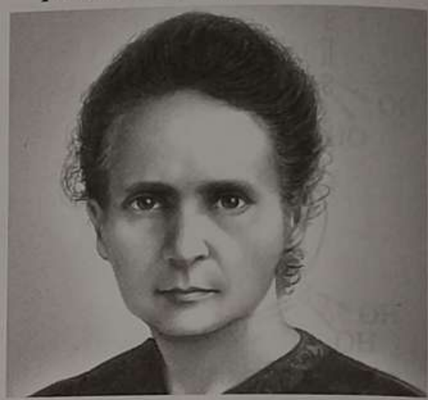
Chapter No.

08 Transition and Inner Transition Elements

Subtopics

Marie Curie: Idol of passion, patience, boldness, persistence, selflessness ……



The Curies undertook the arduous task of separating out radium salt by differential crystallization. From a ton of pitchblende, one-tenth of a gram of radium chloride was separated in 1902. In 1910, Marie Curie isolated pure radium metal.
The extraction was not a simple task. Much more pitchblende was needed to obtain significant quantities of radium and they eventually obtained some 8000 kg of waste ore from Austria. They worked for the next four years under appalling conditions in a leaking unventilated shed, freezing in the winter and dreadfully hot by summer. Marie described life in 'this miserable shed' as 'the best and happiest years of our life', and was much honoured when Lord Kelvin and other famous scientists visited her there. It is remarkable that Curie calculated the atomic weight of radium (as 225) so accurately, given such deplorable conditions. "Large swings in temperature and humidity undoubtedly affected the electrometer...but Marie's patience and tenacity prevailed."

Quick Review

➢ **d and f-Block elements:**

d-block elements
Transition elements
(group 3 to 12)

- **First transition (3d) series elements** (period 4) [Sc(Z = 21) to Zn(Z = 30)]
- **Second transition (4d) series elements** (period 5) [Y(Z = 39) to Cd(Z = 48)]
- **Third transition (5d) series elements** (period 6) [La(Z = 57), Hf(Z = 72) to Hg (Z = 80)]
- **Fourth transition (6d) series elements** (period 7) [Ac(Z = 89), Rf(Z = 104) to Cn (Z = 112)]

f-block elements
Inner transition elements

Lanthanoids
(First inner transition series elements)
(group 3 and period 6)
[Ce(Z = 58) to Lu (Z = 71)]

Actinoids
(Second inner transition series elements)
(group 3 and period 7)
[Th(Z = 90) to Lr (Z = 103)]

Electronic configuration of 3d series of d-block elements:

General electronic configuration of 3d series is **[Ar] 3d $^{1-10}$ 4s^2**.
(Atomic number of Ar = 18)

Element	Symbol	Atomic number	Expected electronic configuration	Observed electronic configuration
Scandium	Sc	21	[Ar] $3d^1 4s^2$	[Ar] $3d^1 4s^2$
Titanium	Ti	22	[Ar] $3d^2 4s^2$	[Ar] $3d^2 4s^2$
Vanadium	V	23	[Ar] $3d^3 4s^2$	[Ar] $3d^3 4s^2$
Chromium	Cr	24	[Ar] $3d^4 4s^2$	[Ar] $3d^5 4s^1$
Manganese	Mn	25	[Ar] $3d^5 4s^2$	[Ar] $3d^5 4s^2$
Iron	Fe	26	[Ar] $3d^6 4s^2$	[Ar] $3d^6 4s^2$
Cobalt	Co	27	[Ar] $3d^7 4s^2$	[Ar] $3d^7 4s^2$
Nickel	Ni	28	[Ar] $3d^8 4s^2$	[Ar] $3d^8 4s^2$
Copper	Cu	29	[Ar] $3d^9 4s^2$	[Ar] $3d^{10} 4s^1$
Zinc	Zn	30	[Ar] $3d^{10} 4s^2$	[Ar] $3d^{10} 4s^2$

Colour of 3d transition metal ions:

Ion	Outer electronic configuration	Number of unpaired electrons	Colour
Sc^{3+}	$3d^0$	0	Colourless
Ti^{3+}	$3d^1$	1	Purple
Ti^{4+}	$3d^0$	0	Colourless
V^{3+}	$3d^2$	2	Green
Cr^{3+}	$3d^3$	3	Violet
Mn^{2+}	$3d^5$	5	Light pink
Mn^{3+}	$3d^4$	4	Violet
Fe^{2+}	$3d^6$	4	Pale green
Fe^{3+}	$3d^5$	5	Yellow
Co^{2+}	$3d^7$	3	Pink
Ni^{2+}	$3d^8$	2	Green
Cu^{2+}	$3d^9$	1	Blue
Cu^+	$3d^{10}$	0	Colourless
Zn^{2+}	$3d^{10}$	0	Colourless

Preparation of $KMnO_4$:

Chemical oxidation:

$$3MnO_2 + 6KOH + KClO_3 \xrightarrow{\Delta} 3K_2MnO_4 + KCl + 3H_2O$$

$$3K_2MnO_4 + 4CO_2 + 2H_2O \longrightarrow 2KMnO_4 + MnO_2 + 4KHCO_3$$

Electrolytic oxidation:

$$2K_2MnO_4 + H_2O + [O] \longrightarrow 2KMnO_4 + 2KOH$$

➢ **Chemical properties of $KMnO_4$:**

Acidic medium	
Oxidation of I^- to I_2	$2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + I_2$
Oxidation of Fe^{2+} to Fe^{3+}	$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$
Oxidation of S^{2-} to S	$5S^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 5S + 8H_2O$
Oxidation of $H_2C_2O_4$ to CO_2	$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$
Neutral or weakly alkaline medium	
Oxidation of I^- to IO_3^-	$2MnO_4^- + H_2O + I^- \longrightarrow 2Mn_2 + 2OH^- + IO_3^-$
Oxidation of $S_2O_3^{2-}$ to SO_4^{2-}	$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$
Oxidation of Mn^{2+} to MnO_2	$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$

➢ **Preparation of $K_2Cr_2O_7$:**

Industrial preparation from chromite ore:

$4(FeO.Cr_2O_3) + 8Na_2CO_3 + 7O_2 \xrightarrow{\Delta} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4.H_2O$

$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

➢ **Chemical properties of $K_2Cr_2O_7$:**

Acidic medium	
Oxidation of I^- to I_2	$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$
Oxidation of S^{2-} to S	$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$

➢ **Minerals and ores of some transition metals:**

Metals	Mineral	Ore
Iron	Haematite: Fe_2O_3 Magnetite: Fe_3O_4 Limonite: $2Fe_2O_3, 3H_2O$ Iron pyrites: FeS_2 Siderite: $FeCO_3$	Haematite
Copper	Chalcopyrite: $CuFeS_2$ Chalcocite: Cu_2S Cuprite: Cu_2O	Chalcopyrite Chalcocite
Zinc	Zinc blende: ZnS Zincite: ZnO Calamine: $ZnCO_3$	Zinc blende

➢ **Different methods used in metallurgy:**

Metallurgy

Pyrometallurgy
Ores are reduced to the metals at high temperatures using suitable reducing agents.

Hydrometallurgy
Metals are extracted from aqueous solutions of their salts using suitable reducing agents.

Electrometallurgy
Metals are extracted by electrolytic reduction of molten metallic compounds.

➢ **Steps involved in the extraction of iron from haematite ore:**

Iron ore → **Crushing and grinding** → **Concentration** → **Roasting** → **Reduction (smelting)** → **Refining** → **Pure iron**

Commercial forms of iron:

Iron

Cast iron	Wrought iron	Steel
Contains 4% C	Contains less than 0.2% C	Contains 0.2 - 2% C
Hard and brittle	Very soft	Neither too hard nor too soft
Uses: making pipes, manufacturing automotive parts, pots, pans, utensils, etc.	**Uses:** making pipes, bars for stay bolts, engine bolts and rivets, etc.	**Uses:** in buildings infrastructure, tools, ships, automobiles, weapons, etc.

Electronic configuration of lanthanoids:

General electronic configuration of lanthanoids is **[Xe] $4f^{0-14}$ $5d^{0-2}$ $6s^2$**.

(Atomic number of Xe = 54)

Element	Symbol	Atomic number	Expected electronic configuration	Observed electronic configuration
Lanthanum	La	57	[Xe] $4f^0 5d^1 6s^2$	[Xe] $4f^0 5d^1 6s^2$
Cerium	Ce	58	[Xe] $4f^2 6s^2$	[Xe] $4f^1 5d^1 6s^2$
Praseodymium	Pr	59	[Xe] $4f^3 6s^2$	[Xe] $4f^3 6s^2$
Neodymium	Nd	60	[Xe] $4f^4 6s^2$	[Xe] $4f^4 6s^2$
Promethium	Pm	61	[Xe] $4f^5 6s^2$	[Xe] $4f^5 6s^2$
Samarium	Sm	61	[Xe] $4f^6 6s^2$	[Xe] $4f^6 6s^2$
Europium	Eu	63	[Xe] $4f^7 6s^2$	[Xe] $4f^7 6s^2$
Gadolinium	Gd	64	[Xe] $4f^8 6s^2$	[Xe] $4f^7 5d^1 6s^2$
Terbium	Tb	65	[Xe] $4f^9 6s^2$	[Xe] $4f^9 6s^2$
Dysprosium	Dy	66	[Xe] $4f^{10} 6s^2$	[Xe] $4f^{10} 6s^2$
Holmium	Ho	67	[Xe] $4f^{11} 6s^2$	[Xe] $4f^{11} 6s^2$
Erbium	Er	68	[Xe] $4f^{12} 6s^2$	[Xe] $4f^{12} 6s^2$
Thulium	Tm	69	[Xe] $4f^{13} 6s^2$	[Xe] $4f^{13} 6s^2$
Ytterbium	Yb	70	[Xe] $4f^{14} 6s^2$	[Xe] $4f^{14} 6s^2$
Lutetium	Lu	71	[Xe] $4f^{14} 5d^1 6s^2$	[Xe] $4f^{14} 5d^1 6s^2$

Chemical reactivity of lanthanoids:

Lanthanoids (Ln)

- $\xrightarrow{H_2O}$ $Ln(OH)_3$ (Hydroxides)
- $\xrightarrow{O_2}$ Ln_2O_3 (Oxides)
- $\xrightarrow{N_2}$ LnN (Nitrides)
- $\xrightarrow{X_2}$ LnX_3 (Halides)
- $\xrightarrow[2800\ K]{C}$ LnC_2 (Carbides)

➢ **Electronic configuration of actinoids:**

General electronic configuration of actinoids is **[Rn] $5f^{0-14}$ $6d^{0-2}$ $7s^2$**.

Atomic number of Rn = 86

Element	Symbol	Atomic number	Observed electronic configuration
Actinium	Ac	89	[Rn] $5f^0 6d^1 7s^2$
Thorium	Th	90	[Rn] $5f^0 6d^2 7s^2$
Protactinium	Pa	91	[Rn] $5f^2 6d^1 7s^2$
Uranium	U	92	[Rn] $5f^3 6d^1 7s^2$
Neptunium	Np	93	[Rn] $5f^4 6d^1 7s^2$
Plutonium	Pu	94	[Rn] $5f^6 6d^0 7s^2$
Americium	Am	95	[Rn] $5f^7 6d^0 7s^2$
Curium	Cm	96	[Rn] $5f^7 6d^1 7s^2$
Berkelium	Bk	97	[Rn] $5f^9 6d^0 7s^2$
Californium	Cf	98	[Rn] $5f^{10} 6d^0 7s^2$
Einsteinium	Es	99	[Rn] $5f^{11} 6d^0 7s^2$
Fermium	Fm	100	[Rn] $5f^{12} 6d^0 7s^2$
Mendelevium	Md	101	[Rn] $5f^{13} 6d^0 7s^2$
Nobelium	No	102	[Rn] $5f^{14} 6d^0 7s^2$
Lawrencium	Lr	103	[Rn] $5f^{14} 6d^1 7s^2$

Formulae

1. Spin-only formula for magnetic moment:

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

where, n = no. of unpaired electrons