Chapter 8

d-and f-Block Elements

General Properties of Transition Elements: The d & f- Block Elements

Transition Elements:

Definition: They are often called "transition elements" because their position in the periodic table is between s-block and p-block elements.
Typically, the transition elements have an incompletely filled d-level. Since Zn group has d^{10} configuration and are not considered as transition elements but they are d-block elements.

General Characteristics:

(i) Metallic character: They are all metals and good conductors of heat & electricity.
(ii) Electronic configuration: $(n-1)\,d^{1-10}ns^{1-2}$

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
other are as usual				$4s^1$ $3d^5$					$4s^1$ $3d^{10}$	

(iii) M.P.

$$\left.\begin{matrix}\mathrm{Cr}\\ \mathrm{Mo}\\ \mathrm{W}\end{matrix}\right\}\xrightarrow[\text{are involved inmetallic bonding}]{\text{Maximum}}\ \text{6 no. of unpaired } e^-\text{ s} \qquad \left.\begin{matrix}\mathrm{Zn}\\ \mathrm{Cd}\\ \mathrm{Hg}\end{matrix}\right\}\xrightarrow[\text{for metallic bonding}]{\text{lowest m.p.}}\ \text{due to no unpaired } e^-$$

(iv) Variation in atomic radius:

$$\mathrm{Sc}\longrightarrow\ \mathrm{Mn}\ \underbrace{\mathrm{Fe\ Co\ Ni}}\ \mathrm{Cu\ Zn}$$

decreases	remains same	increases again

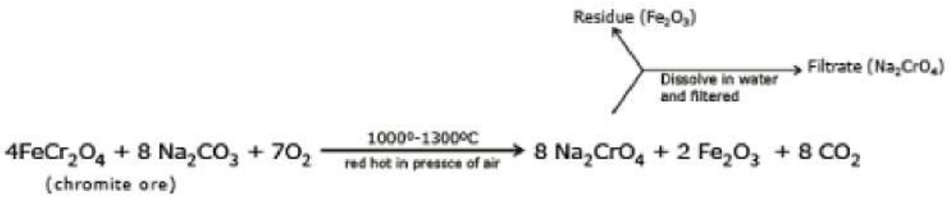
(v) Variable oxidation states possible:

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

Colour : (aquated)	**Colour : (aquated)**
Sc^{3+} → colourless	Ti^{4+} → colourless
Ti^{3+} → purple	V^{4+} → blue
V^{3+} → green	V^{2+} → violet
Cr^{2+} → blue	Cr^{3+} → green
Mn^{3+} violet	Mn^{2+} → light pink
Fe^{2+} → light green	Fe^{3+} yellow
Co^{2+} → pink	Ni^{2+} → green
Cu^{2+} → blue	Zn^{2+} → colourless

CHROMATE - DICHROMATE:

Preparation:



$$\underset{\text{(chromite ore)}}{4FeCr_2O_4} + 8\,Na_2CO_3 + 7O_2 \xrightarrow[\text{red hot in presnce of air}]{1000^{o}\text{-}1300^{o}C} 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2$$

[Lime (CaO) added with Na_2CO_3 which keeps the mass porous so that air has access to all parts and prevents fusion.]
Then,

$$2Na_2CrO_4 + \underset{\text{conc.}}{H_2SO_4} \rightarrow Na_2SO_4\downarrow + Na_2Cr_2O_7 + H_2O$$

It's solubility upto 32°C increases and then decreases } Hence, suitable temp. is to be employed to crystallise out Na_2SO_4 first.

Then $Na_2Cr_2O_7$ is crystallised out as $\underset{\text{(red crystal)}}{Na_2Cr_2O_7.2H_2O}$ on evaporation.

How to get $K_2Cr_2O_7$, $\underset{\text{hot conc.}}{Na_2Cr_2O_7} + KCl \xrightarrow[\text{decomposition}]{\text{double}} K_2Cr_2O_7 + 2NaCl$

NaCl crystallises out first and filtered off. Then $K_2Cr_2O_7$ crystallised out on cooling

- Other props & test of CrO_4^{2-} & $Cr_2O_7^{2-}$: Already discussed
- Similarities between hexavalent Cr & S–compounds.

(i) SO_3 & $CrO_3 \rightarrow$ both acidic.

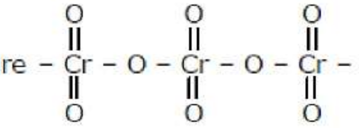
(ii) $S \rightarrow SO_4^{2-}, S_2O_7^{2-}$, $Cr \rightarrow CrO_4^{2-}, Cr_2O_7^{2-}$

(iii) CrO_4^{-2} & SO_4^{2-} are isomorphous

(iv) SO_2Cl_2 & $CrO_2Cl_2 \xrightarrow{OH^-} SO_4^{2-}$ & CrO_4^{2-} respectively

(v) SO_2Cl^- & $CrO_3Cl^- \xrightarrow{OH^-} SO_4^{2-}$ & CrO_4^{2-} respectively

(vi) CrO_3 & $\beta(SO_3)$ has same structure



$$-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{Cr}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{Cr}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{Cr}}-$$

Ques: In laboratory $K_2Cr_2O_7$ is used mainly not $Na_2Cr_2O_7$. Why?

Ans: $Na_2Cr_2O_7$ is deliquescent enough and changes its concentration and cannot be taken as primary standard solution whereas $K_2Cr_2O_7$ has no water of crystallisation and is not deliquescent.

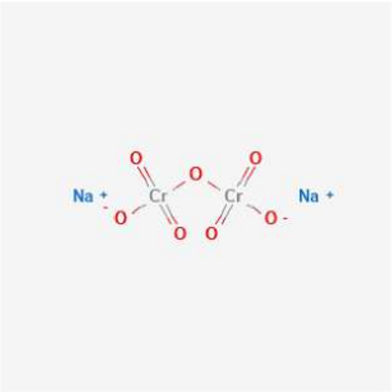


Fig: Structure of $Na_2Cr_2O_7$

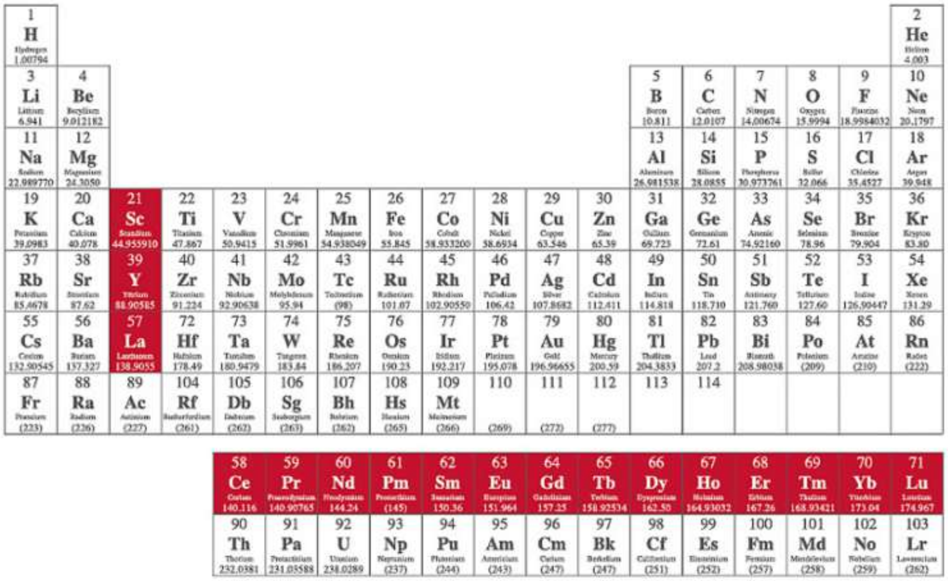
Ques: How to standardise $Na_2S_2O_3$ solution in iodometry?

Ans: $K_2Cr_2O_7$ is the primary standard ⇒ strength is known by weighing the salt in chemical balance and dissolving in measured amount of water.
Then in acidic solution, add KI
$Cr_2O_7^{2-} + 14 H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$
This I_2 is liberated can be estimated with $S_2O_3^{2-}$.

Lanthanides & Actinides

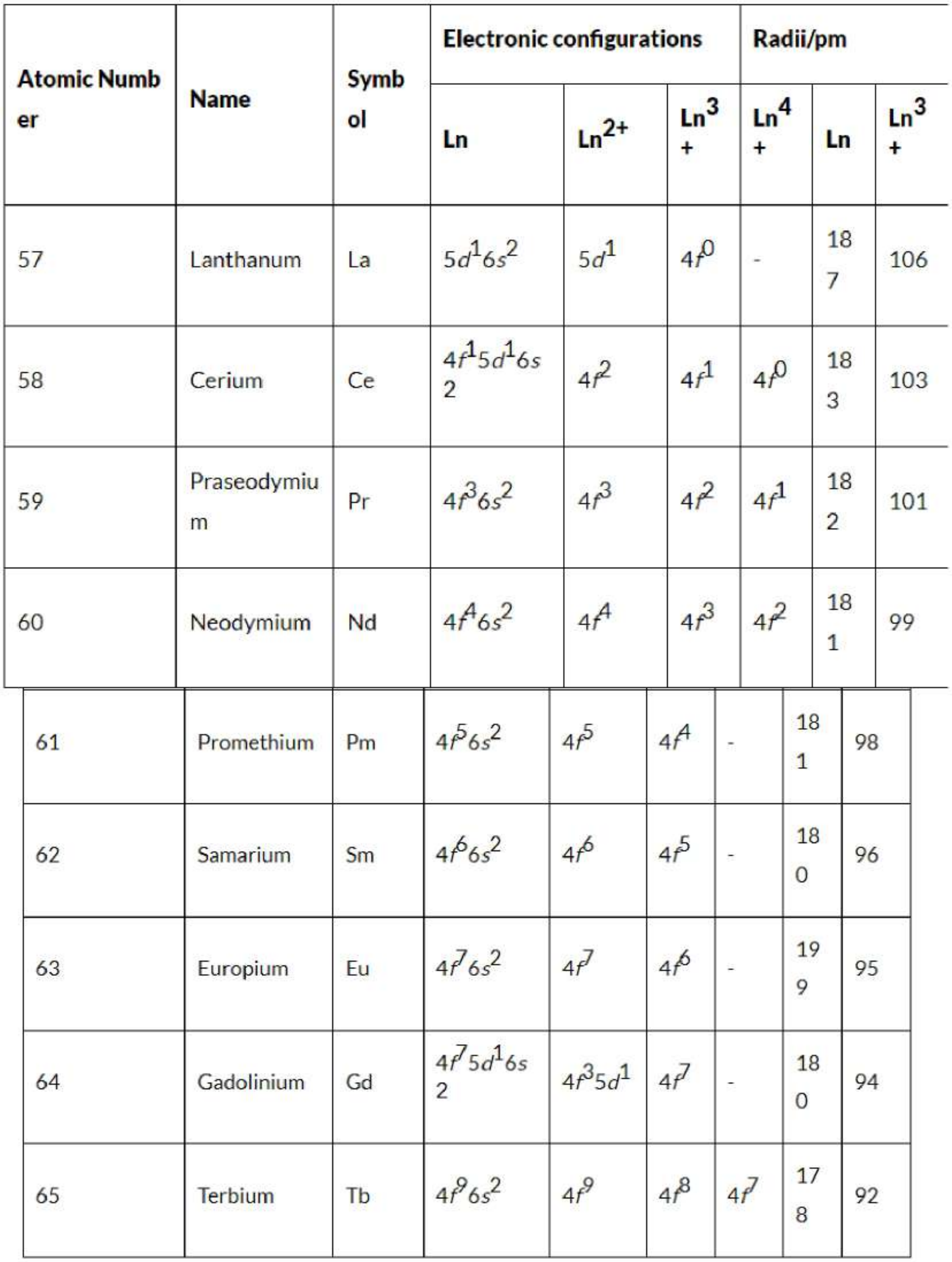
Lanthanides

Lanthanides consist of elements that follow lanthanum and involve the filling of 4f subshell



1 H 1.00794																	2 He 4.003
3 Li 6.941	4 Be 9.012182											5 B 10.811	6 C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050											13 Al 26.981538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	57 La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.96655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.98038	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)	113	114				
				58 Ce 140.116	59 Pr 140.90765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967
				90 Th 232.0381	91 Pa 231.03588	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Electronic Configuration
[Xe] $4f^{n+1}$ $5d^{\circ}$ $6s^2$ or [Xe] $4f^n$ $5d^1$ $6s^2$
The general valence shell electronic configuration of lanthanides is $4f^{1-14}6s^2$.
Electronic configurations of lanthanum and lanthanides are listed in the table



Atomic Number	Name	Symbol	Electronic configurations			Radii/pm		
			Ln	Ln^{2+}	Ln^{3+}	Ln^{4+}	Ln	Ln^{3+}
57	Lanthanum	La	$5d^1 6s^2$	$5d^1$	$4f^0$	-	187	106
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^2$	$4f^1$	$4f^0$	183	103
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^3$	$4f^2$	$4f^1$	182	101
60	Neodymium	Nd	$4f^4 6s^2$	$4f^4$	$4f^3$	$4f^2$	181	99
61	Promethium	Pm	$4f^5 6s^2$	$4f^5$	$4f^4$	-	181	98
62	Samarium	Sm	$4f^6 6s^2$	$4f^6$	$4f^5$	-	180	96
63	Europium	Eu	$4f^7 6s^2$	$4f^7$	$4f^6$	-	199	95
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^3 5d^1$	$4f^7$	-	180	94
65	Terbium	Tb	$4f^9 6s^2$	$4f^9$	$4f^8$	$4f^7$	178	92

66	Dysprosium	Dy	$4f^{10}6s^2$	$4f^{10}$	$4f^9$	$4f^8$	177	91
67	Holmium	Ho	$4f^{11}6s^2$	$4f^{11}$	$4f^{10}$	-	176	89
68	Erbium	Er	$4f^{12}6s^2$	$4f^{12}$	$4f^{11}$	-	175	88
69	Thulium	Tm	$4f^{13}6s^2$	$4f^{13}$	$4f^{12}$	-	174	87
70	Ytterbium	Yb	$4f^{14}6s^2$	$4f^{14}$	$4f^{13}$	-	173	86
71	Lutetium	Lu	$4f^{14}5d^16s^2$	$4f^{14}5d^1$	$4f^{14}$	-	-	-

Atomic and Ionic Sizes of Lanthanides

- Atomic and ionic radii of lanthanides decrease with an increase in atomic number. This gradual decrease is known as lanthanides contraction.
- Because of the lanthanides contraction, the radii of the elements of the 3rd transition series are very similar to those of the corresponding elements of the 2nd transition series elements.

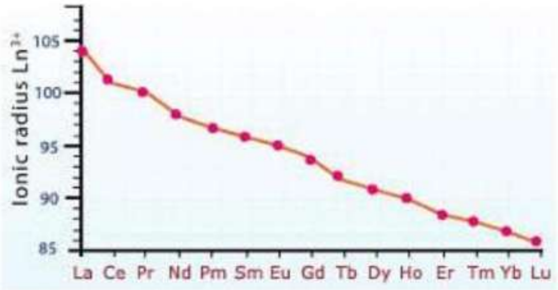
Oxidation States of Lanthanides

Lanthanides exhibit the oxidation state of +3. Some of them also exhibit the oxidation state of +2 and +4.

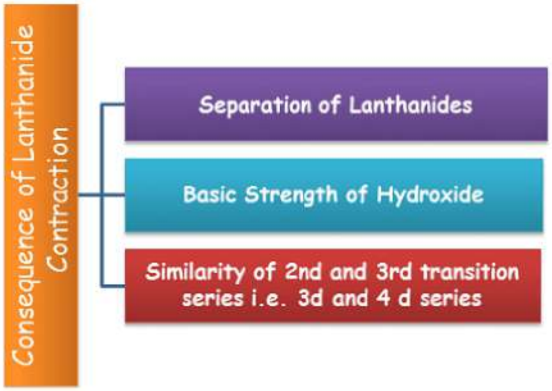
- a noble gas configuration e.g. Ce^{4+} (f^0)
- a half filled f shell e.g. Eu^{2+} (f^7)
- a completely filled f shell e.g. YB^{22+} (f^{14})

Lanthanide contraction

It is observed that in lanthanide series, there is a progressive decrease in the atomic and ionic radii with increasing atomic number . This regular decrease with increase in atomic number is called lanthanide contraction. This is due to the weak shielding of f orbitals. These f orbitals are unable to counter balance the effect of increasing nuclear charge because of which the size keeps on decreasing with increase in atomic number.



Causes of Lanthanide Contraction:



As we move along the period from left to right in lanthanide series, the atomic number increases i.e. number of protons keeps on increasing For every proton added in the nucleus the extra electron goes to the same 4f orbital.
The 4f orbital shows poor shielding effect because of which there is a gradual increase in the effective nuclear charge experienced by the outer electrons. Thus, the attraction of the nucleus for the electrons in the outermost shell increases in atomic number.

Consequence of Lanthanide Contraction

- **Separation of Lanthanides:** Without lanthanide contraction all the lanthanides would have same size because of which if would have been very difficult to separate them but due to lanthanide contraction their properties slightly vary. The variation in the properties is utilized for separating them.
- **Basic Strength of Hydroxide:** Because of the lanthanide contraction, size of M^{3+} ions decreases and there is increase in covalent character in M–OH and hence basic character decreases.
- **Similarity of 2nd and 3rd transition series i.e. 3d and 4 d series:** The atomic sizes of second row transition elements and third row transition elements are almost similar. This is also an effect of lanthanide contraction. As we move down the from form 4d to 5d series, the size must increase but it remains

almost same due to the fact that the 4f electrons present in the 5d elements show poor shielding effect.

Complex formation

- The lanthanides do not show much tendency to form complexes due to low charge density because of their size. However, the tendency to form complex and their stability increases with increasing atomic number.

Chemical Behaviour

The first few members of the series are quite reactive like calcium. However with increasing atomic number, their behaviour becomes similar to that of aluminum.

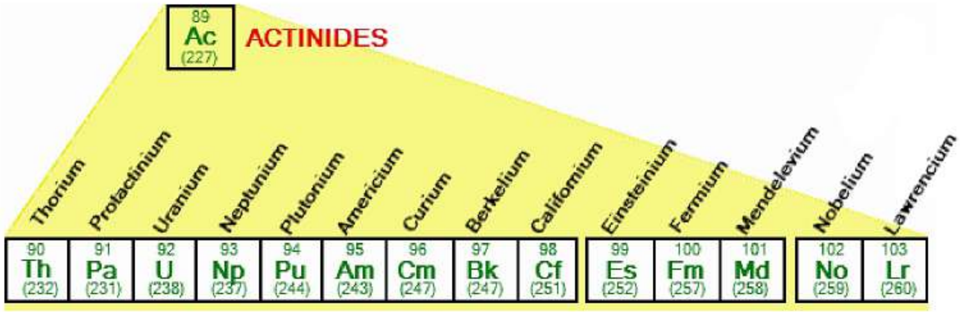
- Lanthanides combine with hydrogen on gentle heating. When they are heated with carbon result in formation of carbides On burning in the presence of halogens, lanthanides form halides.
- Lanthanides react with dilute acids to liberate hydrogen gas.
- Lanthanides form oxides and hydroxides of the type N_2O_3 and $M(OH)_3$ which are basic alkaline earth metal oxides and hydroxides.

Uses of Lanthanides

- Lanthanide are used in the production of alloy steels for plates and pipes.
- Mixed oxides of lanthanides are used as catalysts in petroleum cracking industries.
- Some lanthanum oxides are used as phosphors in television screens and other fluorescing surfaces.

Actinides

Actinides consist of elements that follow actinium and involve the filling of 5f subshell .



Electronic Configuration

[Rn] $5f^{0-14}6d^{0-2}\ 7s^2$

Oxidation States

The dominant oxidation state of these elements is +3 (similar to lanthanides). Besides +3 state, they also exhibit +4 oxidation state. Some actinides show still higher oxidation states. The maximum oxidation state first increases upto the middle of the series and then decreases i.e. it increases from +4 for Th to +5, +6 and +7 for Pa, V and Np but decreases in the succeeding elements.

Melting and boiling point

They have high melting and boiling points like lanthanides but don't show any regular trend with increasing atomic number.

Density:

All actinides except thorium and amercium have high density.

Ionization enthalpies:

The actinides have lower ionization enthalpies as comapre to lanthanides because 5f is more effectively shielded from nuclear charge than 4f.

Magnetic behavior:

All actinides are paramagnetic in nature. The paramagnetic nature which depends on the presence of unpaired electrons.

Radioactivity:

All the actinides are radioactive in nature. Radioactivity increases with increase in atomic number.

Chemical Behaviour

The ability of actinides to exist in different oxidation states has made their chemistry more complex. Moreover, most of these elements are radioactive and the study of their chemistry in the laboratory is difficult.

- They react with boiling water to give a mixture of oxide and hydride.
- The combine with most of the non – metals at moderate temperature.
- All these metals are attacked by HCl but the effect of HNO_3 is very small due to the formation of a protective oxide layer on their surface.

Manganate & Permanganate

Manganate & Permanganate

Preparation of Manganate (MnO_4^{2-}):

$$MnO_2 \xrightarrow[\Delta \text{ or NaOH, in presence of air}]{KOH} \underset{\text{green melt}}{MnO_4^{2-}} \quad \begin{aligned} &[2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O] \\ &MnO_2 + 4KOH + KNO_3 \longrightarrow K_2MnO_4 + KNO_2 + 2H_2O] \\ \backslash\ &3MnO_2 + 6KOH + KClO_3 \longrightarrow 3K_2MnO_4 + KCl + 2H_2O] \end{aligned}$$

In presence of $KClO_3$ & KNO_3 the above reaction is more faster because these two on decomposition provides O_2 easily.
Manganate is also obtained when $KMnO_4$ is boiled with KOH.
$4\,KMnO_4 + 4KOH \xrightarrow{\text{boiled}} 4K_2MnO_4\ \ 2H_2O\ O_2$

Props: The above green solution is quite stable in alkali, but in pure water and in presence of acids, depositing MnO_2 and giving a purple solution of permanganate.
$3K_2MnO_4 + 2H_2O \rightleftharpoons \underset{\text{purple}}{2KMnO_4} + \underset{\text{drak brown}}{MnO_2^-} + 4KOH$

Prob: = $E^0_{MnO_4^{2-}/MnO_2} = 2.26\text{ V}\ \ E^0_{MnO_4^{2-}/MnO_4^-} = -0.56\text{ V}$
Prove that MnO_4^{2-} will disproportionate in acidic medium.

Another Method of Prep^n.: $3K_2MnO_4 + 2H_2SO_4 \rightarrow 2KMnO_4 + MnO_2 + 2K_2SO_4 + 2H_2O$
or $3K_2MnO_4 + 2H_2O + 4CO_2 \rightarrow 2KMnO_4 + MnO_2 + 4KHCO_3$

But in the above method $\frac{1}{3}$ of Mn is lost as MnO_2 but when oxidised either by Cl_2or by O_3
$2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$ [Unwanted MnO_2 does not form]
OR
$2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + 2KOH\ O_2$

Oxidising Prop. of $KMnO_4$: (in acidic medium)

(i) $MnO_4^- + Fe^{+2} + H^+ \rightarrow Fe^{+3} + Mn^{+2} + H_2O$
(ii) $MnO_4^- + I^- + H^+ \rightarrow Mn^{+2} + I_2 + H_2O$
(iii) $MnO_4^- + H_2O_2 + H^+ \rightarrow Mn^{+2} + O_2 + H_2O$
(iv) $MnO_4^- + SO_2 \xrightarrow{H^{\oplus}} Mn^{+2} + H_2SO_4$
(v) $MnO_4^- + NO_2^- + H^+ \rightarrow Mn^{+2} + NO_3^- + H_2O$
(vi) $MnO_4^- + H_2C_2O_4 + H^+ \rightarrow Mn^{+2} + CO_2 + H_2O$
(vii) $MnO_4^- + H_2S \rightarrow Mn^{+2} + S^- + H_2O$
(1) It is not a primary standard since it is difficult to get it in a high degree of purity and free from trances of MnO_2.

(2) It is slowly reduced to MnO_2 especially in presence of light or acid
$4\ MnO_4^- + 4\ H^+ \rightarrow 4\ MnO_2 + 2H_2O + 3O_2$
Hence it should be kept in dark bottles and standardise just before use.
(viii) $2\ KMnO_4 + 16\ HCl \rightarrow 2KCl + 5Cl_2 + 8H_2O + 2MnCl_2$

Oxidising Prop. of $KMnO_4$ in alk. medium:

$2\ MnO_4^- + 2OH^- \rightarrow 2MnO_4^{2-} + H_2O + O.$
Then $2MnO_4^{2-} + 2H_2O \rightarrow 2MnO_2 + 4OH^- + 2O$
(i) $2KMnO_4 + H_2O + KI \rightarrow 2MnO_2 + 2KOH + KIO_3$
(ii) $2KMnO_4 + 3HCO_2K \rightarrow 2MnO_2 + KHCO_3 + 2K_2CO_3 + H_2O$
(iii) $2KMnO_4 + 3H_2O_2 \rightarrow 2MnO_2 + 2KOH + 2H_2O + 3O_2$

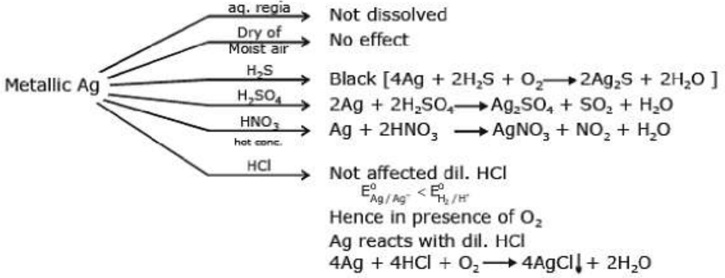
Oxidising Prop. in neutral or weakly acidic solution:

(i) $2KMnO_4 + 3\ MnSO_4 + 2H_2O \xrightarrow{\text{in presence } Zn^{2+} \text{ or } ZnO} 5\ MnO_2 + K_2SO_4 + 2H_2SO_4$
or $MnO_4^- + Mn^{+2} + 2H_2O \rightarrow 5MnO_2 + 4H^+$
In absence of Zn^{+2} ions, some of the Mn^{+2} ion may escape, oxidation through the formation of insoluble $Mn^{II}[Mn^{IV}O_3]$ manganous permanganite.
(ii) $8\ KMnO_4 + 3Na_2S_2O_3 + H_2O \rightarrow 8\ MnO_2 + 3\ Na_2SO_4 + 3\ S + 2\ KOH$

Conversion of Mn^{+2} to MnO_4^-

(i) PbO_2
(ii) $Pb_3O_4 + HNO_3$
(iii) Pb_2O_3
(iv) $NaBiO_3/H^+$
(v) $(NH_4)_2S_2O_8\ /H^+$
(vi) KIO_4/H^+
Heating effect : $2KMnO_4 \xrightarrow[200^\circ C]{\Delta} K_2MnO_4 + MnO_2 + O_2$
green Black
$2K_2MNO_4 \xrightarrow[\text{hot}]{\text{at red}} 2K_2MnO_3 + O_2$

Silver and its compound
(I)



In the same way in presence of O_2, Ag complexes with NaCN/KCN.
$4\ Ag + 8\ KCN + 2H_2O + O_2 \Rightarrow 4K\,[Ag\,(CN)_2] + 4KOH$

Preparation: Already done.

Properties:

(i) It is called as lunar caustic because in contact with skin it produces burning sensation like that of caustic soda with the formation of finely divided silver (black colour)
(ii) Thermal decomposition:
(iii) Props. of $AgNO_3$: [Already done in basic radical]
$6\ AgNO_3 + 3I_2 + 3H_2O \rightarrow 5\ AgI + AgIO_3 + 6HNO_3$
(excess)

(iv) $Ag_2SO_4 \xrightarrow{\Delta} 2Ag + SO_2 + O_2$
(v) $A(AgNO_3) \xrightarrow[\text{added}]{B}$ white ppt appears quickly
$B(Na_2S_2O_3) \xrightarrow[\text{added}]{A}$ It takes time to give white ppt.

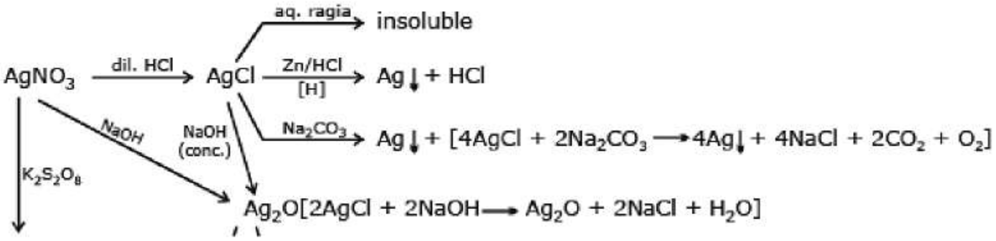
(vi) $Ag_2S_2O_3 + H_2O \xrightarrow{\Delta} Ag_2S + H_2SO_4$
AgCl, AgBr, AgI (but not Ag_2S) are soluble in $Na_2S_2O_3$ forming $[Ag(S_2O_3)_2]^{-3}$ complexes

(vii) $AgBr + AgNO_3 \xrightarrow{\dot{K}Br} AgBr^{-} + KNO_3$
(Pale yellow) ppt.

Heating effect:

$2\ AgNO_3 \xrightarrow{212^\circ C} 2AgNO_2 + O_2$
$2\ AgNO_3 \xrightarrow{500^\circ C} 2Ag\ \ 2NO + O_2$

(VIII)



$Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2$
$K_2S_2O_8 + 2AgNO_3 + 2H_2O \rightarrow 2AgO + 2KHSO_4 + 2HNO_3$

- AgO supposed to be paramagnetic due to d^9 configuration. But actually it is diamagnetic and exists as $Ag^I[Ag^{III}O_2]$
- Reaction involved in developer: $K_2Fe^{II}(C_2O_4)_2 + AgBr \rightarrow KFe^{III}(C_2O_4)_2 + Ag^- + KBr$

ZinC Compounds

ZnO: It is called as phillospher's wool due to its wooly flock type appearance

Preparation:

1] $2Zn + O_2 \rightarrow 2ZnO$

2] $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$

3] $2Zn(NO_3)_2 \xrightarrow{\Delta} 2ZnO + 4NO_2 + O_2$

4] $Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O$

Purest ZnO: $4ZnSO_4 + 4Na_2CO_3 + 3H_2O \rightarrow ZnCO_3.3Zn(OH)_2^- + 4Na_2SO_4 + 3CO_2$

white basic zinc
carbonate

$\downarrow \Delta$

$4ZnO + 3H_2O\uparrow + CO\uparrow$
Pure

Properties : 1) $ZnO(cold) \xrightleftharpoons{\Delta} ZnO(hot)$
white yellow

2) It is insoluble in water
3) It sublimes at 400ºC
4) It is amphoteric oxide
$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$
$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$
$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$
5) $ZnO \rightarrow Zn$ by H_2 & C
$ZnO + H_2 \xrightarrow{>400^\circ C} Zn + H_2O$
$ZnO + C \longrightarrow Zn + CO$
6)It forms Rinmann's green with $Co(NO_3)_2$
$2Co(NO_3)_2 \rightarrow 2CoO + 4NO_2 + O_2$
$CoO + ZnO \rightarrow CoZnO_2$ or CoO - ZnO

Rinmann's green

Uses : (1) As white pigment. It is superior than white lead because it does not turn into black

(2) Rinmann's green is used as green pigment

(3) It is used as zinc ointment in medicine

$ZnCl_2$

Preparation :

$$\left.\begin{aligned} &ZnO + 2HCl \rightarrow ZnCl_2 + H_2O \\ &ZnCO_3 + 2HCl \rightarrow ZnCl_2 + H_2O + CO_2 \\ &Zn(OH)_2 + 2HCl \rightarrow ZnCl_2 + 2H_2O \end{aligned}\right\} \text{It crystallises as } ZnCl_2 \, . \, 2H_2O$$

Anh. $ZnCl_2$ cannot be made by heating $ZnCl_2.2H_2O$ because

$ZnCl_2.2H_2O \xrightarrow{\Delta} Zn(OH)Cl + HCl + H_2O$

$Zn(OH)Cl \xrightarrow{\Delta} ZnO + HCl$

To get anh. $ZnCl_2$: $Zn + Cl_2 \rightarrow ZnCl_2$

$Zn + 2HCl(dry) \rightarrow ZnCl_2 + H_2$

or $Zn + HgCl_2 \rightarrow ZnCl_2 + Hg$

Properties : (i) It is deliquescent white solid (when anhydrous)

(ii) $ZnCl_2 + H_2S \rightarrow ZnS$

$+NaOH \rightarrow Zn(OH)_2 \xrightarrow{\text{excess}} Na_2[Zn(OH)_4]$

$+NH_4OH \rightarrow Zn(OH)_2 \xrightarrow{\text{excess}} [Zn(NH_3)_4]^2$

Uses : 1] Used for impregnating timber to prevent destruction by insects

2] As dehydrating agent when anhydrous

3] $ZnO. ZnCl_2$ used in dental filling

$ZnSO_4$: -

Preparation: →

$Zn + \text{dil. } H_2SO_4 \rightarrow ZnSO_4 + H_2$

$ZnO + \text{dil } H_2SO_4 \rightarrow ZnSO_4 + H_2O$

$ZnCO_3 + \text{dil } H_2SO_4 \rightarrow ZnSO_4 + H_2O + CO_2$

$ZnS + 2O_2 \rightarrow ZnSO_4$

$ZnS + O_2 \rightarrow ZnO + SO_2$

$ZnS + 4O_3 \rightarrow ZnSO_4 + 4O_2$

Props. 1] $ZnSO_4 \, . \, 7H_2O \xrightarrow{39\text{-}70^\circ C} ZnSO_4 \, . \, 6H_2O$

$$\begin{tikzcd} {} \arrow[r, ">70^{o}C"] & ZnSO_4.H_2O \arrow[r, ">280^{o}C"] & ZnSO_4 \arrow[d, ">800^{o}C"] \\ & & \frac{1}{2}O_2 + SO_2 + ZnO \end{tikzcd}$$

Uses: 1] in eye lotion
2] Lithophone making (ZnS $BaSO_4$) as white pigment.

COPPER compounds

CuO:

Preparation: -

(i) $CuCO_3.\ Cu\ (OH)_2 \xrightarrow{\Delta} 2CuO + H_2O + CO_2$ (commercial process)
Malachite Green
(native Cu-carbonate)
(ii) $2Cu\ O_2 \rightarrow 2CuO$ & $Cu_2O + O_2 \rightarrow 2CuO$
(iii) $Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$
(iv) $2Cu(NO_3)_2 \xrightarrow{250ºC} 2CuO + 4NO_2 + O_2$

Properties:

(i) CuO is insoluble in water
(ii) Readily dissolves in dil. acids
$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$
$HCl \rightarrow CuCl_2$
$HNO_3 \rightarrow Cu(NO_3)_2$
(iii) It decomposes when, heated above 1100ºC
$4CuO \rightarrow 2Cu_2O + O_2$
(iv) CuO is reduced to Cu by H_2 or C under hot condition
$CuO + C \rightarrow Cu + CO$
$CuO + H_2 \rightarrow Cu + H_2O$

$CuCl_2$:

Preparation: - $CuO + 2HCl$ (conc.) $\rightarrow CuCl_2 + H_2O$
$Cu\ (OH)_2.CuCO_3 + 4HCl \rightarrow 2CuCl_2 + 3H_2O + CO_2$

Preparation: -
(i) It is crystallised as $CuCl_2.\ 2H_2O$ of Emerald green colour
(ii) Dil. solution in water is blue in colour due to formation of $[Cu(H_2O)_4]^{2}$ complex.
(iii) Conc. HCl or KCl added to dil. solution of $CuCl_2$ the colour changes into yellow, owing to the formation of $[CuCl_4]^{2-}$.
(iv) The conc. aq. solution is green in colour having the two complex ions in equilibrium $2[Cu\ (H_2O)_4]\ Cl_2 \rightleftharpoons [Cu\ (H_2O)_4]^{2} + [CuCl_4]^{2-} + 4H_2O$

(v) $CuCl_2 \rightarrow CuCl$ by no. of reagents

(a) $CuCl_2 + \text{Cu-turnings} \xrightarrow{\Delta} 2CuCl$

(b) $2CuCl_2 + H_2SO_3 + H_2O \rightarrow 2CuCl + 2HCl + 2H_2SO_4$

(c) $2CuCl_2 + Zn/HCl \rightarrow 2CuCl + ZnCl_2$

(d) $CuCl_2 + SnCl_2 \rightarrow CuCl + SnCl_4$

$CuF_2.2H_2O \rightarrow$ light bule

$CuCl_2.2H_2O \rightarrow$ green

* $CuBr_2 \rightarrow$ almost black

{ Anh. $CuCl_2$ is dark brown mass obtained by heating $CuCl_2.2H_2O$ at 150ºC in presence of HCl vap.

CuI_2 does not exist.

$$CuCl_2.2H_2O \xrightarrow[\text{HCl gas}]{150^{\circ}C} CuCl_2 + 2H_2O$$

$CuSO_4$:

Preparation: -

$CuO + H_2SO_4(dil) \rightarrow CuSO_4 + H_2O$

$Cu(OH)_2 + H_2SO_4(dil) \rightarrow CuSO_4 + 2H_2O$

$Cu(OH)_2.CuCO_3 + H_2SO_4(dil) \rightarrow CuSO_4 + 3H_2O + CO_2$

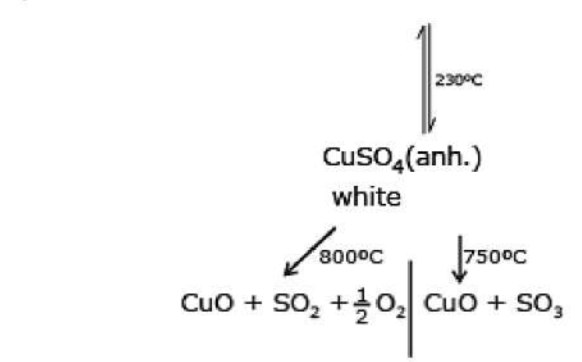
$\underset{\text{(Scrap)}}{Cu}\ H_2SO_4 + O_2 \rightarrow CuSO_4 + H_2O$ [Commercial scale]

Cu dil. $H_2SO_4 \rightarrow$ no reaction {Cu is below H in electrochemical series}

Preparation: -

(i) It is crystallised as $CuSO_4.5H_2O$

(ii)



(iii) Revision with all others reagent

Iron compounds

$FeSO_4.7H_2O$

Preparation: -

(i) Scrap $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$
(dil.)
(ii) From Kipp's waste
$FeS + H_2SO_4$ (dil.) $\rightarrow FeSO_4 + H_2S$
(iii) $FeS_2 + 2H_2O + \frac{7}{2} O_2 \rightarrow FeSO_4 + H_2SO_4$

Properties: -

(i) It undergoes aerial oxidation forming basic ferric sulphate
$4FeSO_4 + H_2O + O_2 \rightarrow 4Fe(OH)SO_4$
(ii) $FeSO_4.7H_2O \xrightarrow{300^\circ C} FeSO_4 \xrightarrow[\text{temp.}]{\text{high}} Fe_2O_3 + SO_2 + SO_3$
anh.white
(iii) Aq. solution is acidic due to hydrolysis
$FeSO_4 + 2H_2O \rightleftharpoons \underset{\text{weak base}}{Fe(OH)_2} + H_2SO_4$
(iv) It is a reducing agent
(a) $Fe^{2+} + MnO_4^{-} + H^{+} \rightarrow Fe^{3+} + Mn^{2+} + H_2O$
(b) $Fe^{2} + Cr_2O_7^{2-} + H^{+} \rightarrow Fe^{3+} + Cr^{3+} + H_2O$
(c) $Au^{3+} + Fe^{2+} \rightarrow Au + Fe^{3+}$
(d) $Fe^{2+} + HgCl_2 \rightarrow Hg_2Cl_2^{-} + Fe^{3+}$
white ppt.
(v) It forms double salt.
Example $(NH_4)_2SO_4. FeSO_4.6H_2O$

FeO (Black):

Prep^{n}: $FeC_2O_4 \xrightarrow[\text{in absence of air}]{\Delta} FeO + CO + CO_2$

Props: - It is stable at high temperature and on cooling slowly disproportionates into
Fe_3O_4 and iron.
$4FeO \rightarrow Fe_3O_4 + Fe$
$FeCl_2$:

Preparation: - $Fe + 2HCl \xrightarrow[\text{a current of HCl}]{\text{heated in}} FeCl_2 + H_2$
OR
$2FeCl_3 + H_2 \xrightarrow{\Delta} 2 FeCl_2 + 2HCl$

Properties: -

(i) It is deliquescent in air like $FeCl_3$

(ii) It is soluble in water, alcohol and ether also because it is sufficiently covalent in nature.

(iii) It volatilises at about 1000ºC and vapour density indicates the presence of Fe_2Cl_4. Above 1300ºC density becomes normal

(iv) It oxidises on heating in air

$12FeCl_2 + 3O_2 \rightarrow 2Fe_2O_3 + 8FeCl_3$

(v) H_2 evolves on heating in steam

$3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2$

(vi) It can exist as different hydrated form

$FeCl_2.2H_2O \rightarrow$ Colourless

$FeCl_2.4H_2O \rightarrow$ pale green

$FeCl_2.6H_2O \rightarrow$ green