron are more poorly shielding than 4f electron.
 Only magnetic property ^{& colour property} are same in lanthanoid & actinoid.

Que Explain giving reasons:

The chemistry of actinoids is not smooth that of lanthanoids.

- Ans:
- (1) Actinoid are radioactive.
 - (2) They are found in very trace amount in nature.
 - (3) They show very high oxidation number.

Que. How would you account for the following:
Actinoid contraction is greater than lanthanoid contraction.

The actinoid contraction is more than lanthanoid contraction because 5f electrons are more poorly shielding than 4f.

Que. Name an important alloy which contains some of the lanthanoid metals. Mention its two uses.

→ Misch metal → 95% La, 5% Th, trace of Ce, Pr, Al, Si

→ Uses:-

a) Magnesium based alloy which is used for making bullet, shield, lighter flint.

Que. What is lanthanoid contraction? What is its effect on the chemistry of the elements which follow the lanthanoid?

Ans: The steady decreases in the atomic & ionic radius of lanthanoid with increase in atomic no. is called lanthanoid contraction. It is caused due to the imperfect shielding of nuclear charge by 4f electrons.

The effect of on the chemistry of the lanthanoid contraction are size of (Zr), (Hf) are approximately same.

Que. Explain the following observations:

La^{3+} ($Z=57$) & Lu^{3+} ($Z=71$) do not show any colour in solutions.

$\text{La}^{3+} \rightarrow f^0$ configuration

$\text{Lu}^{3+} \rightarrow f^{14}$ configuration

all are pair

all are pair

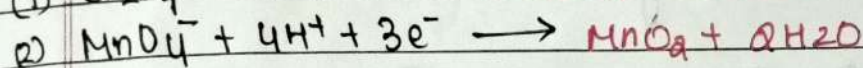
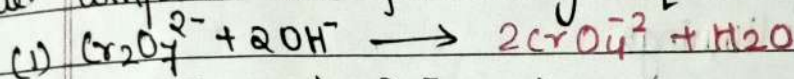
colourless

Que. Account for the following:

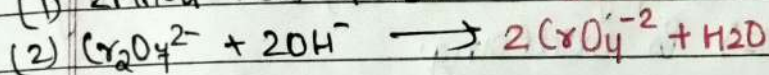
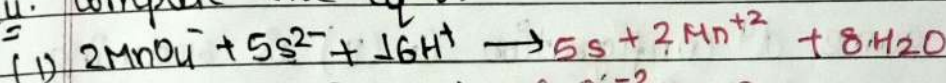
Zr & Hf have almost similar atomic radii.

Ans. due to the lanthanoid contraction.

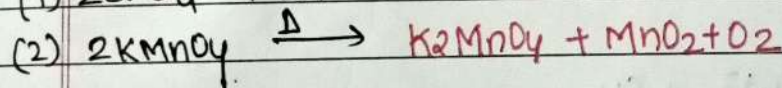
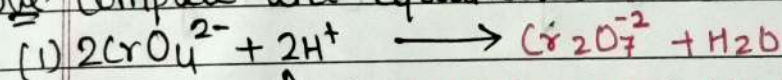
Que. Complete the following eqⁿs:-



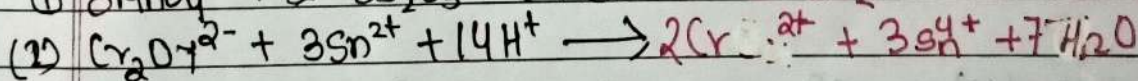
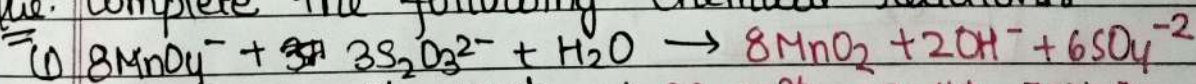
Que. Complete the eqⁿs:-



Que. Complete the equations:-



Que. Complete the following chemical reactions:



Que: Complete the following equations:-
 $2\text{MnO}_4^- + 6\text{H}^+ + 5\text{NO}_2^- \rightarrow 5\text{NO}_3^- + 3\text{H}_2\text{O} + 2\text{Mn}^{+2}$

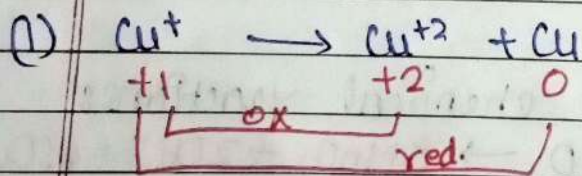
Que: Complete the following eq^s :-
 $3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow \text{Mn}^{+2} + 2\text{MnO}_4^- + 2\text{H}_2\text{O} + \text{O}_2$

Que:- Complete the following eqⁿ -
 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{+2} + 4\text{H}_2\text{O}$

Que: Complete the following
 $\text{SO}_2 + \text{MnO}_4^- + \text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + \text{Mn}^{+2} + 2\text{H}^+$

Que: Explain the following:

- (1) Copper(I) ion is not stable in an aqueous solⁿ.
- (2) With same d^4 configuration Cr(II) is reducing whereas Mn(III) is oxidising.
- (3) Transition metals in general act as good catalyst.



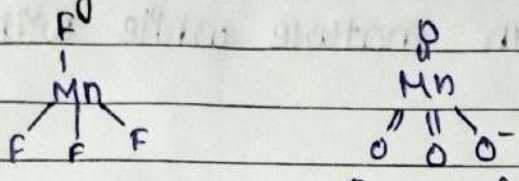
(2) $\text{Cr(II)} - E^\circ = -\text{ve}$, $\therefore$ reducing agent, Mn(III) is oxidizing agent

(3) catalyst $\left\{ \begin{array}{l} \text{variable oxidation no.} \\ \text{provide surface to reactant.} \end{array} \right.$

Que. Account for the following:-

(1) Mn shows the highest oxidation state of +7 with oxygen but with fluorine, P shows the highest oxidation state of +4.

Ans.



- The valency of F is 1 & max. capacity to hold element by Mn are 4.
- The valency of O are 2. That's why Mn show +7 oxidation state oxygen & with +4 with F.

(2) Cr^{2+} is strong reducing agent.

(2) Cr^{+2} are strong reducing agent coz P.S. of Cr^{+2} is -ve

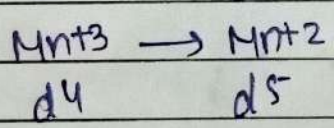
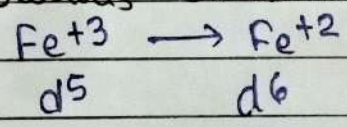
(3) Cu^{2+} salts are produced coloured, while Zn^{+2} are white.

(3) Cu^{2+} have d^9 configuration with one unpaired e^- that's why it's is colourfull d^{10} configuration of Zn^{+2} that's why it is colourless.

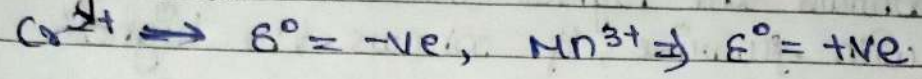
Que Account the following:-

(1) Mn^{+2} compounds are more stable than Fe^{2+} compound towards oxidation to their +3 state.

Ans.



(2) Cr^{2+} is reducing & Mn^{3+} oxidizing when both have d^4 configuration



Que. Cr^{2+} is reducing in nature while with the same d-orbital configuration (d^4) Mn^{3+} is an oxidizing agent

Que. In transition series of metal, the metal which exhibits states occurs in the middle of the series. Middle element contains lot of u.p. electron. Thus why they show max. O.S.
egs- Mn, Os, Ru