

d- and f- block elements

d-Block elements

Those elements in which the last e^- enters in the d-subshell of penultimate shell

General Electronic Configuration $\rightarrow (n-1)d^{1-10} ns^{0-2}$

Periodic Table of the Elements

1 IA 1A																	18 VIIIA 8A
1 H Hydrogen 1.008	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.906	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.905	54 Xe Xenon 131.29
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71 Lanthanide Series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.222	78 Pt Platinum 195.084	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine [210]	86 Rn Radon [222]
87 Fr Francium [223]	88 Ra Radium [226]	89-103 Actinide Series	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [277]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [285]	111 Rg Roentgenium [282]	112 Cn Copernicium [285]	113 Nh Nihonium [284]	114 Fl Flerovium [289]	115 Mc Moscovium [288]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]
		57 La Lanthanum 138.905	58 Ce Cerium 140.12	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium [145]	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.930	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.967	
		89 Ac Actinium [227]	90 Th Thorium 232.038	91 Pa Protactinium [231]	92 U Uranium 238.029	93 Np Neptunium [237]	94 Pu Plutonium [244]	95 Am Americium [243]	96 Cm Curium [247]	97 Bk Berkelium [247]	98 Cf Californium [251]	99 Es Einsteinium [252]	100 Fm Fermium [257]	101 Md Mendelevium [258]	102 No Nobelium [259]	103 Lr Lawrencium [260]	

They are subdivided into four series.

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn

→ The d-block elements in which the atoms or ions have incomplete d-orbitals are called transition elements.

→ Zn, Cd and Hg have completely filled (n-1) d-orbitals so they do not show much resemblance with other transition elements.

↳ There are four series of d-block elements.

3d Series (Sc to Zn)

4d Series (Y to Cd)

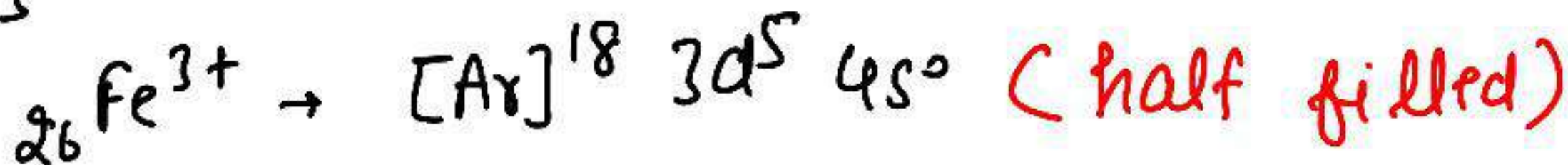
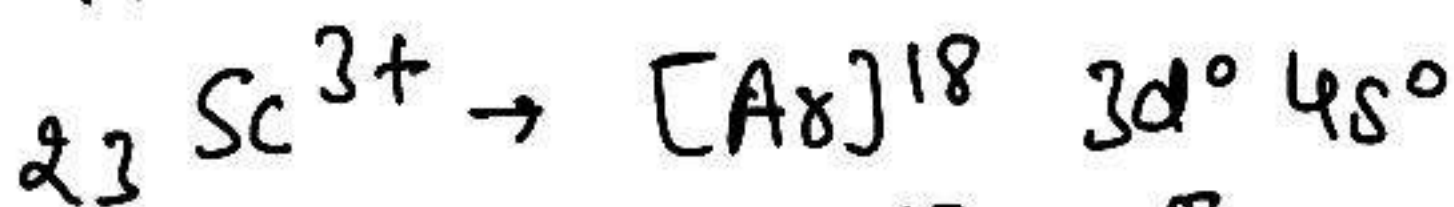
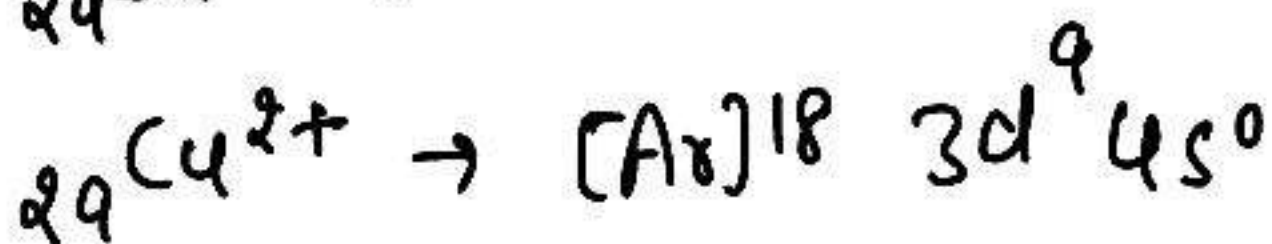
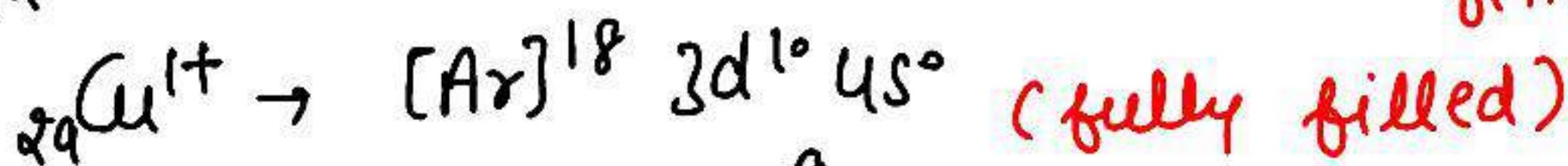
5d Series (La and Hf to Hg)

6d Series (Ac and Rf to U)

Electronic Configuration:

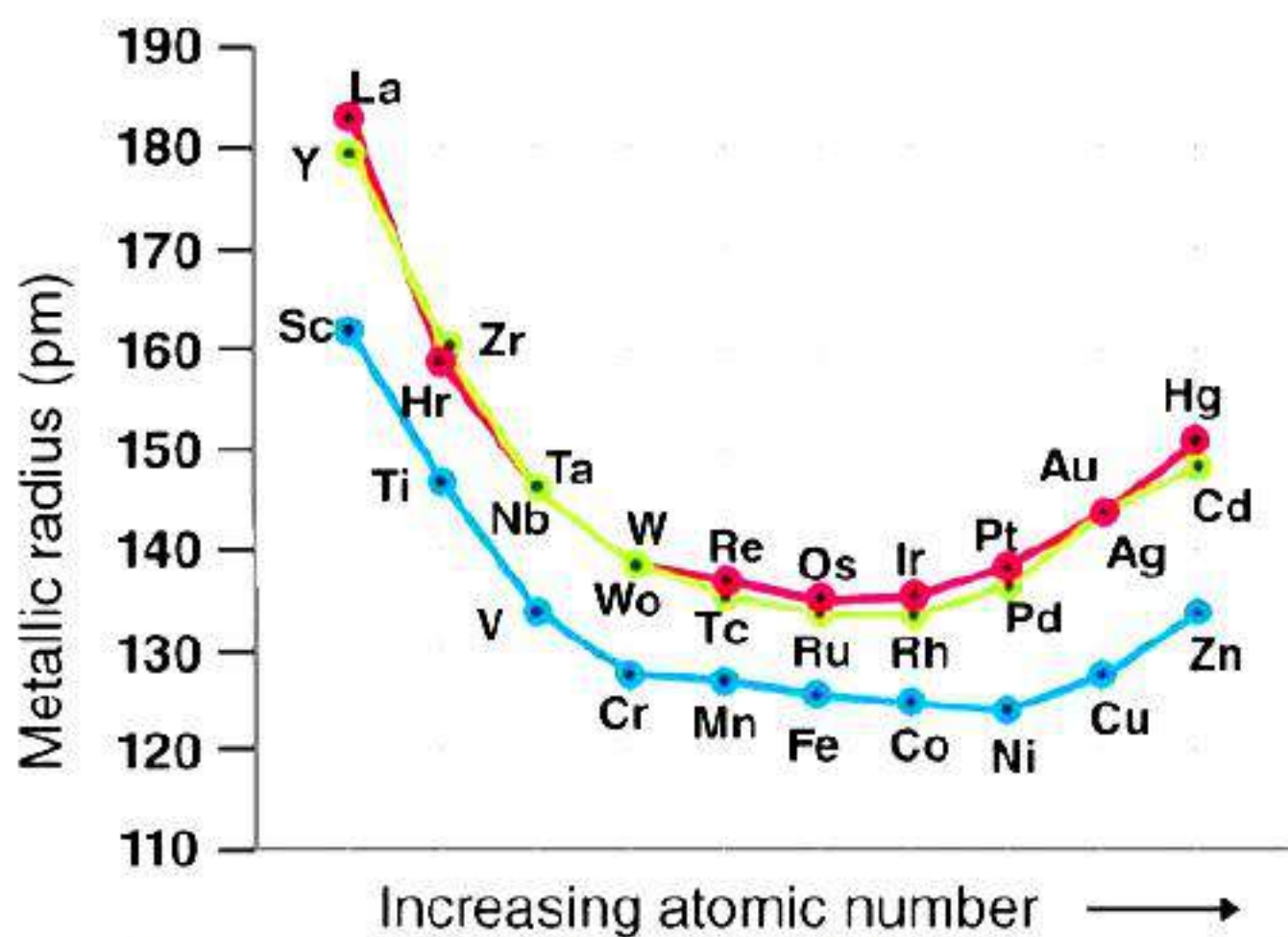
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21. Sc - Scandium	$[\text{Ar}]^{18} 3d^1 4s^2$
22. Ti - Titanium	$[\text{Ar}]^{18} 3d^2 4s^2$
23. V - Vanadium	$[\text{Ar}]^{18} 3d^3 4s^2$
24. Cr - Chromium	$[\text{Ar}]^{18} 3d^5 4s^1$
25. Mn - Manganese	$[\text{Ar}]^{18} 3d^5 4s^2$
26. Fe - Iron	$[\text{Ar}]^{18} 3d^6 4s^2$
27. Co - Cobalt	$[\text{Ar}]^{18} 3d^7 4s^2$
28. Ni - Nickel	$[\text{Ar}]^{18} 3d^8 4s^2$
29. Cu - Copper	$[\text{Ar}]^{18} 3d^{10} 4s^1$
30. Zn - Zinc	$[\text{Ar}]^{18} 3d^{10} 4s^2$



Atomic Radius

As we go from left to right, atomic radii first decrease largely, then decrease slowly and increase in the end of the series.



This decrease in atomic radii in the beginning is due to the increase in effective nuclear charge with the increase in atomic number.

With the increase in number of e^- in $(n-1)d$ subshell the screening effect of these d -electrons on the outermost ns -electrons also increases. This increased screening effect counterbalances the effect of increased nuclear charge, therefore the atomic radii remains almost same.

In the end of the series $e^- - e^-$ repulsion takes place so the size of atom increases.

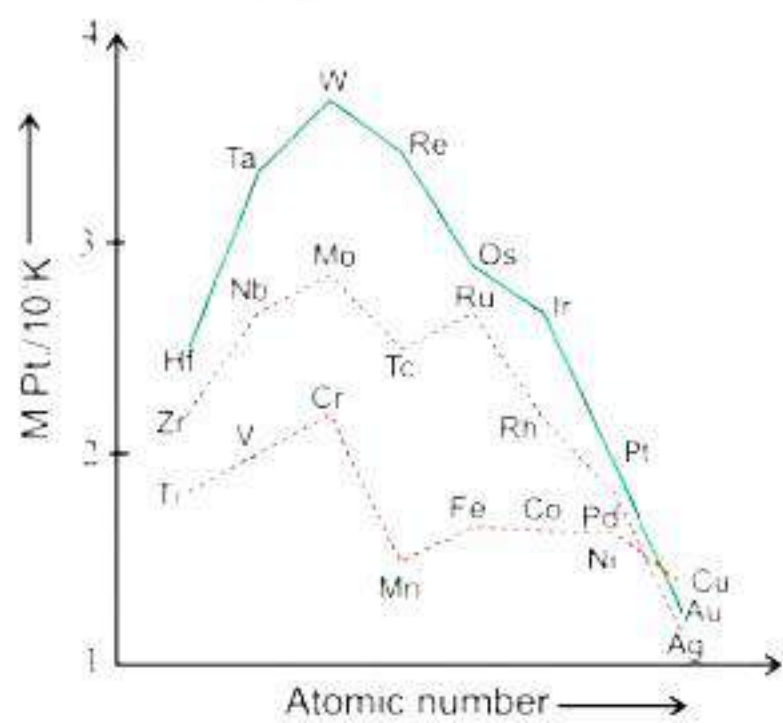
IONIC RADIUS

In general, ions of the same oxidation state in a given series show progressive decrease in radius with increase in atomic number due to the increase in effective nuclear charge.

Ionic Radius $\propto \frac{1}{\text{Oxi. State}}$ [ionic radii $Fe^{2+} > Fe^{3+}$]

Melting and Boiling Point

High m.pt and B.pt



First increase and then decrease due to increase and decrease in number of unpaired electrons because the strength of bond depends on number of unpaired e^- .

Note

→ Tungsten (W) has the highest m.p.t

→ Mercury (Hg) is the only metal in liquid form.

Metallic Character

- Show all the properties of general metals.
- Strength of metallic bond \propto number of unpaired e^- which increase the chance and make the bond strong.
- Cr is a hard metal while Zn is a soft metal.

Enthalpy of Atomisation:

They have strong metallic bond due to which they have high enthalpy of atomization

Ionisation Energy:-

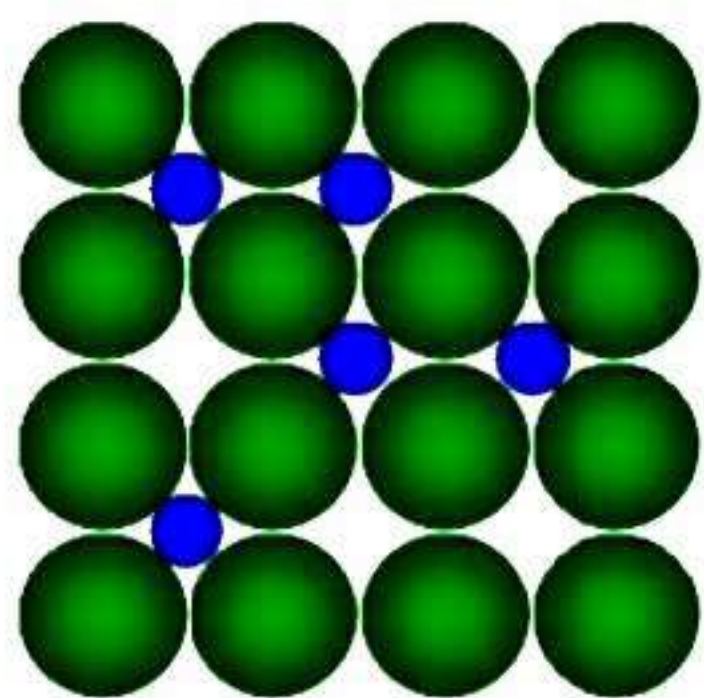
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Lies b/w s- and d-block elements (more than s-block but less than d-block elements)
I.E increases from left to right in a period as the effective nuclear charge increases.

$I.E \propto$ Effective Nuclear charge

- I.E of Zn, Cd and Hg is very high due to fully filled orbitals
- I.E of 5d and 6d series elements is more than 3d and 4d elements due to lanthanide and Actinide contraction.

Formation of Interstitial Compounds:-



Transition metals have a tendency to form interstitial compounds with H, C, B or N atoms.

They are usually non-stoichiometric and are neither typically ionic nor covalent.

e.g. TiC , Mn_4N , Fe_3N , $VH_{0.56}$ and $TiH_{1.7}$ etc

→ The interstitial compounds are very hard, retain metallic conductivity, have high m.pt and are chemically inert.

Alloy Formation :-

Alloys are homogeneous solid solution. Many of d-block elements form alloys because they have similar atomic radii due to which they can easily replace the atom of other metal.

Alloys thus formed and often have high m.pt.

e.g. Brass (Cu + Zn) & Bronze (Cu + Sn)

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Magnetic Properties :-

Diamagnetic substances are repelled by magnetic field while paramagnetic substances are attracted by magnetic field.

→ Those substance which are attracted very strongly by the applied field are called **ferromagnetic**

Many of the d-block elements and their compounds are paramagnetic in nature it is due to the presence of unpaired e^- in incomplete d-orbitals

→ The paramagnetic nature of no. of unpaired e^-

$$\text{Magnetic moment } (\mu) = \sqrt{n(n+2)} \quad \text{B.M}$$

n is number of unpaired e^-

↓
Bohr
Magneton

Complex Formation:-

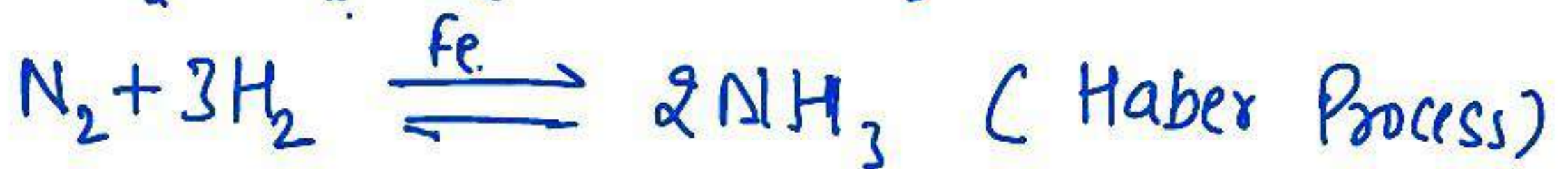
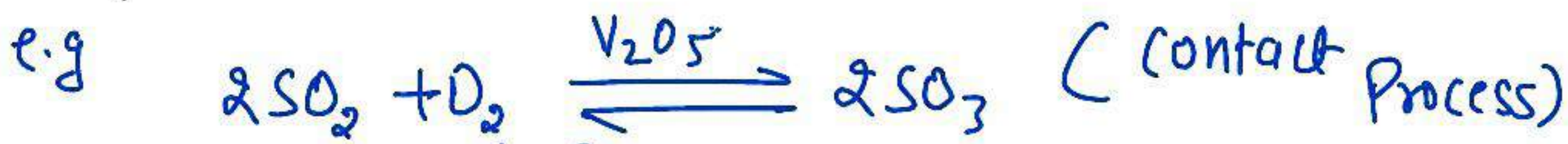
Many of d-block elements form complex compounds. because

- (i) They have small atomic radii
- (ii) High Nuclear charge
- (iii) Presence of vacant d-orbital so they can accept lone pair of e^- from ligands.

Catalytic Properties:-

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Transition elements and their compounds show catalytic properties due to variable oxidation state and their ability to adopt multiple oxidation state.



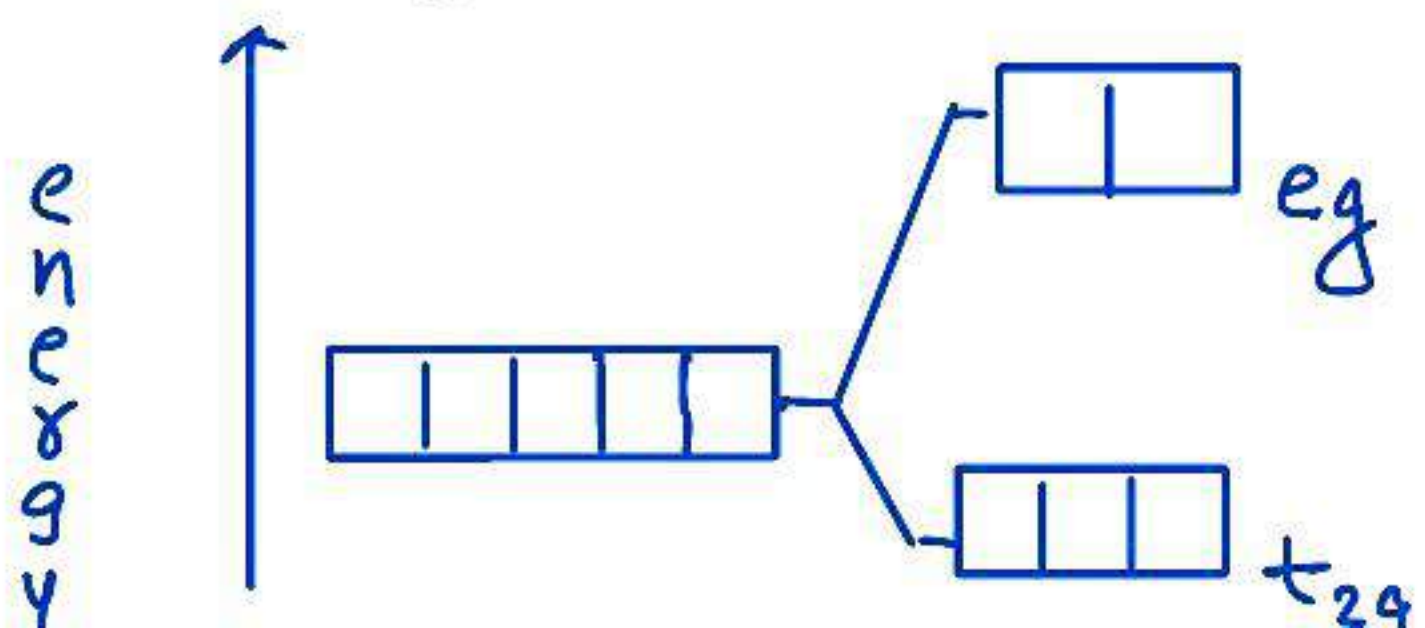
The presence of unpaired e^- 's in incomplete d-orbitals, hence possess the capacity to absorb and re-emit wide range of energies which is used as an activation energy.

Formation Of Coloured Ions:-

• if unpaired e^- is present, complex is coloured due to d-d transition and also paramagnetic in nature

if unpaired e^- is absent, complex or compound is due to the absence of d-d transition and diamagnetic in nature

e.g $CuSO_4$ is blue in colour while $ZnSO_4$ is colourless

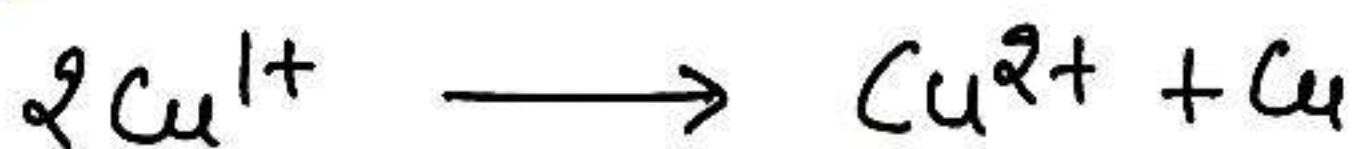


Oxidation State:-

Show large number of oxidation state due to the participation of both $(n-1)d$ and ns electrons in bonding in different compounds.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+1	+2
+3	+3	+3	+3	+3	+3	+3	+3	+2	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

- Mn shows maximum number of oxidation state due to the presence of maximum number of unpaired e^-
- Osmium (Os) show +8 oxidation state
- Cu^{2+} is more stable than Cu^+ because it undergoes disproportionation Reaction in aqueous soln



NOTE The ability of oxygen to stabilise these high oxidation state exceeds that of fluorine because oxygen can form double bond while fluorine form single bond.

As a result highest Mn fluoride is MnF_4 whereas the highest oxide is Mn_2O_7 .

Electrode Potential:-

The stability of a compound depends upon electrode potential and it further depends upon.

- (i) Enthalpy of atomisation/sublimation
- (ii) Ionisation enthalpy
- (iii) Hydration enthalpy

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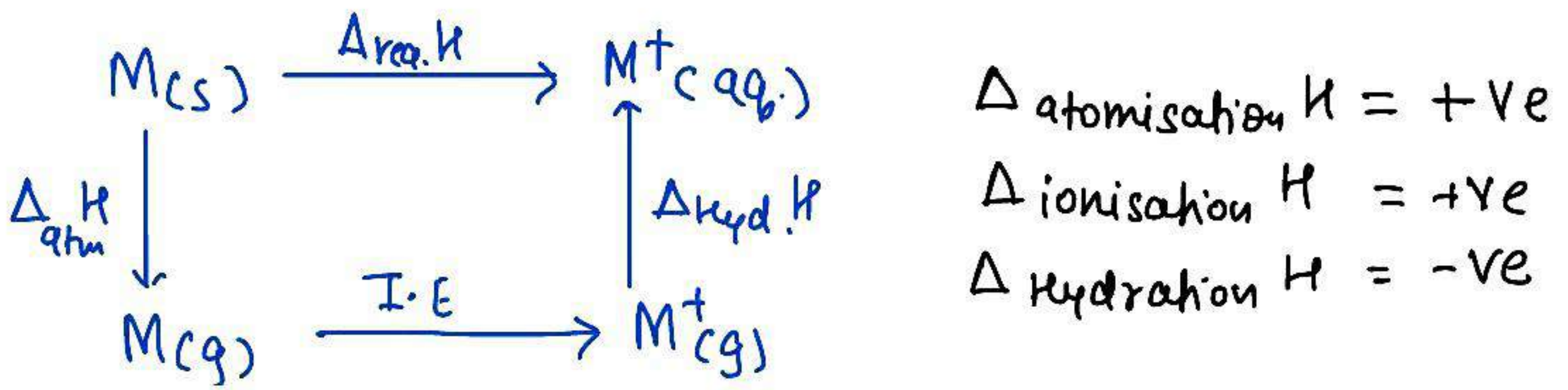


Table 8.4: Thermochemical data (kJ mol^{-1}) for the first row Transition Elements and the Standard Electrode Potentials for the Reduction of M^{II} to M .

Element (M)	$\Delta_{\text{atm}} H^\circ (M)$	$\Delta_1 H_1^\circ$	$\Delta_1 H_2^\circ$	$\Delta_{\text{hyd}} H^\circ (M^{2+})$	E° / V
Ti	469	661	1310	-1866	-1.63
V	515	648	1370	-1895	-1.18
Cr	398	653	1590	-1925	-0.90
Mn	279	716	1510	-1862	-1.18
Fe	418	762	1560	-1998	-0.44
Co	427	757	1640	-2079	-0.28
Ni	431	736	1750	-2121	-0.25
Cu	339	745	1960	-2121	0.34
Zn	130	908	1730	-2059	-0.76

There is no regular trend for M^{2+}/M standard electrode potential due to the irregularities in ionisation enthalpies and enthalpy of atomisation

→ Copper is the only metal having positive value of E° so it does not liberate the hydrogen gas from acids

Chemical Reactivity:-

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$$\text{chemical reactivity} \propto \frac{1}{E^\circ}$$

- $E^\circ (M^{2+}/M)$ is very less (more -ve) except Cu so these metals are highly reactive
- Oxidising power $\propto E^\circ$
- Reducing power $\propto \frac{1}{E^\circ}$

Oxide Formation:-

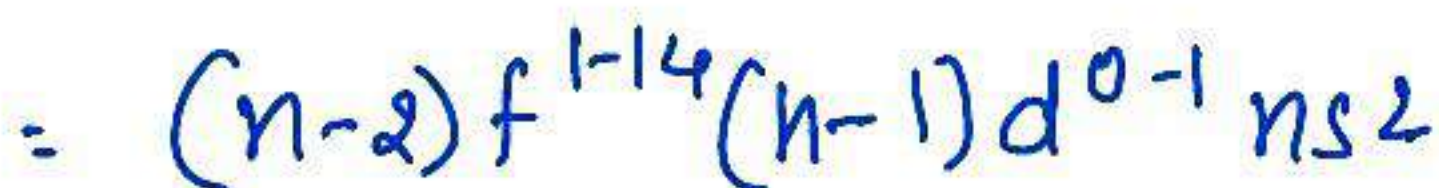
Many of the d-block elements form oxides of different types because of the presence of so many different oxidation states.

Note Acidic character \propto Oxi. State
Ionic character \propto Oxi. State.

f-Block Elements :-

Elements in which last e⁻ enters in f-orbital of pre-penultimate shell

General Electronic Configuration



57 138,9 La lantani	58 140,1 Ce ceri	59 140,9 Pr praseodimi	60 144,2 Nd neodimi	61 [145] Pm prometi	62 150,4 Sm samari	63 152,0 Eu europi	64 157,3 Gd gadolini	65 158,9 Tb terbi	66 162,5 Dy disprosi	67 164,9 Ho holmi	68 167,3 Er erbi	69 168,9 Tm tuli	70 173,1 Yb iterbi	71 175,0 Lu luteci
89 [227] Ac actini	90 232,0 Th tori	91 231,0 Pa protactini	92 238,0 U urani	93 [237] Np neptuni	94 [244] Pu plutoni	95 [243] Am americ	96 [247] Cm curi	97 [247] Bk berkeli	98 [251] Cf californi	99 [252] Es einstein	100 [257] Fm fermi	101 [258] Md mendelevi	102 [259] No nobeli	103 [262] Lr lawrenci

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4f Series

OR

Lanthanoid Series

OR

1st Inner Transition Series

4f-block elements (lanthanides)

Valence shell electronic Configuration $4f^{0-14} 5d^{0-1} 6s^2$

57 La lanthanum 138.905 $4f^0 5d^1 6s^2$	58 Ce Cerium 140.116 $4f^1 5d^1 6s^2$	59 Pr Praseodymium 140.908 $4f^3 5d^0 6s^2$	60 Nd Neodymium 144.243 $4f^4 5d^0 6s^2$	61 Pm Promethium 144.913 $4f^5 5d^0 6s^2$	62 Sm Samarium 150.360 $4f^6 5d^0 6s^2$	63 Eu Europium 151.964 $4f^7 5d^0 6s^2$	64 Gd Gadolinium 157.250 $4f^7 5d^1 6s^2$
65 Tb Terbium 158.925 $4f^9 5d^0 6s^2$	66 Dy Dysprosium 162.500 $4f^{10} 5d^0 6s^2$	67 Ho Holmium 164.930 $4f^{11} 5d^0 6s^2$	68 Er Erbium 167.259 $4f^{12} 5d^0 6s^2$	69 Tm Thulium 168.934 $4f^{13} 5d^0 6s^2$	70 Yb Ytterbium 173.055 $4f^{14} 5d^0 6s^2$	71 Lu Lutetium 174.967 $4f^{14} 5d^1 6s^2$	

Oxidation State:-

The common oxidation state of lanthanoids is +3 with +2 and +4.

Electronic Configuration

General electronic configuration of lanthanoids are $6s^2 5d^{0-1} 4f^{1-14}$

→ Only Cerium, Gadolinium and Lutetium have e^- in $5d$ -orbital as well.

Name	Symbol	Atomic#	Electron configuration
Lanthanum	La	57	(Xe) $5d^1 6s^2$
Cerium	Ce	58	(Xe) $4f^1 5d^1 6s^2$
Praseodymium	Pr	59	(Xe) $4f^3 6s^2$
Neodymium	Nd	60	(Xe) $4f^4 6s^2$
Promethium	Pm	61	(Xe) $4f^5 6s^2$
Samarium	Sm	62	(Xe) $4f^6 6s^2$
Europium	Eu	63	(Xe) $4f^7 6s^2$
Gadolinium	Gd	64	(Xe) $4f^7 5d^1 6s^2$
Terbium	Tb	65	(Xe) $4f^9 6s^2$
Dysprosium	Dy	66	(Xe) $4f^{10} 6s^2$
Holmium	Ho	67	(Xe) $4f^{11} 6s^2$
Erbium	Er	68	(Xe) $4f^{12} 6s^2$
Thulium	Tm	69	(Xe) $4f^{13} 6s^2$
Ytterbium	Yb	70	(Xe) $4f^{14} 6s^2$
Lutetium	Lu	71	(Xe) $4f^{14} 5d^1 6s^2$

Atomic and Ionic Radii -

The atomic and ionic radii decreases from Lanthanum to Lutetium. Which is known as LANTHANOID CONTRACTION.

CAUSE -

In case of lanthanide series elements, the last e^- enters into the $4f$ -orbital. Since, the shielding or screening effect of "f-orbitals" is much less than 's' and 'p' orbital even less than that of d-orbital.

the effective nuclear charge increases by one at each step. Hence, the size of entire 4f subshell reduces.

CONSEQUENCES OF LANTHANOID CONTRACTION -

• Increase in Covalent character -

Covalent properties of lanthanide metal hydroxide compounds regularly increases according to Fajans Rule.

• Similar Size and Charge

Since all the lanthanide ions are of about the same size and also carry the same charge due to lanthanoid contraction, their properties are almost identical. This makes separation of lanthanides from one another is very difficult.

• Basic Character of Hydroxides of Lanthanoids

As we move from left to right basic character of hydroxides of lanthanoids decreases.

• Atomic and Ionic Radii of 4d & 5d Series

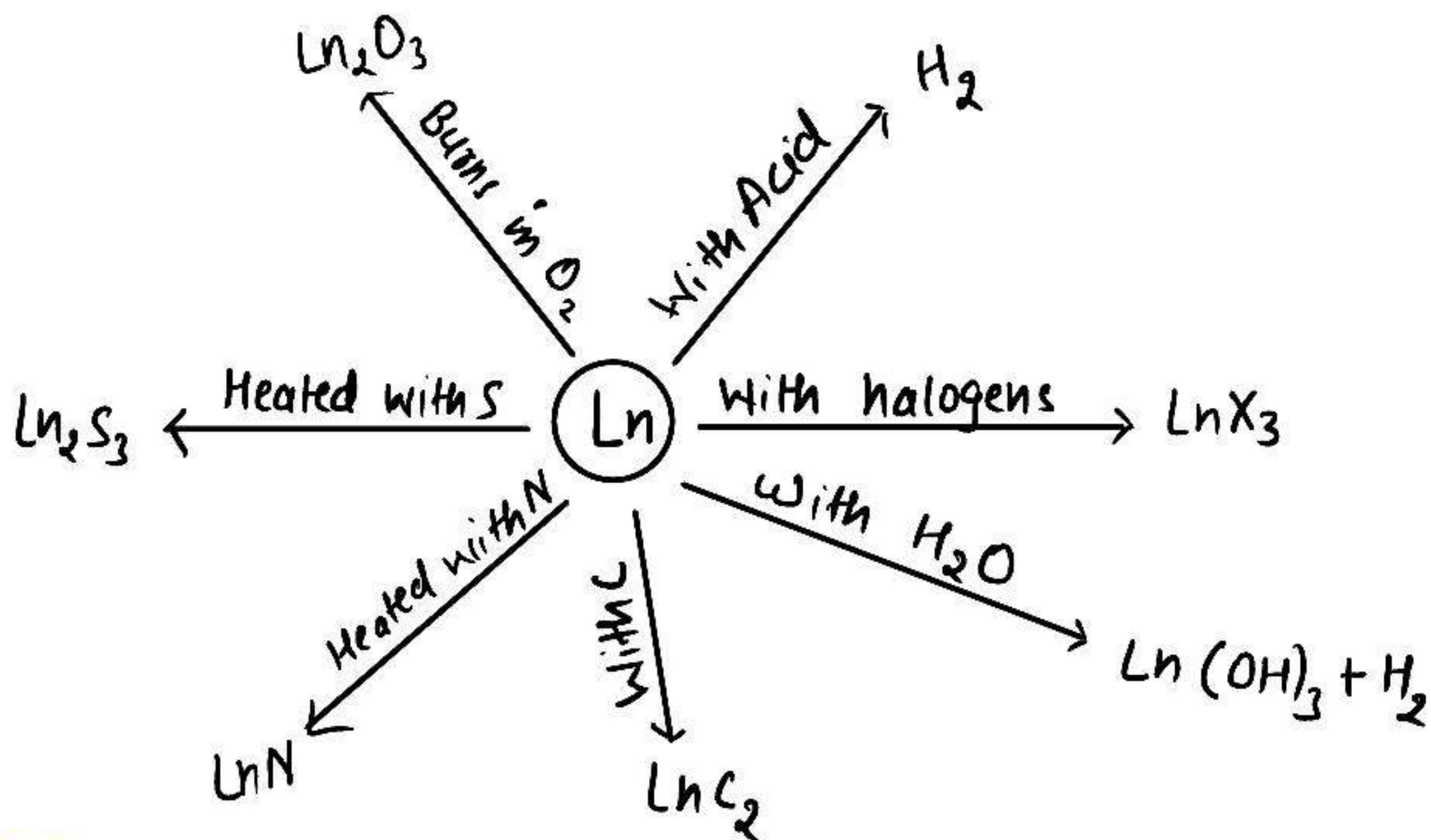
Due to lanthanide contraction, the atomic and ionic radii of the next and before on the lanthanide elements with same group

4d	Zr 145	Nb 134	Mo 129
5d	Hf 144	Ta 134	W 120

• The decrease in chemical reactivity

Due to lanthanoid contraction, the ionization energy of the next on the lanthanoid elements increases. This decreases their chemical reactivity.

Chemical Reactivity



Uses

- i) Lanthanoids are used for the production of alloy steels for plates and pipes.
- ii) Mischmetal alloy of lanthanoid is used in Mg-based alloy to produce bullets, shell and lighter flint.
- (iii) Mixed oxides of lanthanoids are used as catalyst in cracking of petroleum.
- (iv) Some lanthanum oxides are used as phosphorus in television screen.

ACTINIDS

These are the elements in which last e^- filled in $5f$ -orbitals. The actinoids are radioactive elements.

Electronic Configⁿ

The general electronic confi. $5f^{1-14}6d^{0-1}7s^2$

Irregularities in the electronic configuration of actinoids is due to stabilities of f^0, f^7, f^{14} occupancies of $5f$ -orbital.

Similarities btw Lanthanoids and Actinoids

- Both exhibit +3 oxidation state predominantly.
- Both are electropositive and have high reactivity.
- Like Lanthanoid contraction, there is actinoid contraction also.

Difference b/w Lanthanoids and Actinoids

Lanthanoids

- They show mainly +3 Oxi. State. +2 and +4 Oxidation State also exist
- They have poor shielding effect
- They are paramagnetic and their paramagnetic character can be explained easily
- They have less tendency to form complexes
- These are non-radioactive except promethium

Actinoids

- They show +3 Oxi. State. Higher oxidate like +4, +5, +6 and +7
- They have even poor shielding effect
- They are also paramagnetic but their magnetic character can't be explained easily
- They have more tendency to form complexes
- These are radioactive substance.

Application of Actinoids

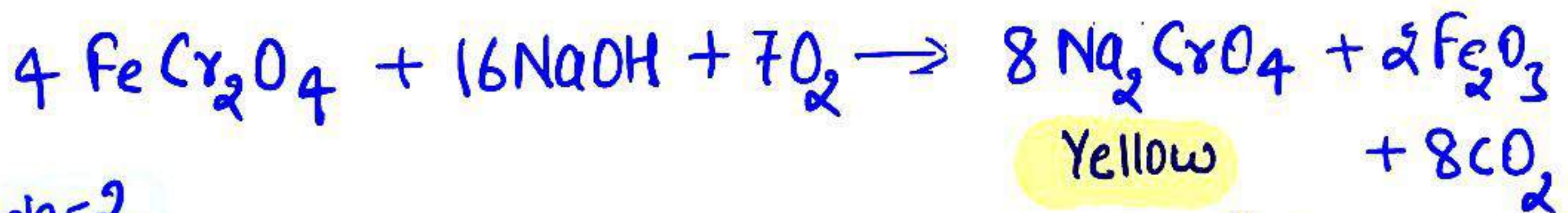
- Actinoids are used in nuclear reactors for the production of electricity.
- Actinoids are also used for the synthesis of transuranic elements.

COMPOUNDS OF TRANSITION ELEMENTS

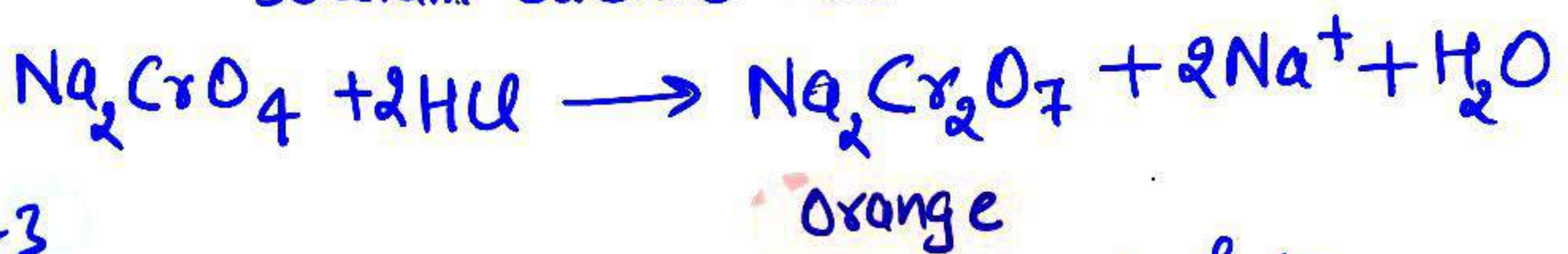
- Potassium Dichromate $(K_2Cr_2O_7)$
- Potassium Permanganate $(KMnO_4)$

→ Potassium Dichromate $(K_2Cr_2O_7)$ it is prepared from chromite ore

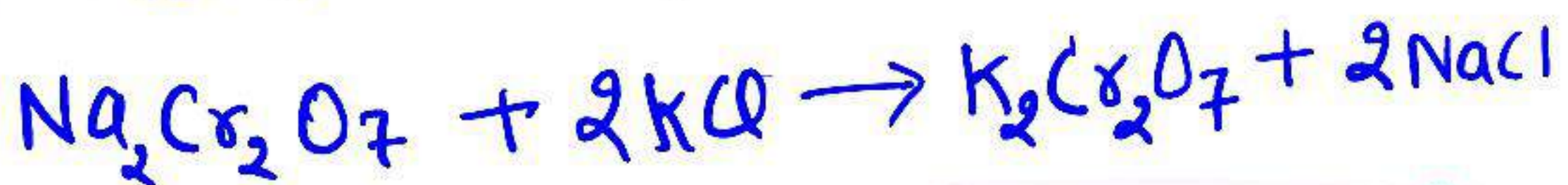
Step-1 Conversion of ferrochromite into sodium chromate



Step-2 Conversion of sodium chromate into sodium dichromate

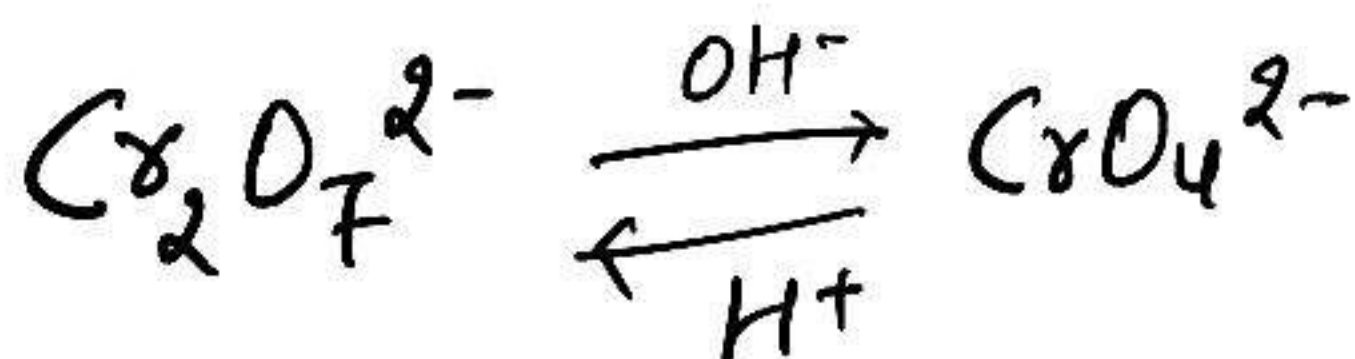


Step-3 Conversion of sodium dichromate into potassium dichromate



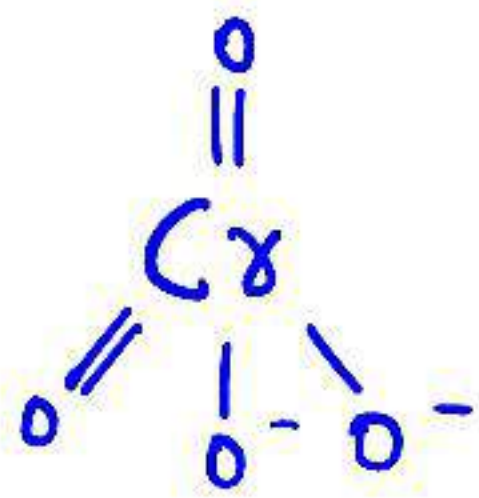
Orange Crystals

→ Chromates and dichromates are interconvertible

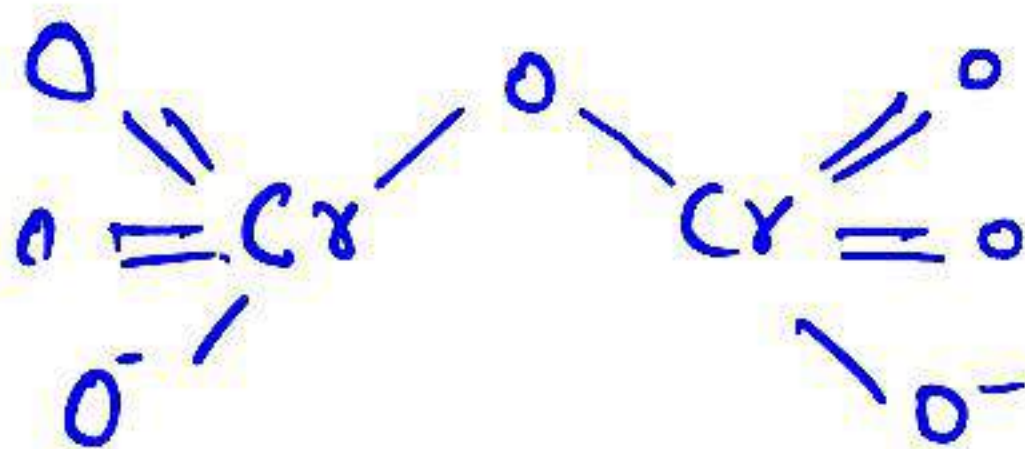


Structure..

chromate ion (CrO_4^{2-})



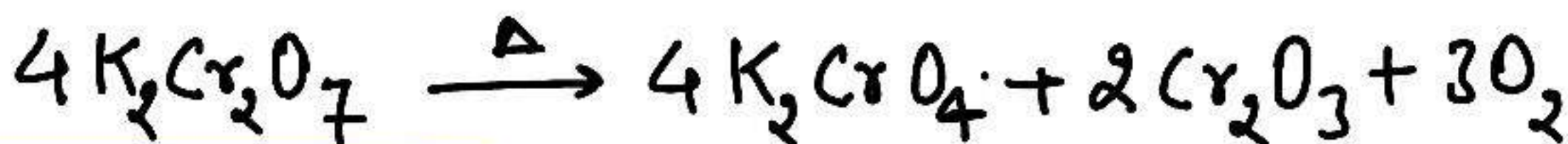
dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$)



Properties

1.) These are orange red crystals, moderately soluble in cold water but readily soluble in hot water

2.) Action of heat



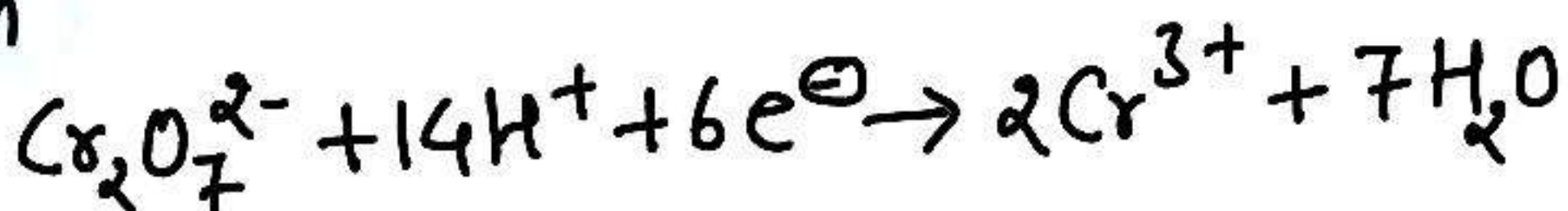
3.) Action of Alkali -



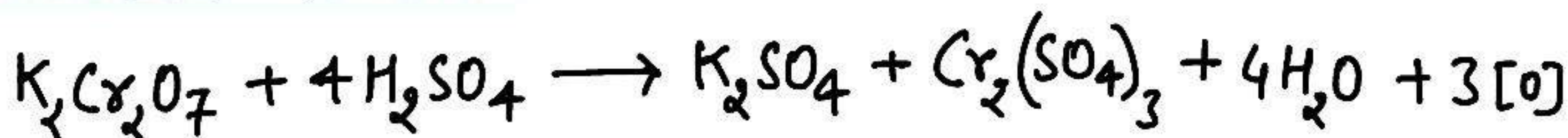
4.) Oxidising Property -

$\text{K}_2\text{Cr}_2\text{O}_7$ behave as a powerful oxidising agent in $\text{Cr}(\text{VI})$ is changed into $\text{Cr}(\text{III})$

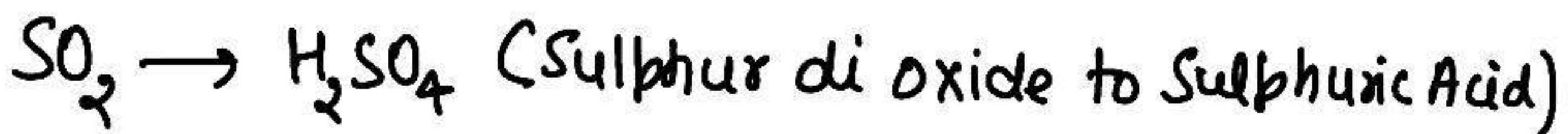
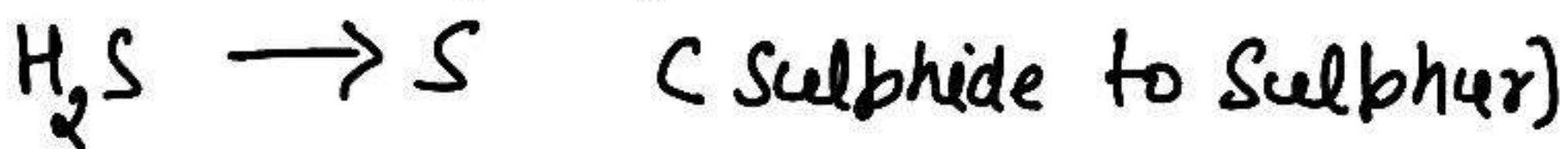
Ionic Reaction



Molecular Reaction

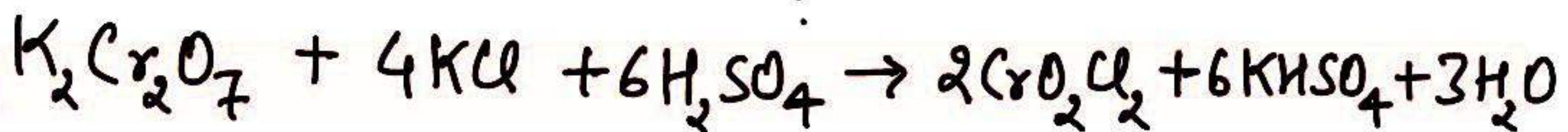


↳ It oxidise



→ CHROMYL CHLORIDE TEST

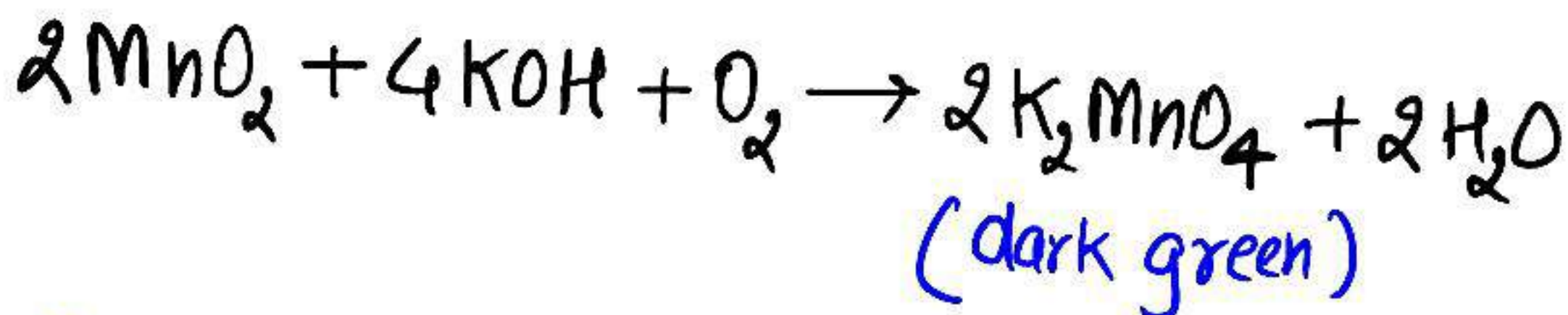
This test is done for the identification of Cl^- ions during salt analysis, potassium dichromate is heated with conc. H_2SO_4 and a salt having Cl^- (eg. $NaCl$, KCl) and reddish brown vapours of chromyl chloride are obtained.



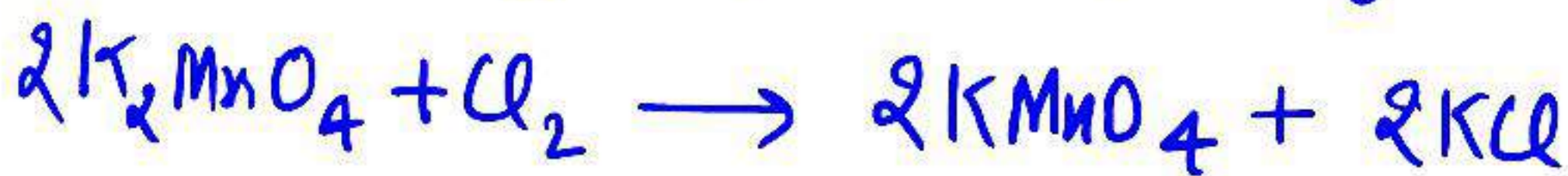
→ Potassium Permanganate (KMnO_4)

pyrolusite (MnO_2) ore. KMnO_4 is prepared from

↳ Pyrolusite (MnO_2) react with alkali metal hydroxide (KOH) to give potassium manganate



↳ Potassium manganate disproportionate in acid or alkali to give potassium permanganate

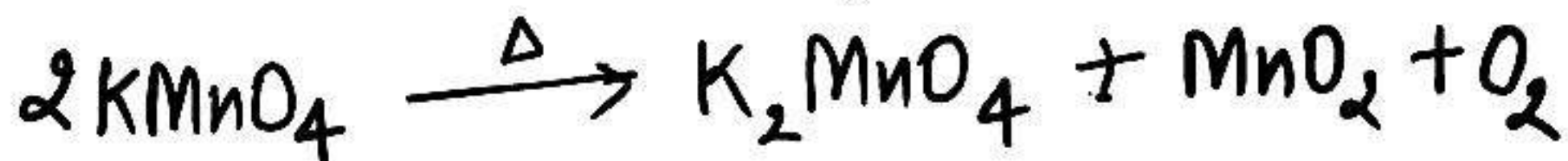


Properties

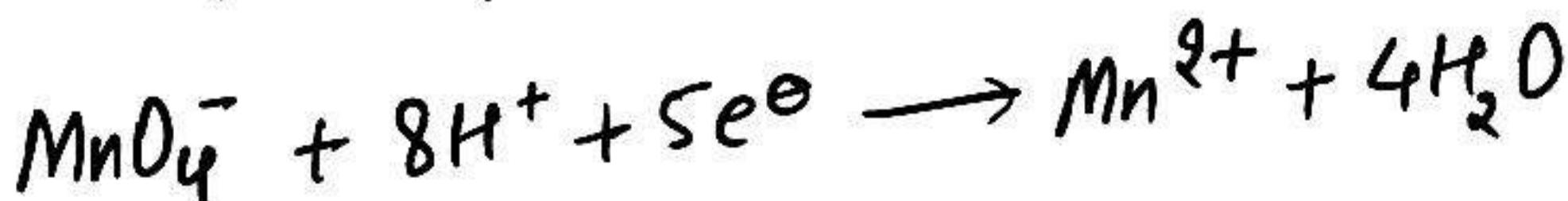
KMnO_4 is dark purple-black crystalline solid, soluble in warm water.

2.) Action of Heat -

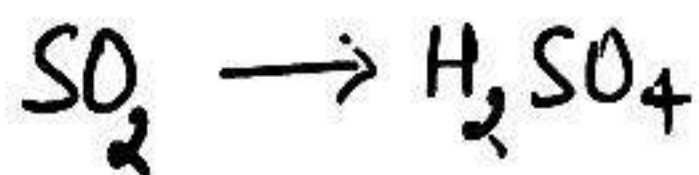
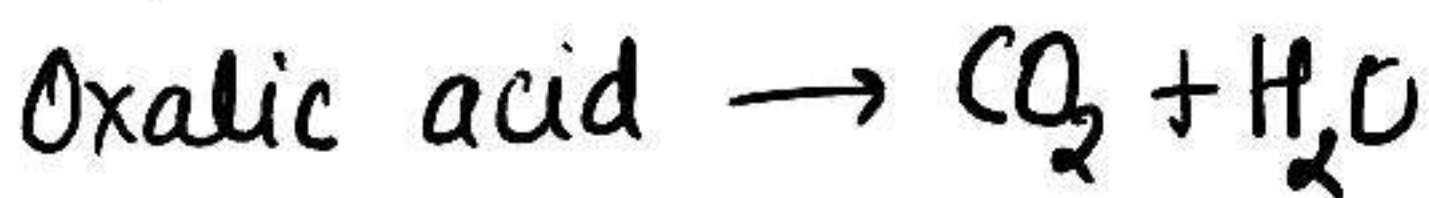
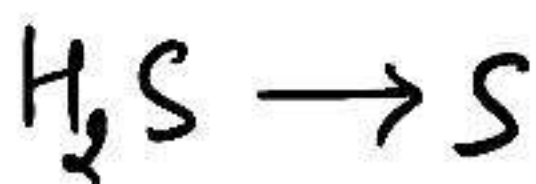
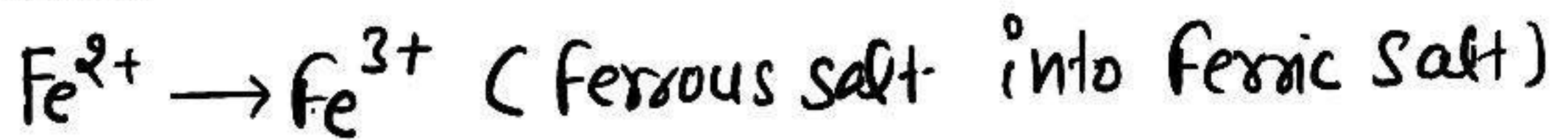
On heating, it decomposes



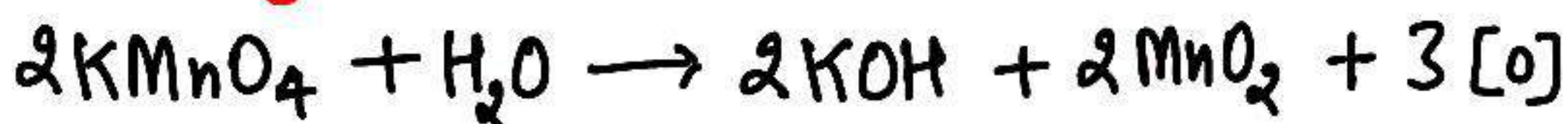
3.) In Acidic Medium



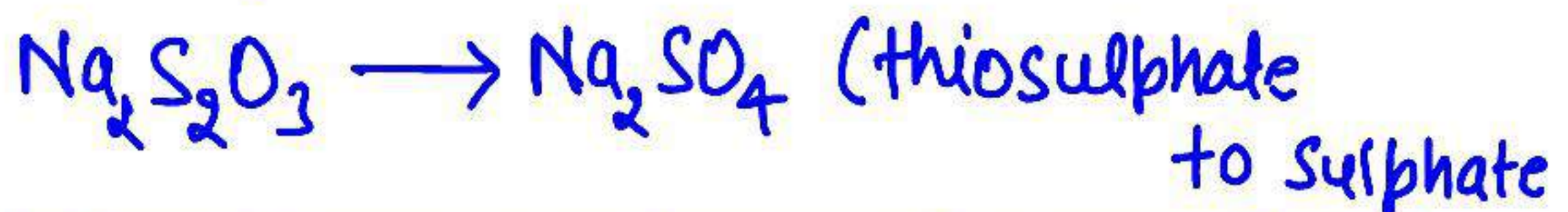
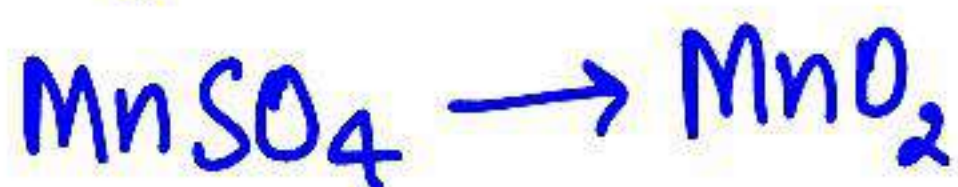
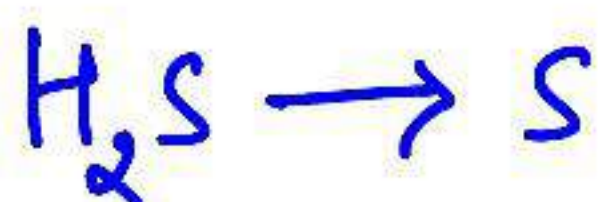
→ it oxidise



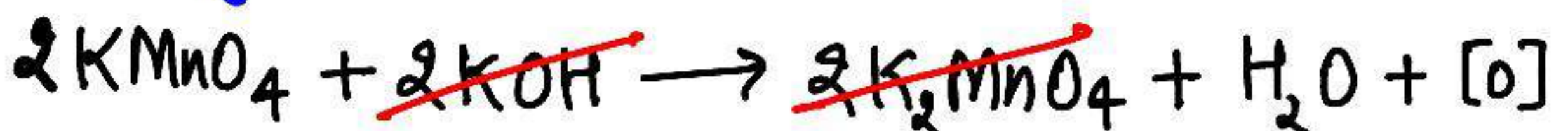
→ Oxidising Reactions in Neutral Medium...



→ It oxidise



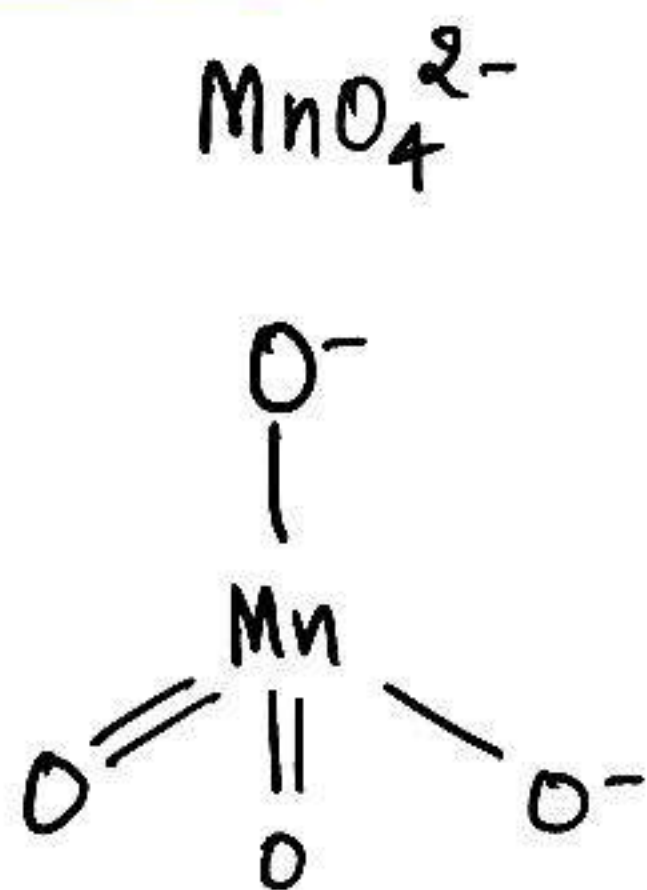
→ Oxidising Reactions in Alkaline Medium



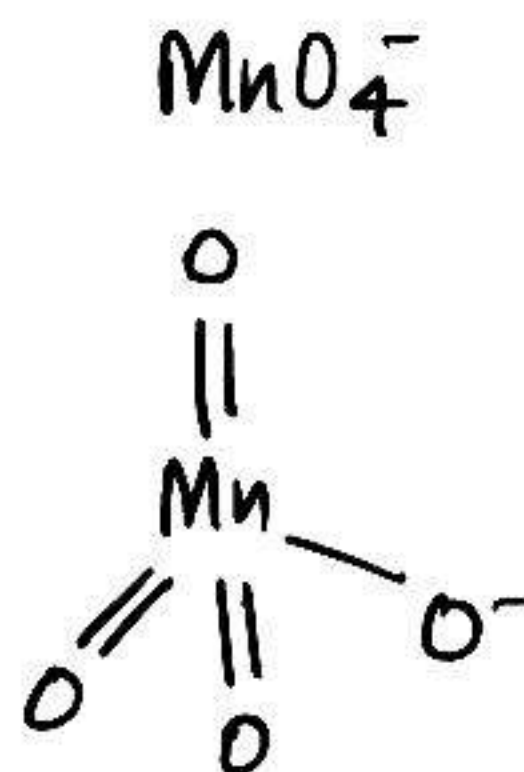
NOTE

The overall reactions in alkaline medium is same as in neutral medium.

Structure of



Tetrahedral manganate ion
(green) (paramagnetic)



Tetrahedral permanganate ion
purple (Diamagnetic)