"The d- and f- Block Elements"

for Class XII Board Exams

• General Introduction

→ d-block elements : 3rd Group - 12th Group
- → d-orbitals are progressively filled in each of the four long periods.
- → filled from 4th period
- → Transition elements
- → Metals.

FAQ

↳ Transition elements : The one which has incompletely filled d-orbitals in its ground state or in any of its oxidation states.

GROUP 12
Zn, Cd, Hg } not typical transition elements because they have full d^{10} configuration in their G.S. as well as in their common oxd^n state.

However, being the last members of three transition series, their chemistry is studied along with the chemistry of transition metals.

→ f-block elements
- → are those in which the 4f and 5f orbitals are progressively filled
- → placed below the table in two long periods
- → formal members of Group 3 but taken out.
- → Inner transition metals
- → Lanthanoids and Actinoids.

The Transition Elements (d-block)

The very name 'transition' given to the elements of d-block is only because of their position b/w s- and p-block elements.

• **Electronic Configurations of the d-block elements**

General E.C. is

for 3d series : $3d^{1-10}\,4s^{1-2}$ → Anomalous configuration

* $_{24}Cr = [Ar]^{18}\,3d^5\,4s^1$
* $_{29}Cu = [Ar]^{18}\,3d^{10}\,4s^1$

for 4d series : $4d^{1-10}\,5s^{0-2}$

for 5d series : $5d^{1-10}\,6s^{1-2}$

for 6d series : $6d^{1-10}\,7s^{1-2}$

Outer E.C. of the Transition Elements (Ground State)

1st Series (3d) : $_{21}Sc$ to $_{30}Zn$

$_{21}Sc$	$_{22}Ti$	$_{23}V$	$_{24}Cr$	$_{25}Mn$	$_{26}Fe$	$_{27}Co$	$_{28}Ni$	$_{29}Cu$	$_{30}Zn$
$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$

2nd Series (4d) : $_{39}Y$ to $_{48}Cd$

$_{39}Y$	$_{40}Zr$	$_{41}Nb$	$_{42}Mo$	$_{43}Tc$	$_{44}Ru$	$_{45}Rh$	$_{46}Pd$	$_{47}Ag$	$_{48}Cd$
$4d^1 5s^2$	$4d^2 5s^2$	$4d^4 5s^1$	$4d^5 5s^1$	$4d^6 5s^1$	$4d^7 5s^1$	$4d^8 5s^1$	$4d^{10} 5s^0$	$4d^{10} 5s^1$	$4d^{10} 5s^2$

f-block (58-71)

3rd Series (5d) : $_{57}La$ to $_{80}Hg$

$_{57}La$	$_{72}Hf$	$_{73}Ta$	$_{74}W$	$_{75}Re$	$_{76}Os$	$_{77}Ir$	$_{78}Pt$	$_{79}Au$	$_{80}Hg$
$5d^1 6s^2$	$5d^2 6s^2$	$5d^3 6s^2$	$5d^4 6s^2$	$5d^5 6s^2$	$5d^6 6s^2$	$5d^7 6s^2$	$5d^9 6s^1$	$5d^{10} 6s^1$	$5d^{10} 6s^2$

f-block (90-103)

4th series (6d) : $_{89}Ac$ to $_{112}Cn$

$_{89}Ac$	$_{104}Rf$	$_{105}Db$	$_{106}Sg$	$_{107}Bh$	$_{108}Hs$	$_{109}Mt$	$_{110}Ds$	$_{111}Rg$	$_{112}Cn$
$6d^1 7s^2$	$6d^2 7s^2$	$6d^3 7s^2$	$6d^4 7s^2$	$6d^5 7s^2$	$6d^6 7s^2$	$6d^7 7s^2$	$6d^8 7s^2$	$6d^{10} 7s^1$	$6d^{10} 7s^2$

Q1. Explain why zinc is not regarded as a transition element?

Ans1. Zinc in its ground state and common oxidation state of +2 has completely filled d-orbitals. Hence, it is considered as non transition element.

😊 **TRY YOURSELF**: INTEXT 8.1 ; Example 8.1 ; Back Exercise 8.1 (i to iv) (FROM NCERT)

• General Properties of the Transition Elements (d-Block)

1. Physical Properties:

→ All are metals
→ Malleable & ductile (except mercury → liquid)
→ High thermal & electrical conductivity
→ Metallic Lustre & Sonorous.

2. Atomic Radii:

➤ s-block > d-block > p-block (In a period)

➤ In a transition series as atomic no. ↑, the atomic radii first ↓ses upto middle, becomes constant & then ↑ses towards end of the period.

eg: from Sc to Cr : atomic radii ↓ (inc. in nuclear charge)
from Cr to Cu : almost constant (Shielding effect of d e⁻s neutralise the nuclear charge)
from Cu to Zn : size ↑ses
[Zn has higher atomic radius
$_{30}Zn$: $3d^{10}\ 4s^2$
⇅⇅⇅⇅⇅ inter e^- repulsion exist
↓
expansion of e^- cloud.]

V. Imp

•)) 3d → 4d → 5d : size ↑ses due to introduction of new principal shell.

Note: The size of 4d elements is almost the same size of the 5d series elements.

This is due to filling of 4f before 5d orbitals which results in regular decrease in atomic radii & called as Lanthanoid Contraction. eg. (Zr 160pm, Hf 159pm)

3. Ionic Radii : ↓se with ↑se in oxidation state.

4. Ionisation Enthalpy :

- from Left to Right along the series, I.E. ↑se.

(However, irregular trend in the 1st I.E of 3d metals is due to irregularity in E.C. of 4s and 3d orbitals).

- In a group,

$$3d \xrightarrow{\text{I.E. } \downarrow \text{ses}} 4d \xrightarrow{\text{I.E. } \uparrow \text{ses}} 5d$$

(Lanthanoid Contraction)
↳ poor screening of 4f orbital e⁻s

Hg : highest I.E₁ (1007 KJ/mol)

La : lowest I.E. (540 KJ/mol)

FAQ

5. Oxidation State : d-block elements show variable O.S (except 1st & last member) due to similar energies of ns and (n-1)d electrons

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					

Q2. Name the transition element which doesnot exhibit variable oxdⁿ state.

Ans. Sc (Z=21)

Q3: Calculate the oxidation state of Fe in $Fe(CO)_5$ and

Ni in $Ni(CO)_4$.

Ans3: Zero

Q4: Name any two transition metals which exhibit oxd^n state of +8.

Ans4: Ru and Os exhibit +8 Oxd^n state.

TRY YOURSELF : INTEXT (8.3) ; Back Exercise (8.2, 8.5, 8.9, 8.13) (FROM NCERT)

6. Trends in the M^{2+}/M Standard Electrode Potentials:

E^o/V (M^{2+}/M)	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	−1.63	−1.18	−0.90	−1.18	−0.44	−0.28	−0.25	0.34	−0.76

* $E^o(M^{2+}/M)$ values: irregular due to irregular variation of I.E ($\Delta_i H_1 + \Delta_i H_2$) and also sublimation enthalpies which are relatively much less for Mn & V.

* Cu : positive E^o

High energy to transform Cu (s) to Cu^{2+}(aq.) is not balanced by its hydration energy.

Q5: Why is Cr^{2+} reducing and Mn^{3+} oxidising when both have d^4 configuration?

Ans5: Cr^{2+} is reducing (lose e^-) as its config^n changes from $d^4 \to d^3$.

d^3 : half filled t_{2g} level

$Mn^{3+} \longrightarrow Mn^{2+}$: half-filled d^5 config^n : Extra stability.

oxidising → (gain e^-)

TRY YOURSELF : EXAMPLE (8.6, 8.7) ; INTEXT (8.6 + 8.7) ; BACK EXERCISE (8.17) (FROM NCERT)

FAQ

TRANSITION ELEMENTS

Density
Left → Right; density ↑ses.
eg. Ti to Cu (Z=22) (Z=29) density ↑ses.

Metallic bonding
Greater the no. of valence e⁻s, stronger is the resultant bonding.

M.Pt and B.Pt.
↓
High (except Zn, Cd, Hg)
↓
due to strong metallic bonds & presence of partially filled d-orbitals
↓
High M.Pt & B.Pt.

Enthalpy of atomisation
↓
High
It first ↑ses (upto middle) & then ↓ses in a series.

⇒ No. of unpaired e^-s ∝ Enthalpy of Atomisation

TRANSITION ELEMENTS

Magnetic Properties

By MAGNET

Diamagnetic : no unpaired e^- (repelled)
Paramagnetic : one/more unpaired e^- (weakly attracted)
Ferromagnetic : (strongly attracted)

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

Complex formation

(due to high charge on Transition metal & availability of d-orbitals)

eg $[Fe(CN)_6]^{3-}$, $[Mn(H_2O)_4]^{2+}$ etc.

Catalytic properties

(due to their ability to adopt multiple oxdn states & ability to form complexes.

eg Fe : Haber Process
V_2O_5 : Contact Process ($SO_2 \longrightarrow SO_3$)
$PdCl_2$: Wacker Process etc.

FAQ

Formation of Coloured Ions

Colour : due to unpaired e^-s $\rightarrow$ excitation (d-d transition)

$\boxed{d^0 \ \& \ d^{10}}$: Colourless

(no d e^-s) (all e^-s are paired up)

Alloy formation

(due to almost similar size of metal ions ($\sim 15\%$) high ionic charges & availability of d-orbitals)

eg. Steel, brass, Stainless steel etc.

Formation of Interstitial Compounds

(small-sized atoms of H, B, C, N etc. can easily occupy positions in the voids present in the crystal lattices of transition metals.)

$\rightarrow$ usually non-stoichiometric & are neither typically ionic nor covalent. eg. TiC, Mn_4N, $VH_{0.56}$ etc.

• Characteristics of interstitial compounds:

1. High M.Pt (higher than those of pure metals)
2. Very hard
3. They retain metallic conductivity
4. Chemically inert.

7. Trends in the M^{3+}/M^{2+} Standard Electrode Potentials:

$E^0_{M^{3+}/M^{2+}}$ (in V)	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	–	−0.37	−0.26	−0.41	+1.57	+0.77	+1.97	–	–	–

$E^0(M^{3+}/M^{2+})$ values show varying trend.

- Low value for Sc : shows Sc in +3 ⟶ noble gas E.C.
- Highest value for Zn : due to removal of an e^- from stable d^{10} config^n of Zn^{2+}.
- High values for Mn : shows that Mn^{2+} (d^5) : more stable

8. Trends in Stability of Higher Oxidation States :

Oxd^n No.										
+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'''	

Key : $X = F \rightarrow I$; $X' = F \rightarrow Br$; $X'' = F, Cl$; $X''' = Cl \rightarrow I$

Table 1 : Formulae of Halides of 3d Metals

→ The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy (as in case of CoF_3) or higher bond enthalpy terms for the higher covalent compounds (eg. VF_5 and CrF_6)

→ Another feature of fluorides is their instability in the low oxidation states (eg. VX_2 ; X = Cl, Br or I) and the same applies to CuX.

All Cu^{II} halides are known (except the iodide). In this case, Cu^{2+} oxidises I^- to I_2

$$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2(s) + I_2$$

However, many copper (I) compounds are unstable in aqueous solution & undergo disproportionation.

Imp. $2Cu^+ \longrightarrow Cu^{2+} + Cu$

Note: The stability of $Cu^{2+}(aq.)$ rather than $Cu^+(aq.)$ is due to the much more –ve $\Delta H^\ominus_{hyd}$ of $Cu^{2+}(aq.)$ than Cu^+, which more than compensates the second I.E. of Cu.

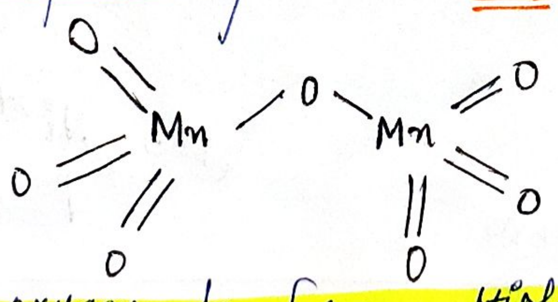
Table 2: Oxides of 3d metals

Oxdn No.	3	4	5	6	7	8	9	10	11	12
				GROUPS						
+7					Mn_2O_7					
+6				CrO_3						
+5			V_2O_5							
+4		TiO_2	V_2O_4	CrO_2	MnO_2					
+3	Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_2O_3				
					Mn_3O_4*	Fe_3O_4*	Co_3O_4*			
+2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO
+1									Cu_2O	

* mixed oxides

- The highest oxidation no. in the oxides coincides with the group no. and is attained in Sc_2O_3 to Mn_2O_7.
- The ability of oxygen to stabilise these high O.S. > fluorine.

Thus; Highest fluoride of Mn is MnF_4 but oxide is Mn_2O_7.



; Mn_2O_7

The ability of oxygen to form multiple bonds to metals explains its superiority.

Q6. MnF_7 is not stable while Mn_2O_7 is stable. why?
↳ because of overcrowding of F.

67

9. Chemical Reactivity and E° Values :

Transition metals vary widely in their chemical reactivity.

→ Metals of 1^{st} series (3d) are relatively more reactive (exception Cu) & are oxidised by 1M H^+.

Note: Ti & V : passive to dilute non-oxidising acids at room temp.

→ E° values for M^{2+}/M : indicate a ↓sing tendency to form divalent cations across the series. (This is related to the ↑se in sum of 1^{st} & 2^{nd} I.E.

→ E° values for Mn^{2+}/Mn, Ni^{2+}/Ni and Zn^{2+}/Zn are more −ve than expected.

(d^5) Mn^{2+} & Zn^{2+} (d^{10}) : due to half-filled & full filled E.C

Ni^{2+} : E°_{value} is related to highest −ve $\Delta H_{hydration}$;

★ Mn^{3+} & Co^{3+} : strong oxidising agents in aq. solⁿ

★ Ti^{2+}, V^{2+} & Cr^{2+} : strong reducing agents & liberate H_2 from a dil. acid.

eg. $2Cr^{2+}(aq.) + 2H^+(aq.) \longrightarrow 2Cr^{3+} + H_2(g)$

Q7 Calculate spin only magnetic moment of given ions :

(i.) $_{29}Cu^{2+}$: $3d^9$ [↑↓|↑↓|↑↓|↑↓|↑]

$\mu_s = \sqrt{n(n+2)} = \sqrt{1(1+2)}$
$= \sqrt{3} = 1.73$ B.M.

(ii.) $_{24}Cr^{2+}$: $3d^4$ [↑|↑|↑|↑|]

$\mu_s = \sqrt{4 \times 6} = \sqrt{24}$
$= 4.90$ B.M.

(iii.) $_{26}Fe^{3+}$: $3d^5$

$\sqrt{5 \times 7} = 5.92$ B.M.

(iv.) $_{28}Ni^{2+}$: $3d^8$

$\sqrt{2 \times 4} = 2.84$ B.M.

TRY ☺ YOURSELF !	INTEXT (8.2, 8.4, 8.5, 8.8, 8.9); EXAMPLE (8.5), (8.9); BACK EXERCISE (8.11, 8.12, 8.18, 8.21, 8.22, 8.24) (FROM NCERT)

The Inner Transition Elements (f-block)

- The elements in which filling of electrons takes place in (n-2)f-subshell which belongs to anti-penultimate (third to the outermost) energy shell.
- The f-block consists of two series of elements known as Lanthanoids and Actinoids.

The general electronic configuration of the f-block elements is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

for Lanthanoids, n is 6 while its value is 7 for Actinoids. There are many exceptions in the electronic configuration.

LANTHANOIDS: The series involving the filling of 4f-orbitals following lanthanum (Z = 57) is called the lanthanoid series. There are 14 elements in this series starting with Ce (Z=58) to Lu (Z=71)

- Electronic Configuration: $[Xe]\,4f^{1-14}\,5d^{0-1}\,6s^2$

Atomic No.	Name	Symbol	Ln	Ln^{2+}	Ln^{3+}
57	Lanthanum	La	$5d^1 6s^2$	$5d^1$	$4f^0$
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^2$	$4f^1$
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^3$	$4f^2$
60	Neodymium	Nd	$4f^4 6s^2$	$4f^4$	$4f^3$
61	Promethium	Pm	$4f^5 6s^2$	$4f^5$	$4f^4$
62	Samarium	Sm	$4f^6 6s^2$	$4f^6$	$4f^5$
63	Europium	Eu	$4f^7 6s^2$	$4f^7$	$4f^6$
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7 5d^1$	$4f^7$
65	Terbium	Tb	$4f^9 6s^2$	$4f^9$	$4f^8$
66	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^{10}$	$4f^9$

67	Holmium	Ho	$4f^{11} 6s^2$	$4f^{11}$	$4f^{10}$
68	Erbium	Er	$4f^{12} 6s^2$	$4f^{12}$	$4f^{11}$
69	Thulium	Tm	$4f^{13} 6s^2$	$4f^{13}$	$4f^{12}$
70	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{14}$	$4f^{13}$
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14} 5d^1$	$4f^{14}$

FAQ * Only electrons outside [Xe] core are indicated.

1. Atomic and ionic sizes : With ↑ing atomic no., the atomic and ionic radii decreases from one element to the other but the decrease is very small.

A steady decrease in the size of lanthanoids with ↑se in atomic no. is known as **Lanthanoid Contraction**.

★ Consequences of Lanthanoid contraction :

(a.) It leads to similar physical & chemical properties among lanthanoids.

(b.) Zr and Hf have similar properties due to similar atomic radii.

(c.) Chemical separation of lanthanoids becomes difficult.

Properties of Lanthanoids

- → Oxidation State
  - Mainly give +3 O.S. but some elements show +2 and +4 O.S.
- → Silvery white soft metals & tarnish rapidly.
- → Hardness ↑ as atomic no. ↑
  - Samarium (Sm) being steel hard.
- → Malleable, ductile, High M.Pt, good conductor of electricity; Highly dense metals.
- → form alloys with other metals easily. eg Mischmetall
- → Colour
  - Many trivalent lanthanoid ions are coloured both in solid & in aq. sol^n.
  - (Colour → presence of f-electrons; f-f trans^n)

→ Magnetic Properties

- La^{3+} $(4f^0)$ and Lu^{3+} $(4f^{14})$: Diamagnetic
- Other trivalent Lanthanoid ions : Paramagnetic ↓ due to presence of unpaired $\bar{e}$'s

Q8. Name a member of the Lanthanoid series which is well known to exhibit +4 O.S.

Ans8. Cerium (Z = 58)

TRY YOURSELF : Back Exercise 8.20 (i, ii, iii), 8.27, 8.31, 8.32 (FROM NCERT)

→ BOARDS Ke liye

1. Solve NCERT Exemplar (except deleted portion)

2. Some Important & F. A. Questions : MUST TRY

Q1. What is meant by 'Lanthanoid Contraction'?

Q2. Why do transition elements show variable oxd^n states?

Q3. Give reasons :

(i.) Generally, there is an increase in density of elements from Ti (Z=22) to Cu (Z=29)

(ii.) Transition elements generally form coloured compounds.

(iii.) Transition elements & their compounds are generally found to be good catalysts.

Q4. Assign reasons:

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

(ii.) Zn^{2+} salts are colourless.

(iii.) Copper (I) ion is not known to exist in aqueous solutions.

Q5. Explain the following:

(i.) The enthalpies of atomization of transition metals are quite high.

(ii.) Transition metals and their compounds generally exhibit a paramagnetic behaviour.

Q6. Which of the following cations are coloured in aqueous solutions and why?

Sc^{3+}, V^{3+}, Ti^{4+}, Mn^{2+}

Q7. Mention two main consequences of Lanthanoid contraction.

Q8. In the 3d series ($Sc = 21$ to $Zn = 30$)

(i.) which element shows maximum no. of Oxidation states?

(ii.) which element shows only +3 O.S.?

(iii.) which element has the lowest enthalpy of atomization?