Transition Elements

(Chemistry-DSE-1002D: Inorganic and Physical Chemistry, Section-II)

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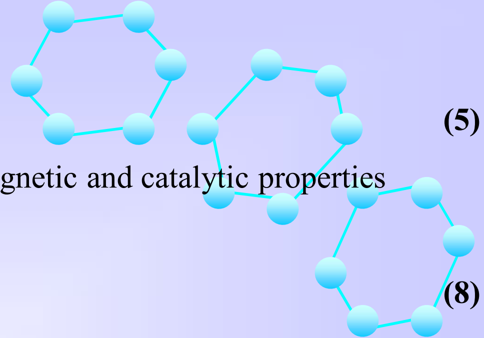
Syllabus



Unit-1 Transition Elements (3d series) **(5)**

General group trends with special reference to electronic configuration, variable valency, colour, magnetic and catalytic properties and ability to form complexes.

Unit-2 Lanthanoids and Actinoids **(8)**

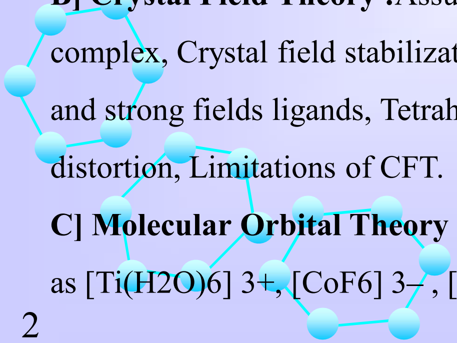
A] Lanthanoids: Introduction, electronic configurations, oxidation states, colour and spectra, magnetic properties, lanthanide contraction, occurrence and separation of lanthanides (ion exchange method only).

B] Actinoids: Introduction, position in periodic table, electronic configuration, oxidation states; General methods of preparation of Transuranic elements- i) Neutron capture followed by β decay ii) Accelerated projectile bombardment iii) Heavy ion bombardment; IUPAC nomenclature of the super heavy elements with atomic number (Z) greater than 100.

Unit-3 Unit 3: Coordination Chemistry: Theories of Metal Complexes

A] Valence Bond Theory : Definition and formation of co-ordinate covalent bond in BF_3-NH_3 and $[NH_4]^*$, Distinguish between double salt and complex salt, Werner's theory i) Postulates, ii) theory as applied to cobalt amines complexes; Description of the terms: ligands, co-ordination compounds, Coordination number; IUPAC system of nomenclature, Structural and stereoisomerism in complexes with coordination numbers 4 and 6; postulates of VBT, Inner and outer orbital complexes w. r .t. coordination numbers 4 and 6; Drawbacks of VBT. **(9)**

B] Crystal Field Theory : Assumptions of CFT, Crystal field splitting of 'd' orbital in octahedral, tetrahedral and square planar complex, Crystal field stabilization energy (CFSE), Comparison of CFSE for Oh and Td complexes, Crystal field effects for weak and strong fields ligands, Tetrahedral symmetry, Factors affecting the Magnitude of 10 Dq, Spectrochemical series, Jahn-Teller distortion, Limitations of CFT. **(10)**



C] Molecular Orbital Theory [MOT] : Introduction, Salient features of MOT of octahedral complexes with sigma bonding such as $[Ti(H_2O)_6]^{3+}$, $[CoF_6]^{3-}$, $[Co(NH_3)_6]^{3+}$, Merits and demerits of MOT. **(5)**

Transition Elements

1 Introduction

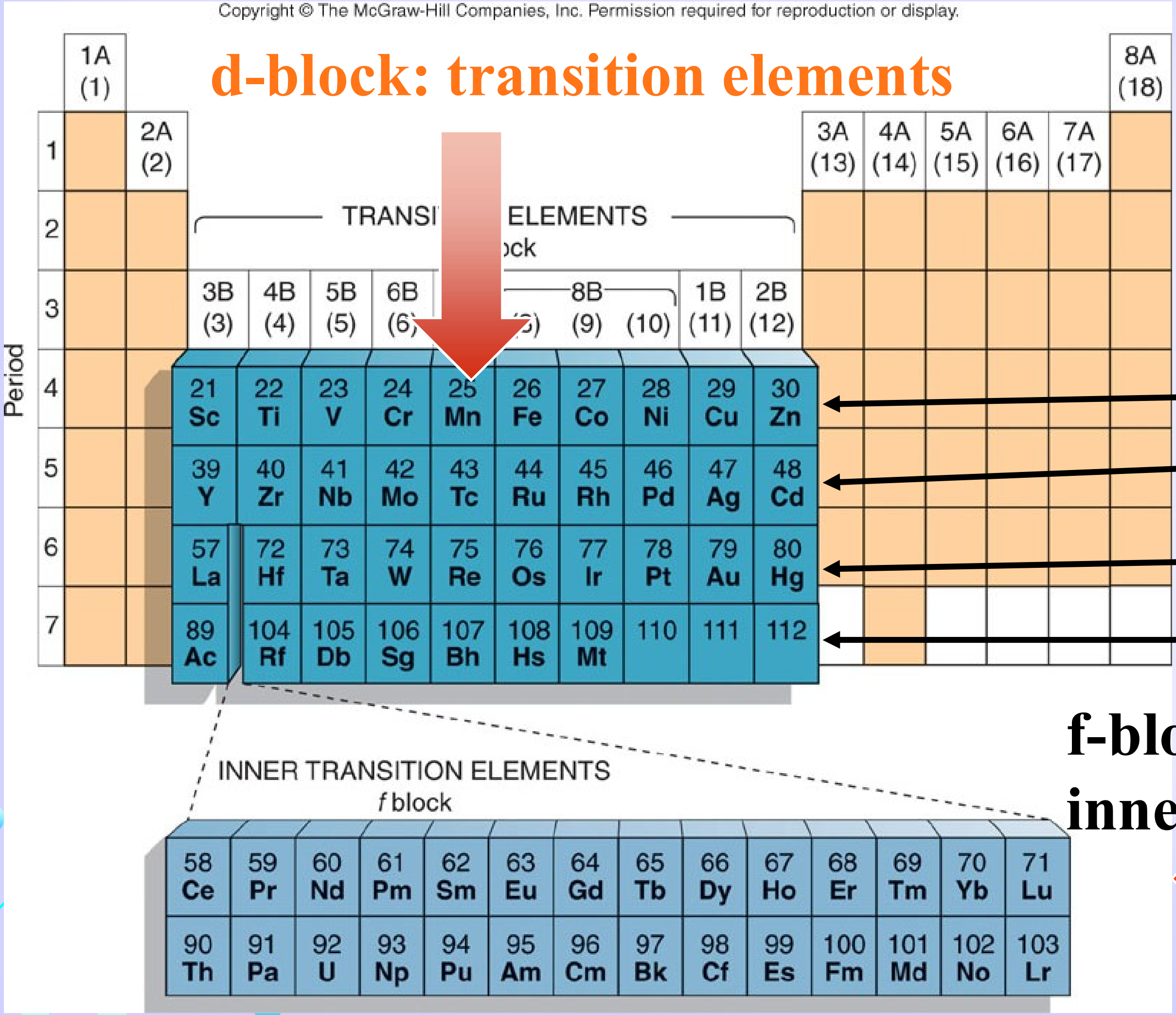
2 General Features of the *d*-Block Elements from Sc to Zn

2 Characteristic Properties of the *d*-Block Elements

  a. Electronic Configuration
  b. Oxidation states
  c. Color
  d. Magnetic behavior
  e. Complex formation
  f. Catalytic property

What is a transition metal?

"an element with valance d- electrons"



d-block: transition elements

3d

4d

5d

6d

f-block:
inner transition eleme

What’s interesting about Transition Metals??

biological activity

colour

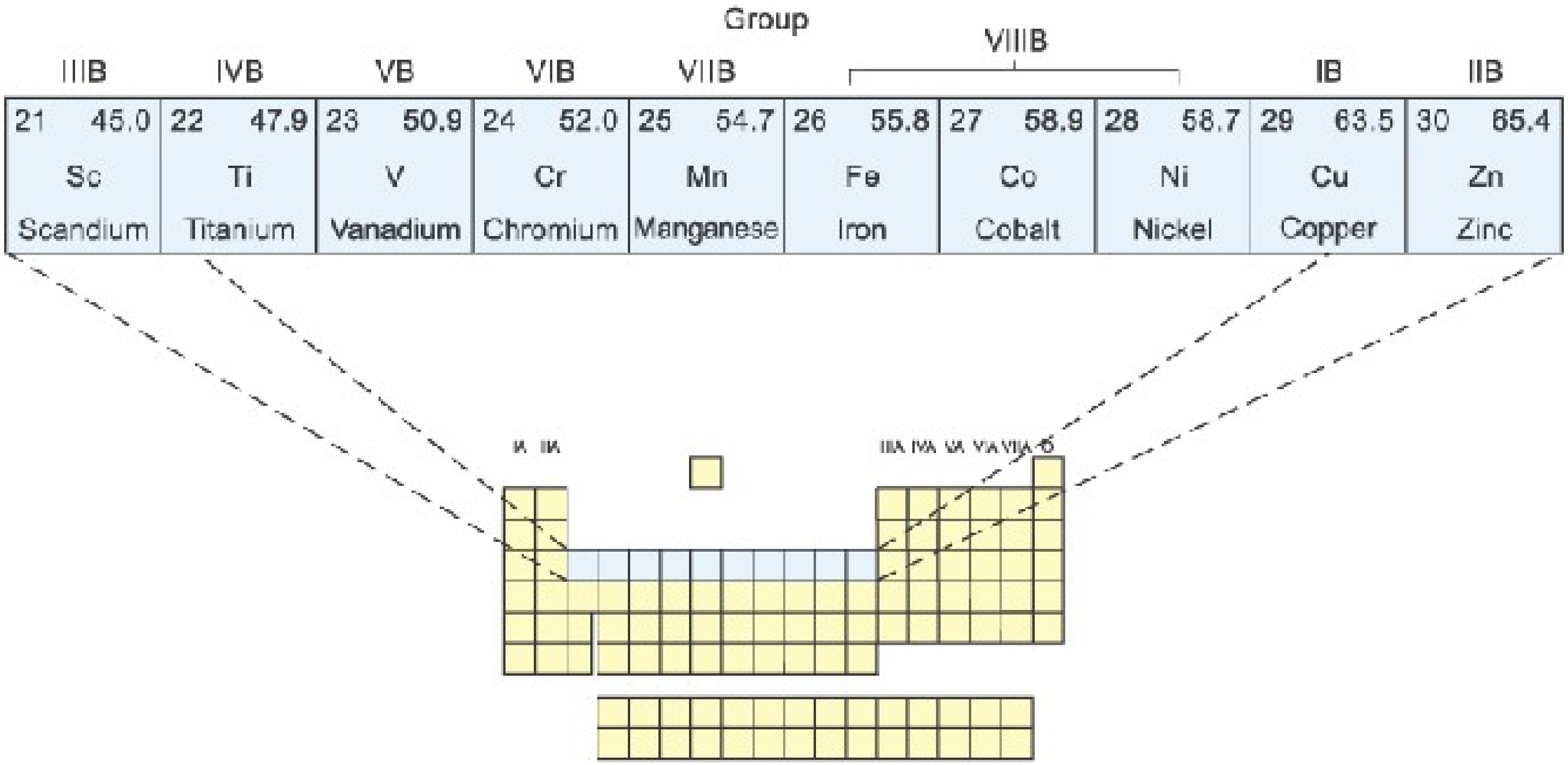
magnetic behaviour

geometry

coordination number

oxidation states

medical applications



IIIB	IVB	VB	VIB	VIIB	VIIIB	VIIIB	VIIIB	IB	IIB
21 45.0	22 47.9	23 50.9	24 52.0	25 54.7	26 55.8	27 58.9	28 58.7	29 63.5	30 65.4
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc

The first transition series

Scandium, Sc; 3B(3)

Titanium, Ti; 4B(4)

Vanadium, V; 5B(5)

Chromium, Cr; 6B(6)

Manganese, Mn; 7B(7)

Iron, Fe; 8B(8)

Cobalt, Co; 8B(9)

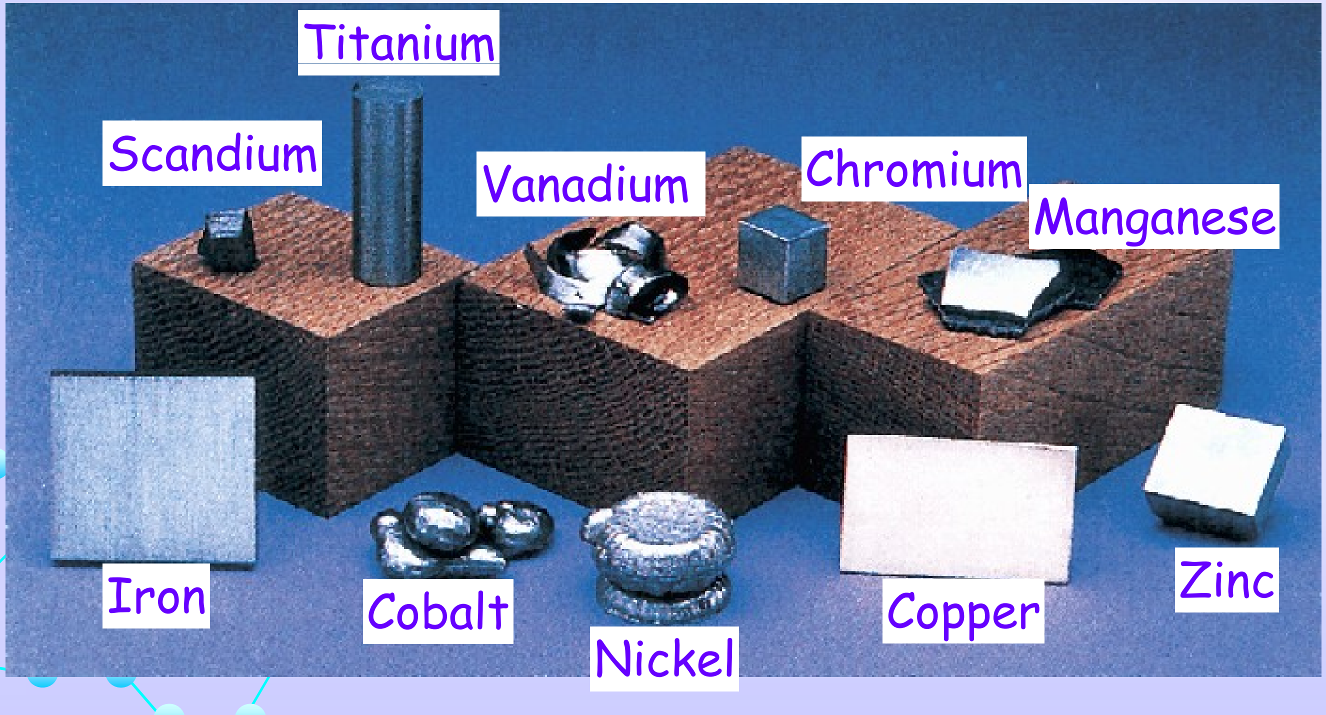
Nickel, Ni; 8B(10)

Copper, Cu; 1B(11)

Zinc, Zn; 2B(12)

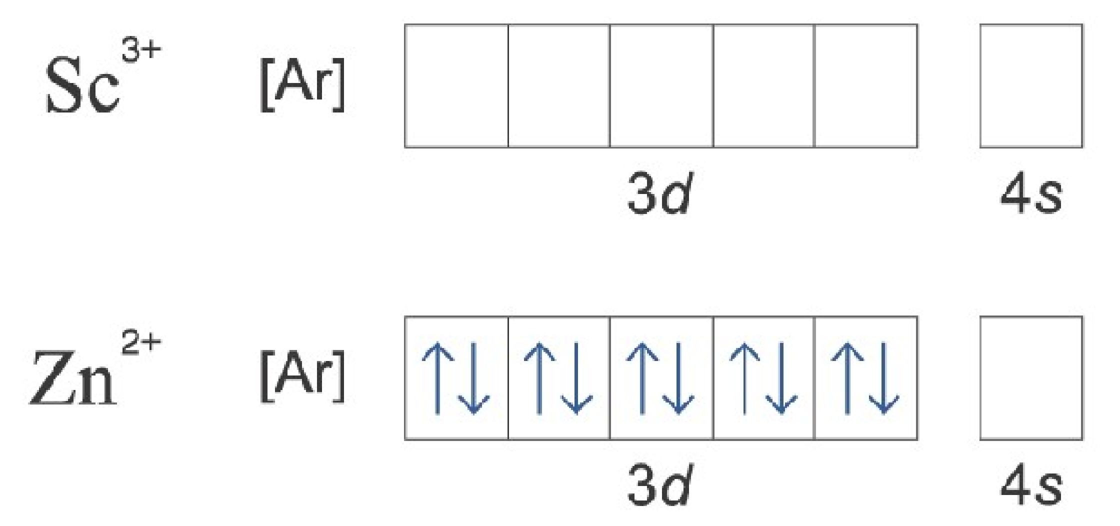
d-Block elements (transition elements):

- Lie **between *s*-block and *p*-block** elements
- Occur in the **fourth and subsequent periods**
- All contains **incomplete *d* sub-shell** (i.e. 1 – 9 electrons) in at least one of their oxidation state



- Strictly speaking, **scandium (Sc) and zinc (Zn) are not transitions elements**

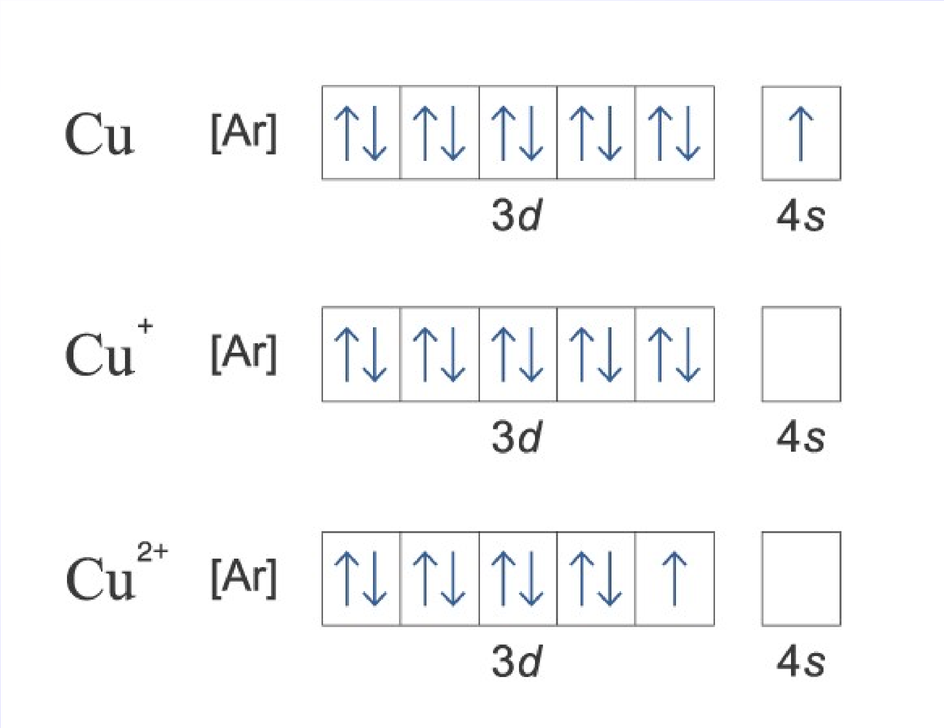
  ∵ Sc forms **Sc^{3+} ion which has an empty *d* sub-shell ($3d^0$)**
  Zn forms **Zn^{2+} ion which has a completely filled *d* sub-shell ($3d^{10}$)**



- Cu shows some **intermediate behaviour** between transition and non-transition elements because of two oxidation states, **Cu(I)** & **Cu(II)**

- **Cu^+** is **not a transition metal ion** as it has a **completely filled *d* sub-shell**

- **Cu^{2+}** is **a transition metal ion** as it has an **incompletely filled *d* sub-shell**



General Features of the *d*-Block Elements from Sc to Zn

- all **metals**

- **good conductors** of heat and electricity, **hard**, **strong**, **malleable**, **ductile** and **lustrous**

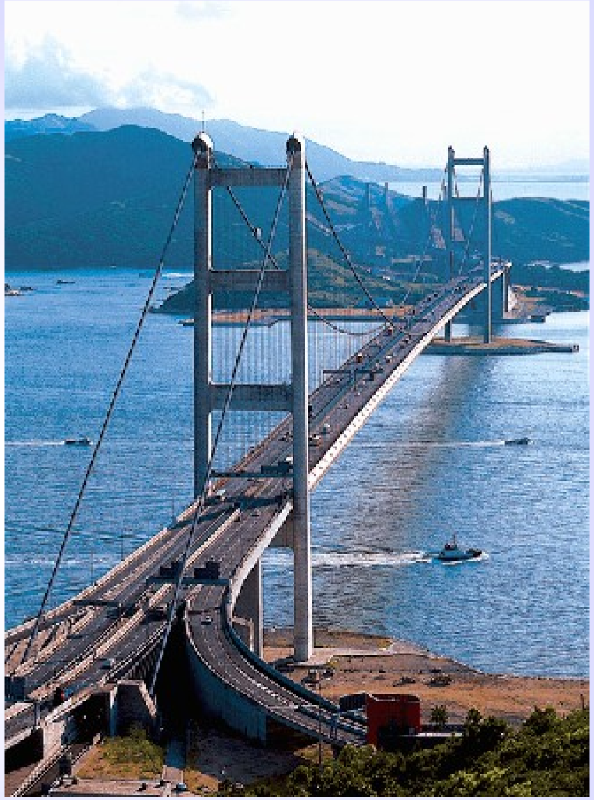
- **high melting and boiling points** except Hg is a liquid at room temperature
- all have **partially filled** *d* subshells
- exhibit horizontal & vertical similarities
- alloys & compounds are important components of materials in modern world
- most **first-row** transition metals are essential for **life**

- Transition metals become **less reactive** (more “Noble”) going from left to right across a row

- Many transition metal compounds are colored and paramagnetic, whereas most main-group ionic compounds are colorless and diamagnetic.

General Features of the *d*-Block Elements from Sc to Zn

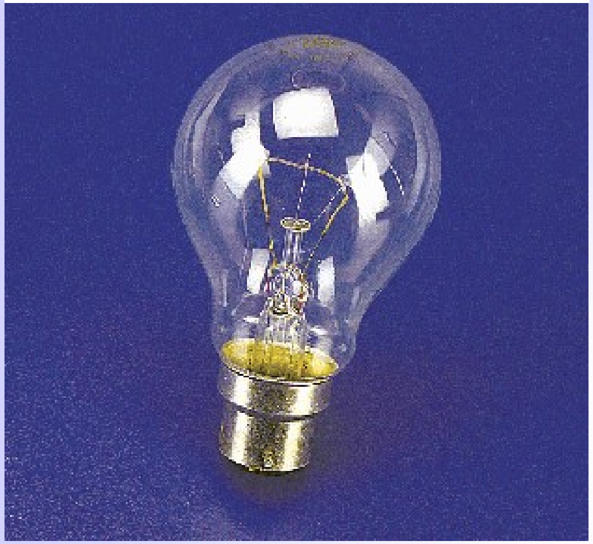
Iron is used to make ships



Tsing Ma Bridge is constructed of steel

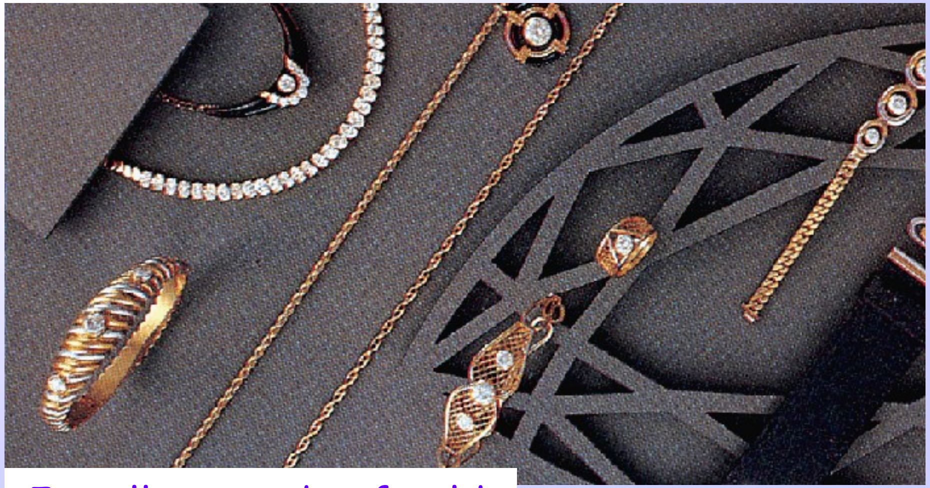
General Features of the *d*-Block Elements from Sc to Zn

Tungsten in a light bulb



The statue is made of alloy of copper and zinc

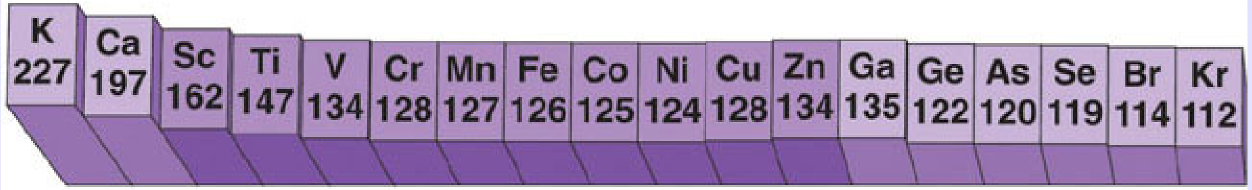
Titanium is used in making aircraft



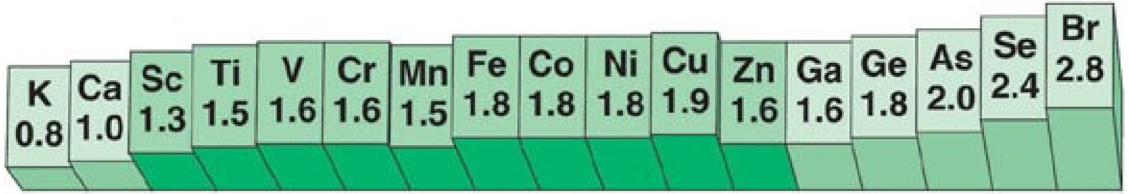
Jewellery made of gold

- The atomic radii **decrease initially**, **remain almost constant in the middle** and then **increase at the end of series**
- Electronegativity and ionization energies also increase relatively little across the transition metals of a particular period.
- The ***lower*** the oxidation state of the transition metal, the ***more metallic*** its behavior.
- ***Ionic*** bonding is more prevalent for the ***lower*** oxidation states, whereas ***covalent*** bonding occurs more frequently for ***higher*** oxidation states.
- Metal oxides become ***less basic*** (more acidic) as the oxidation state ***increases***.
- *d*-block metals have **close-packed structures** hence densities **increase** generally across the first series of *d*-block metals. This is in agreement with the general **decrease in atomic radius** across the series

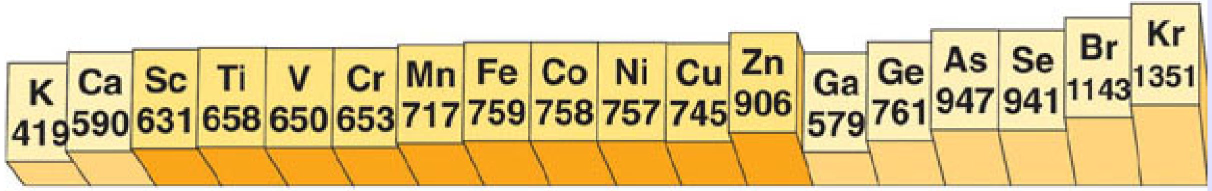
Trends in key atomic properties of Period 4 elements.



A Atomic radius (pm)

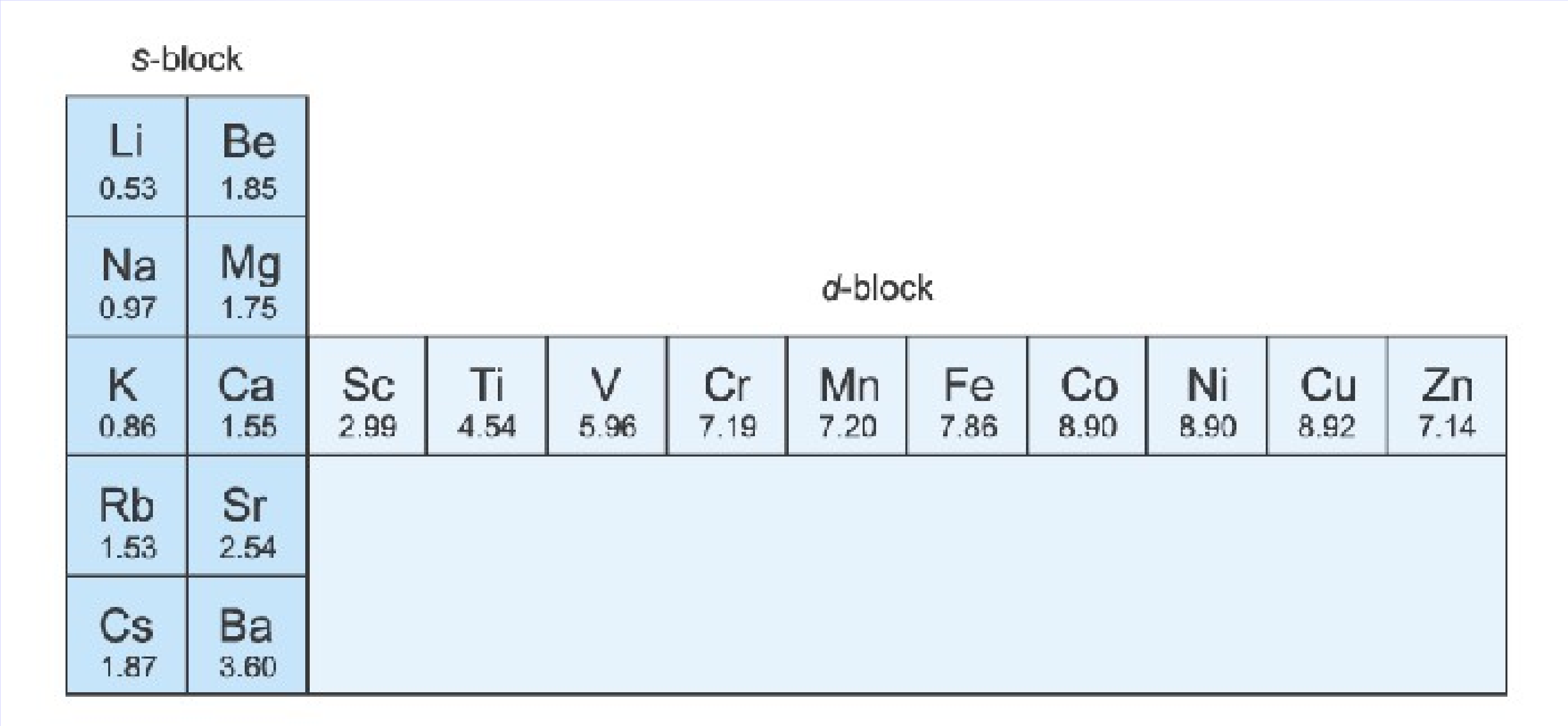


B Electronegativity



C First ionization energy (kJ/mol)

Density

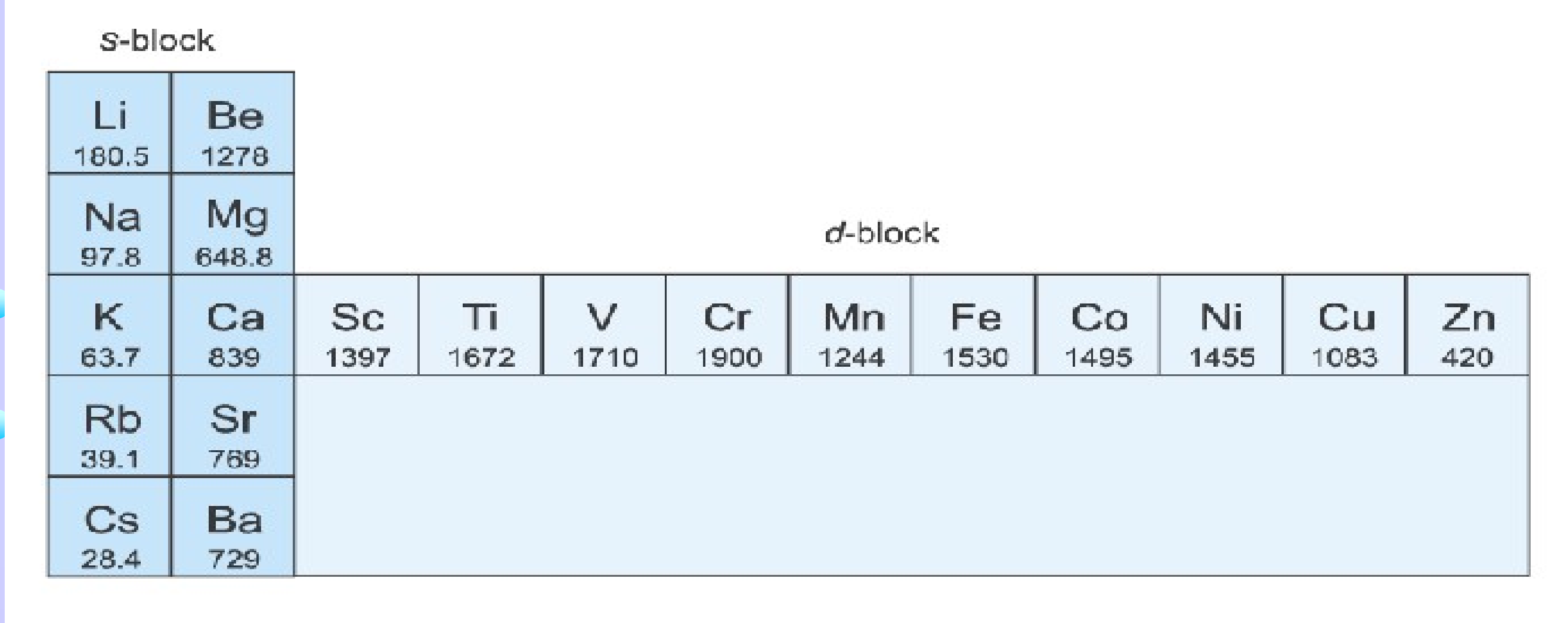


s-block

d-block

Li 0.53	Be 1.85										
Na 0.97	Mg 1.75										
K 0.86	Ca 1.55	Sc 2.99	Ti 4.54	V 5.96	Cr 7.19	Mn 7.20	Fe 7.86	Co 8.90	Ni 8.90	Cu 8.92	Zn 7.14
Rb 1.53	Sr 2.54										
Cs 1.87	Ba 3.60										

Densities (in g cm^{-3}) of the *s*-block metals and the first series of *d*-block metals

- The melting points of the *d*-block metals are much **higher because** *d*-block metal atoms are **small in size** and **closely packed** in the metallic lattice.
- Both **3*d* and 4*s* electrons** of *d*-block metals **participate in metallic bonding** by delocalizing into the electron sea, and thus the **metallic bond strength is very strong**
- The **hardness of a metal** depends on the **strength of the metallic bonds.** The metallic bond of *d*-block metals is **stronger. So** *d*-block metals are **much harder**
- 

s-block

d-block

Li 180.5	Be 1278										
Na 97.8	Mg 648.8										
K 63.7	Ca 839	Sc 1397	Ti 1672	V 1710	Cr 1900	Mn 1244	Fe 1530	Co 1495	Ni 1455	Cu 1083	Zn 420
Rb 39.1	Sr 769										
Cs 28.4	Ba 729										

They act as good catalysts by using the extra electrons in third energy level. So metal forms temporary bonds which aid reactions.

Forms alloys because they dissolve freely in molten conditions in any proportion to form solid solutions.

Ability to form numerous complexes because they have suitable size, charge and incompletely filled valence orbital's to form bonds with ligands.

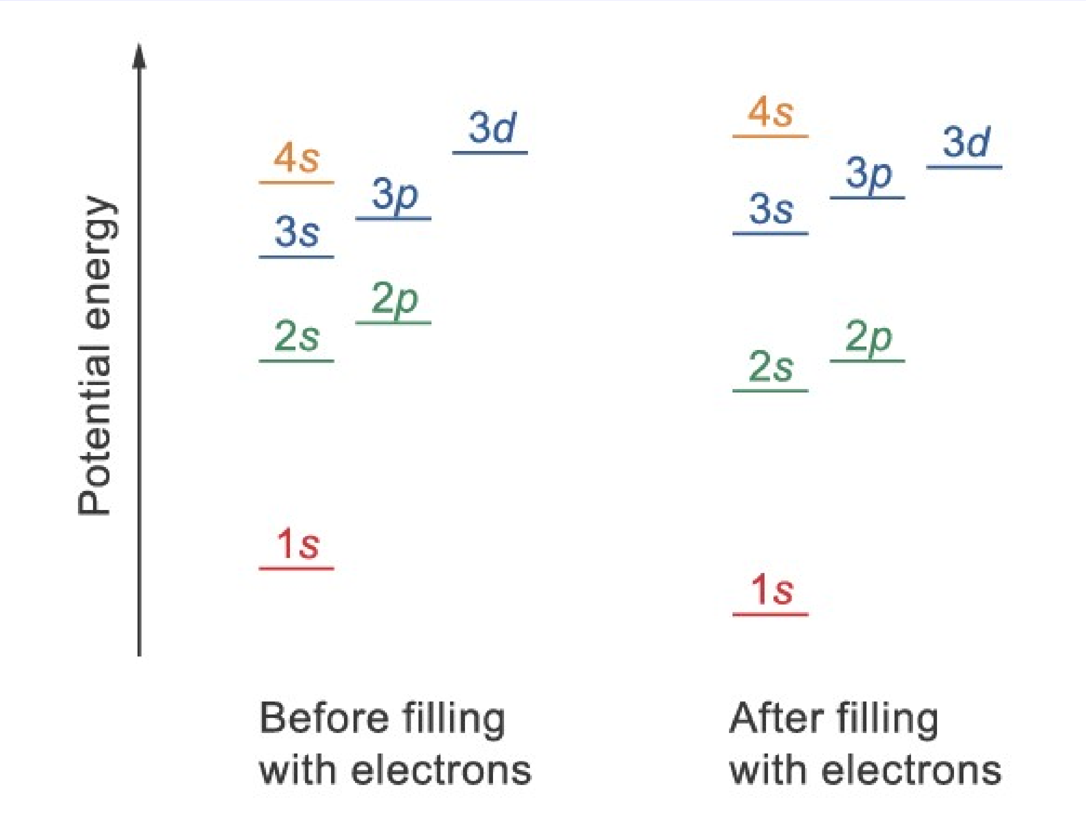
Electron Configurations of Transition Metals and their Ions

The *d*-block elements have the general condensed ground-state configuration [noble gas]$ns^2(n-1)d^x$ where $n = 4$ to 7 and $x = 1$ to 10.

Periods 6 and 7 elements include the *f* sublevel:
[noble gas]$ns^2(n-2)f^{14}(n-1)d^x$ where $n = 6$ or 7.

Transition metals form ions through the ***loss of the ns electrons before the (n – 1)d electrons.***

Electronic Configurations



Relative energy levels of orbitals before and after filling with electrons

- **Before filling electrons**, the energy of 4*s* sub-shell is **lower** than that of 3*d* sub-shell

  ⇒ 4*s* sub-shell is **filled before** 3*d* sub-shell

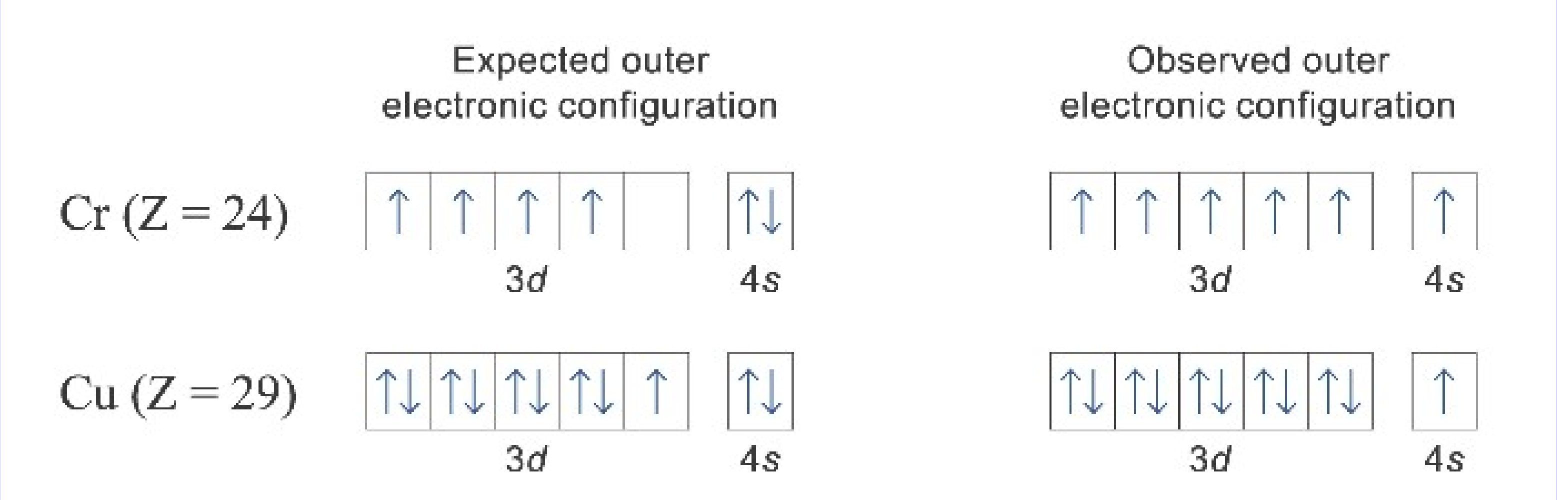
- **Once the 4*s* sub-shell is filled, the energy will increase**

  ⇒ The lowest energy sub-shell becomes 3*d* sub-shell, so the next electron is put into 3*d* sub-shell

Electronic configurations of the first series of *d*-block elements

Element	**Atomic number**	**Electronic configuration**
Scandium	21	$[\mathrm{Ar}]3d^{1}4s^{2}$
Titanium	22	$[\mathrm{Ar}]3d^{2}4s^{2}$
Vanadium	23	$[\mathrm{Ar}]3d^{3}4s^{2}$
Chromium	24	$[\mathrm{Ar}]3d^{5}4s^{1}$
Manganese	25	$[\mathrm{Ar}]3d^{5}4s^{2}$
Iron	26	$[\mathrm{Ar}]3d^{6}4s^{2}$
Cobalt	27	$[\mathrm{Ar}]3d^{7}4s^{2}$
Nickel	28	$[\mathrm{Ar}]3d^{8}4s^{2}$
Copper	29	$[\mathrm{Ar}]3d^{10}4s^{1}$
Zinc	30	$[\mathrm{Ar}]3d^{10}4s^{2}$

- **Cr** is expected to be **[Ar] $3d^4 4s^2$** but **the actual configuration is [Ar] $3d^5 4s^1$**
- **Cu** has the electronic configuration of **[Ar] $3d^{10} 4s^1$ instead of [Ar] $3d^9 4s^2$**



- This can be explained by the fact that **a half-filled** or **fully-filled *d* sub-shell provides extra stability**

Variable Oxidation States

- *d*-block elements has ability to show **variable oxidation states**

  ∵ **3*d* & 4*s* electrons** are of **similar energy levels**, the electrons in both of them are **available for bonding**

  ⇒ When the first transition elements react to form compounds, they can **form ions** of roughly the **same stability** by **losing different numbers of electrons**

  ⇒ Form compounds with **a wide variety of oxidation states**

Oxidation states of the elements of the first transition series in their oxides and chlorides

Oxidation state	Oxide/Chloride									
+1									Cu_2O Cu_2Cl_2	
+2		TiO $TiCl_2$	VO VCl_2	CrO $CrCl_2$	MnO $MnCl_2$	FeO $FeCl_2$	CoO $CoCl_2$	NiO $NiCl_2$	CuO $CuCl_2$	ZnO $ZnCl_2$
+3	Sc_2O_3 $ScCl_3$	Ti_2O_3 $TiCl_3$	V_2O_3 VCl_3	Cr_2O_3 $CrCl_3$	Mn_2O_3 $MnCl_3$	Fe_2O_3 $FeCl_3$		$Ni_2O_3 \cdot xH_2O$		
+4		TiO_2 $TiCl_4$	VO_2 VCl_4	$CrCl_4$	MnO_2					
+5			V_2O_5							
+6				CrO_3						
+7					Mn_2O_7					

Oxidation states of the elements of the first transition series in their compounds

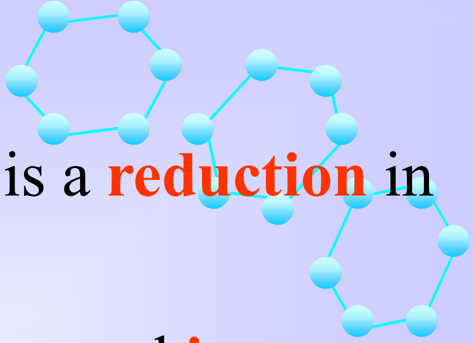
Element	Possible oxidation state						
Sc		+2	+3				
Ti		+2	+3	+4			
V		+2	+3	+4	+5		
Cr		+2	+3	+4	+5	+6	
Mn		+2	+3	+4	+5	+6	+7
Fe		+2	+3	+4	+5	+6	
Co		+2	+3	+4	+5		
Ni		+2	+3	+4			
Cu	+1	+2	+3				
Zn		+2					

Significant features:

1. Sc and Zn **do not** exhibit variable oxidation states. **Sc^{3+}** has electronic configuration of argon (i.e. **$1s^2 2s^2 2p^6 3s^2 3p^6$**). **Zn^{2+}** has the electronic configuration of **[Ar] $3d^{10}$**. *Other oxidation states are not possible.*

2. **Common oxidation states are +2, +3**

3. The **highest oxidation state is +7 at Mn**. This corresponds to removal of all 3*d* & 4*s* electrons. **Minimum oxidation state is +1 for Cu.**

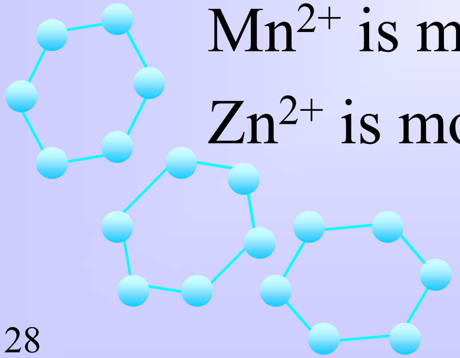


4. Oxidation states increases from Sc to Mn. There is a **reduction** in the number of oxidation states after Mn.

∵ **decrease** in the number of **unpaired electrons** and **increase** in **nuclear charge** which holds the 3*d* electrons more firmly

5. The **relative stability of various oxidation states** can be correlated -with the **stability of empty, half-filled and fully-filled configuration**

e.g. Ti^{4+} is more stable than Ti^{3+} (∵ $[Ar]3d^0$ configuration)
Mn^{2+} is more stable than Mn^{3+} (∵ $[Ar]3d^5$ configuration)
Zn^{2+} is more stable than Zn^{+} (∵ $[Ar]3d^{10}$ configuration)



6. Unstable higher oxidation states are stabilized by forming complexes with small, highly electronegative ligands like F^-, O^{2-} etc.

Unstable lower oxidation states are stabilized by forming complexes with π acid ligands like NO, CO, N_2, C_6H_6 etc.

7. The **stability of +2 oxidation state increases from Sc to Zn while +3 oxidation state decreases from Sc to Zn.**

Nature of compounds in different oxidation states

- In higher oxidation states +6, +7, compounds are **good oxidizing agents and are acidic** e.g. CrO_3, Mn_2O_7 etc. while lower oxidation states +2, compounds are **good reducing agents and basic e.g. Fe^{2+}, Cr^{2+} etc.**

- Compounds in 3+, 4+ oxidation states are amphoteric e.g. Cr_2O_3, MnO_2.

- ***Ionic*** bonding is more prevalent for the ***lower*** oxidation states, whereas ***covalent*** bonding occurs more frequently for ***higher*** oxidation states.

Coloured Ions

- The natural colours of precious gemstones are due to the **existence of small quantities of *d*-block metal ions**

- Most of the *d*-block metals form **coloured** compounds and most of their complexes are **coloured** too

∵ the presence of **incompletely filled *d* orbitals** in the *d*-block metal ions

- When a substance **absorbs visible light of a certain wavelength**, light of wavelengths of **other regions** of the visible light spectrum will be **reflected** or **transmitted**.

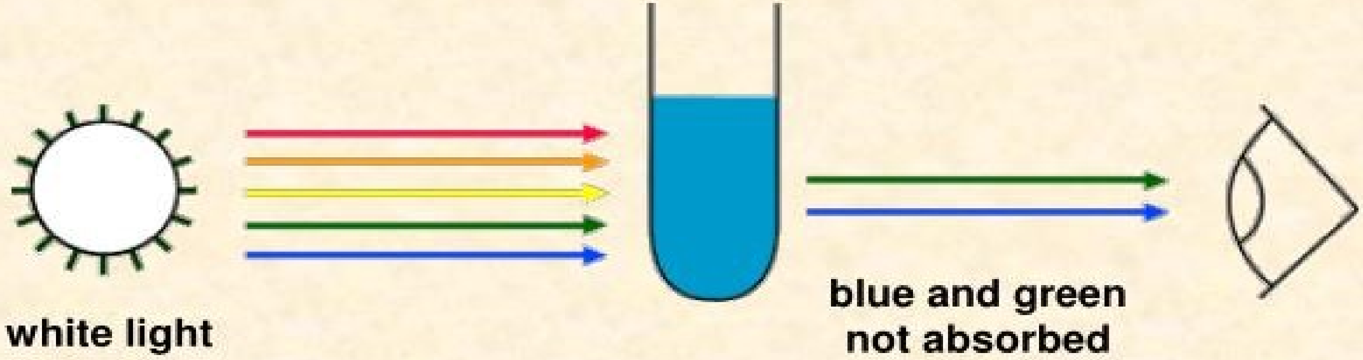
  ⇒ the substance will appear **coloured**

- The absorption of light energy is associated with **electronic transition** (i.e. electron jumping from a lower energy level to a higher one). The **energy required** for electronic transition is **quantized**

- If the **energy** involved in electronic transition **does not fall** into **visible light region**, the substance **will not** appear **coloured**

COLOURED IONS

a solution of copper(II)sulphate is blue because red and yellow wavelengths are absorbed

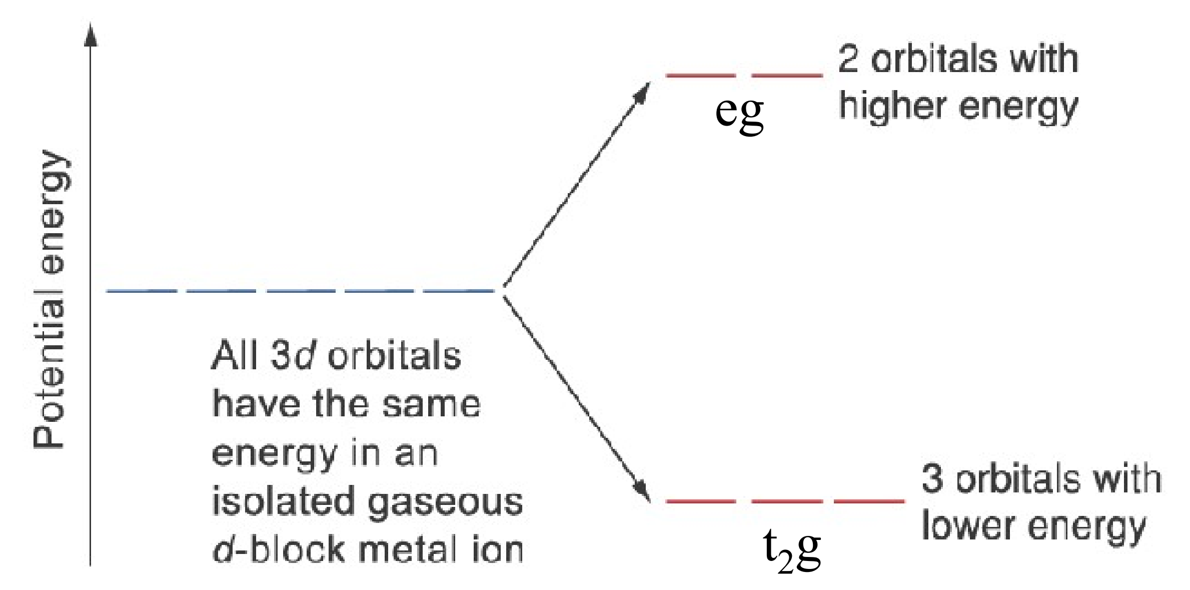


white light

blue and green not absorbed

- For the *d*-block elements, the five 3*d* orbitals are **degenerate** in **gaseous ions**
- However, under **the influence of a ligand**, the 3*d* orbitals will **split into 2 groups** of orbitals with **slightly different energy** levels

⇒ due to the **interaction of the 3*d* orbitals with the electron clouds of the ligands**



- When a sufficient amount of energy is absorbed, **electrons** will be promoted **from 3*d* orbitals at lower energy level** to those at the **higher energy level**
- The **energy** required for the ***d*-*d* transition** falls within the **visible light** spectrum.

⇒ This leads to light absorption, and **reflects or transmit the remainder** of the visible light

⇒ *d*-block metal ions have specific **colours**

$[Ti(H_2O)_6]^{3+}$ absorbs green radiation appears purple colour

- For *d*-*d* electronic transition and absorption of visible light to occur, there must be **unpaired *d* electrons** in the *d*-block metal atoms or ions

  ⇒ **Sc^{3+} and Zn^{2+} are colorless** due to the **empty 3*d* sub-shell** and the **fully-filled 3*d* sub-shell** respectively

- All the coloured ions in 3d-block are not due to d-d transition but charge transfer transition also play important roles. In charge transfer transition an electron is transferred from ligand to metal, charge transfer transition always produces intense colour as compared to d-d transition.

- MnO_4^- is dark purple coloured though Mn is in (+VII) oxidation state with $3d^0$ configuration.

The colours of some hydrated 3*d*-block metal ions

Ion aq.	**Outer electronic configuration**	**No. of unpaired electrons**	**Colour**
Sc^{3+}, Ti^{4+}	$3d^0$	0	⬜
Ti^{3+}	$3d^1$	1	🟪
V^{4+}	$3d^1$	1	🟦
V^{3+}	$3d^2$	2	🟩
V^{2+}	$3d^3$	3	🟪
Cr^{3+}	$3d^3$	3	🟩
Cr^{2+}	$3d^4$	4	🟦
Mn^{3+}	$3d^4$	4	🟪
Mn^{2+}	$3d^5$	5	🟥
Fe^{3+}	$3d^5$	5	🟨
Fe^{2+}	$3d^6$	4	🟩
Co^{2+}	$3d^7$	3	🟥
Ni^{2+}	$3d^8$	2	🟩
Cu^{2+}	$3d^9$	1	🟦
Zn^{2+}, Cu^{+}	$3d^{10}$	0	⬜

Colors of representative compounds of the Period 4 transition metals.

titanium(IV) oxide

sodium chromate

potassium ferricyanide

nickel(II) nitrate hexahydrate

zinc sulfate heptahydrate

scandium oxide

vanadyl sulfate dihydrate

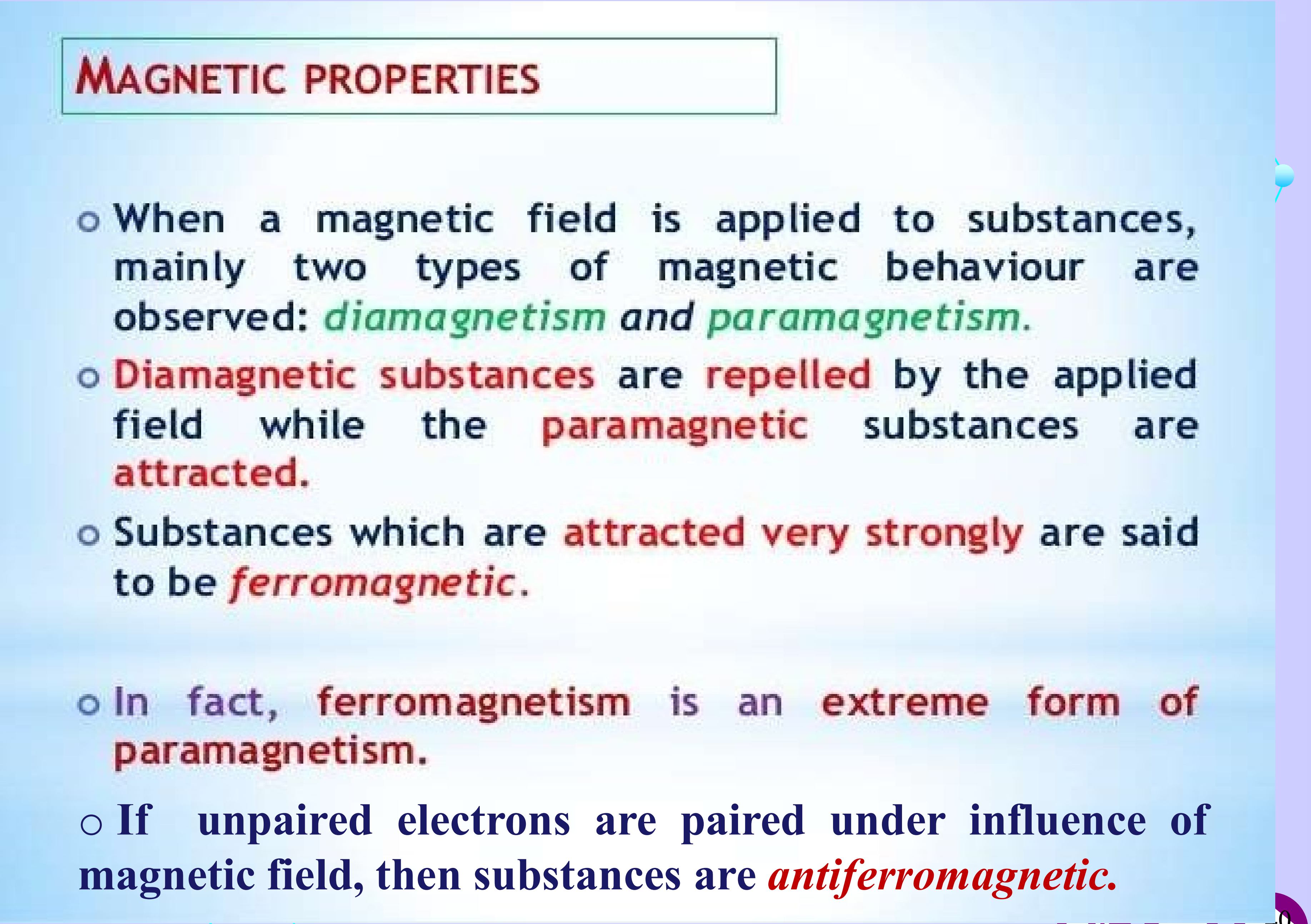
manganese(II) chloride tetrahydrate

cobalt(II) chloride hexahydrate

copper(II) sulfate pentahydrate

Factors affecting the colour of the complexes

1. Number of 3d electrons
2. Field strength of ligand
3. Geometry of complex
4. Defects in solids
5. Cutting of the crystal
6. Charge transfer spectra
7. Role of anions



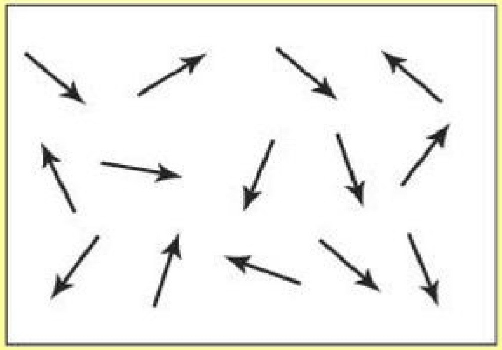
MAGNETIC PROPERTIES

- When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed: *diamagnetism and paramagnetism.*
- Diamagnetic substances are repelled by the applied field while the paramagnetic substances are attracted.
- Substances which are attracted very strongly are said to be *ferromagnetic*.
- In fact, ferromagnetism is an extreme form of paramagnetism.

○ If unpaired electrons are paired under influence of magnetic field, then substances are *antiferromagnetic.*

Paramagnetism

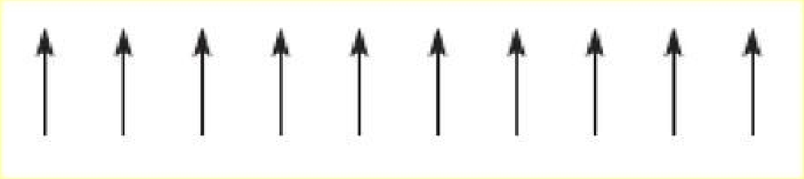
In a paramagnet, the magnetic moments tend to be randomly orientated due to thermal fluctuations when there is no magnetic field. In an applied magnetic field these moments start to align parallel to the field such that the magnetisation of the material is proportional to the applied field



Diamagnetism

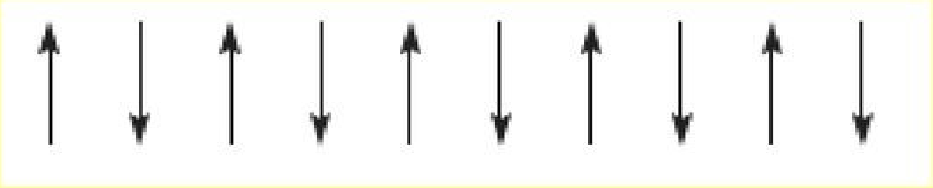
Substances are align perpendicular to the applied magnetic field.

The interaction may give rise to ferromagnetism or antiferromagnetism:



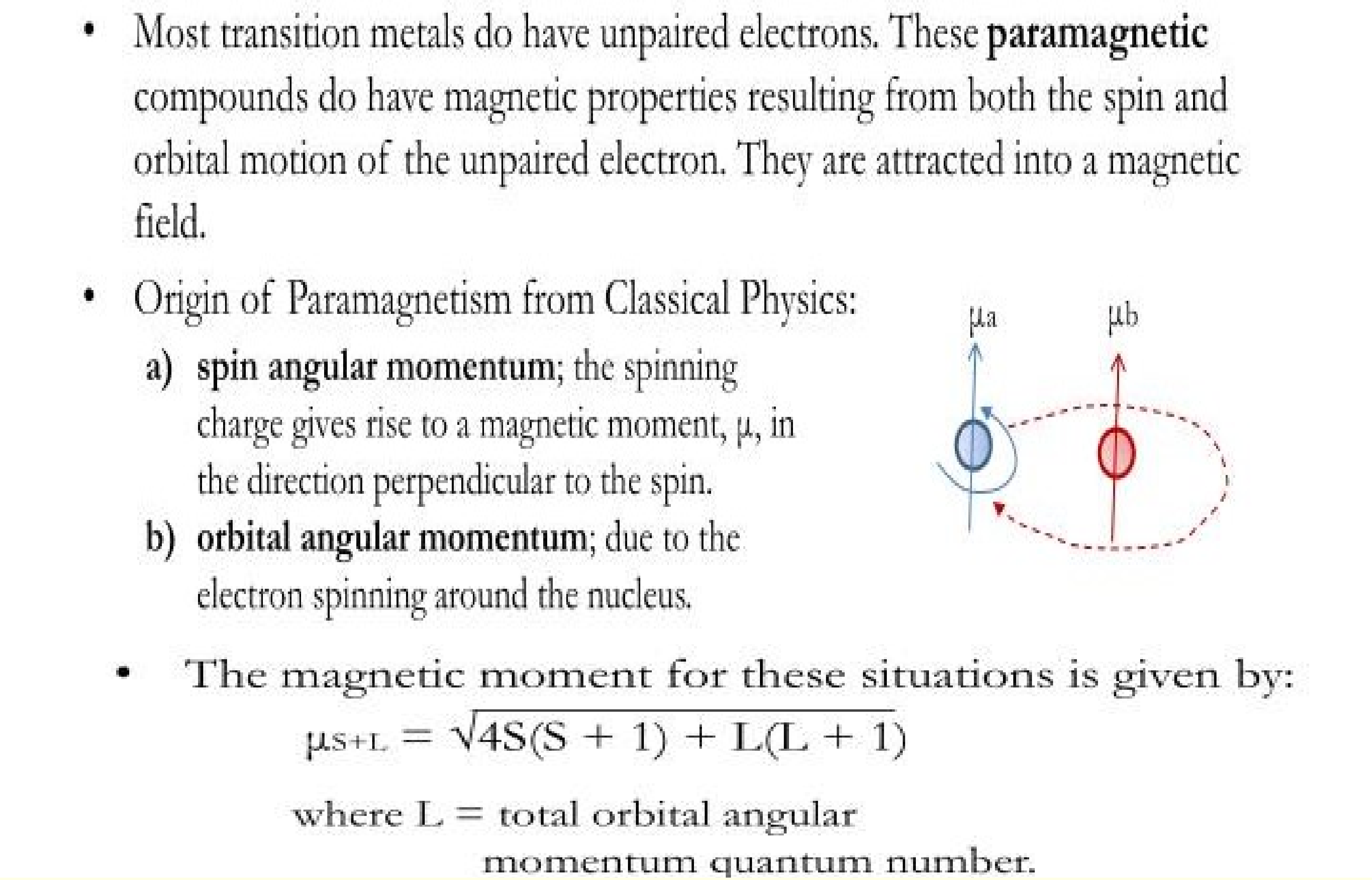
Ferromagnetism

Antiferromagnetism



In a ferromagnetic material, large domains of magnetic dipoles are aligned in the same direction;

in an antiferromagnetic material, neighbouring magnetic dipoles are aligned in opposite directions



- Most transition metals do have unpaired electrons. These **paramagnetic** compounds do have magnetic properties resulting from both the spin and orbital motion of the unpaired electron. They are attracted into a magnetic field.
- Origin of Paramagnetism from Classical Physics:
  - a) **spin angular momentum**; the spinning charge gives rise to a magnetic moment, μ, in the direction perpendicular to the spin.
  - b) **orbital angular momentum**; due to the electron spinning around the nucleus.

- The magnetic moment for these situations is given by:

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$$

where L = total orbital angular momentum quantum number.

S = total spin quantum number
μ = Bohr magneton

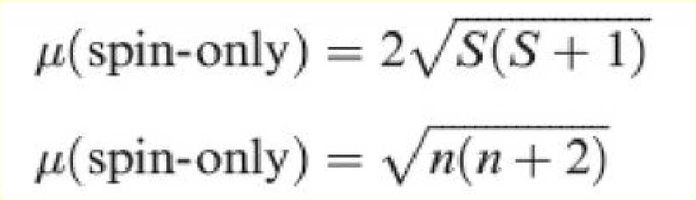
Magnetic properties

Paramagnetism arises from unpaired electrons

Each electron has a magnetic moment with one component associated with the *spin angular momentum* of the electron and (except when the quantum number l = 0) a second component associated with the *orbital angular momentum*

For many complexes of first row d-block metal ions we can ignore the second component and the magnetic moment, μ, can be regarded as being determined by the number of unpaired electrons, n

$$\mu_s = \sqrt{4s(s+1)}$$

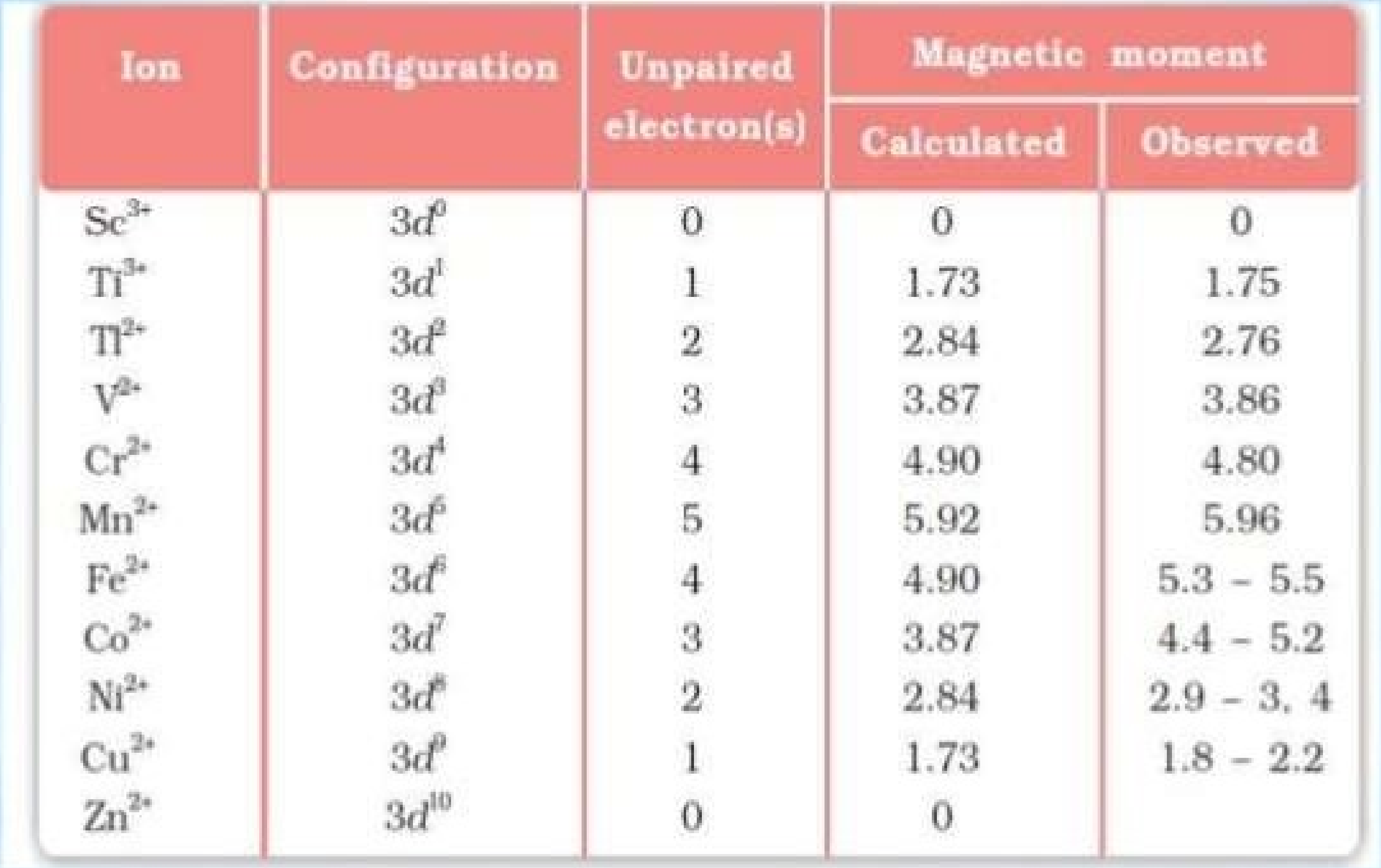


$$\mu(\text{spin-only}) = 2\sqrt{S(S+1)}$$

$$\mu(\text{spin-only}) = \sqrt{n(n+2)}$$

μ_S

for one electron spin, s = ½ then for n electrons s = n/2



Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.73	1.75
Ti^{2+}	$3d^2$	2	2.84	2.76
V^{2+}	$3d^3$	3	3.87	3.86
Cr^{2+}	$3d^4$	4	4.90	4.80
Mn^{2+}	$3d^5$	5	5.92	5.96
Fe^{2+}	$3d^6$	4	4.90	5.3 – 5.5
Co^{2+}	$3d^7$	3	3.87	4.4 – 5.2
Ni^{2+}	$3d^8$	2	2.84	2.9 – 3. 4
Cu^{2+}	$3d^9$	1	1.73	1.8 – 2.2
Zn^{2+}	$3d^{10}$	0	0	

- The paramagnetism first increases in any transition element series, and then decreases. The maximum paramagnetism is seen around the middle of the series.

CATALYTIC PROPERTIES

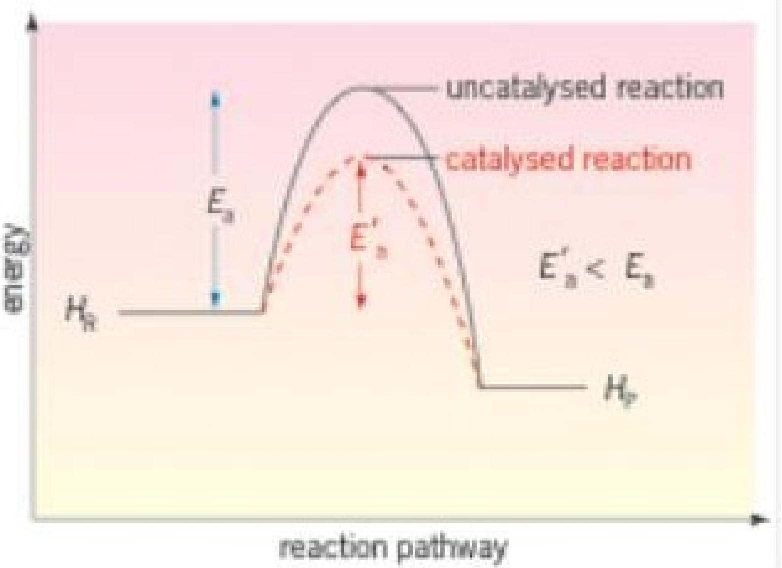
- ✓Vanadium(V) oxide, V_2O_5 (in Contact Process)
- ✓Finely divided iron (in Haber's Process)
- ✓Nickel (in Catalytic Hydrogenation)
- ✓Cobalt (Synthesis of gasoline)

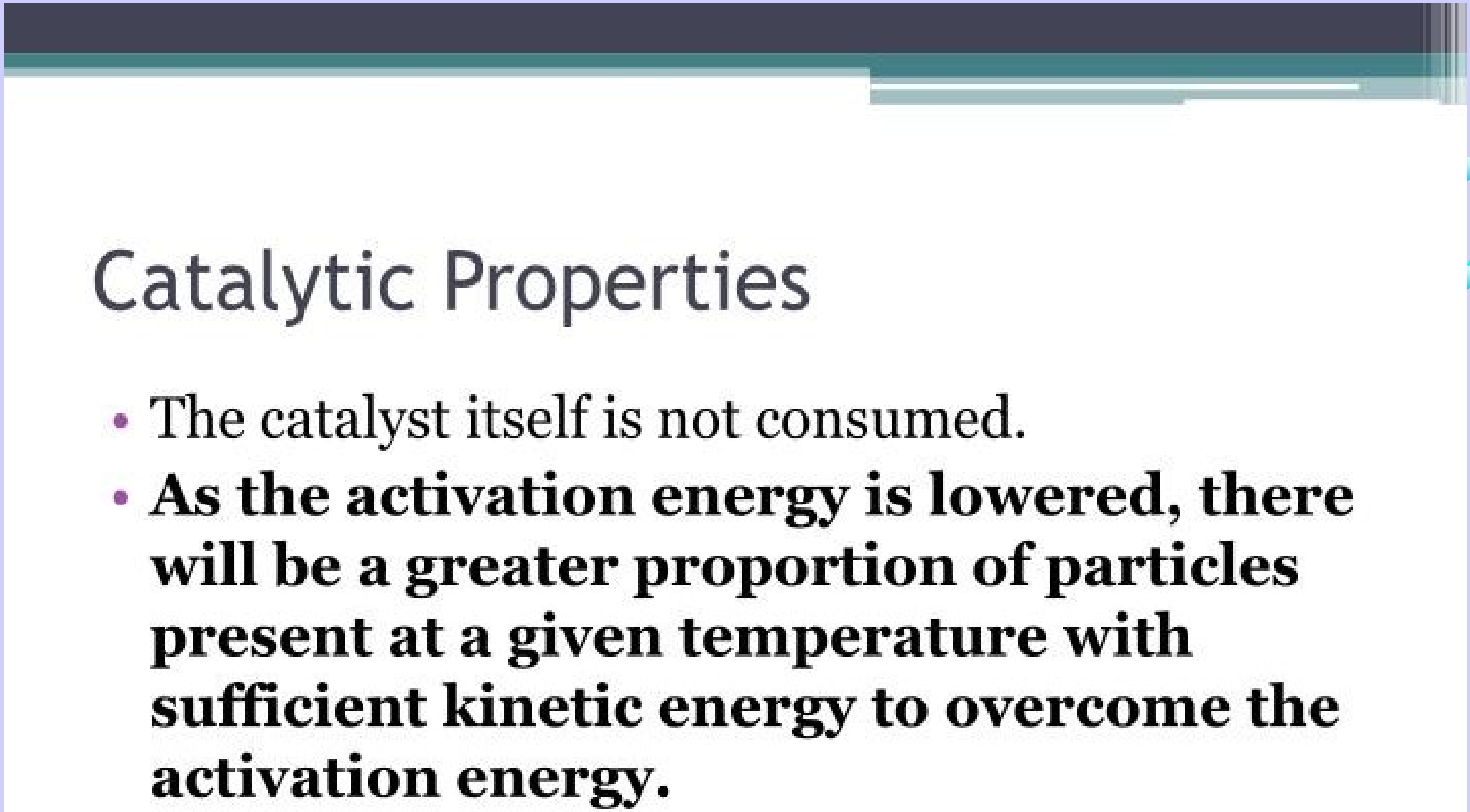
- ➢ This property is due to-
- ➢ Presence of unpaired electrons in their incomplete d orbitals.
- ➢ Variable oxidation state of transition metals.
- ➢ In most cases , provide large surface area with free valencies.

Catalytic Properties

- **A catalyst increases the rate of a chemical reaction by providing an alternative reaction pathway with a lower activation energy.**

➢**enabling the reaction to proceed faster than the uncatalyzed one**



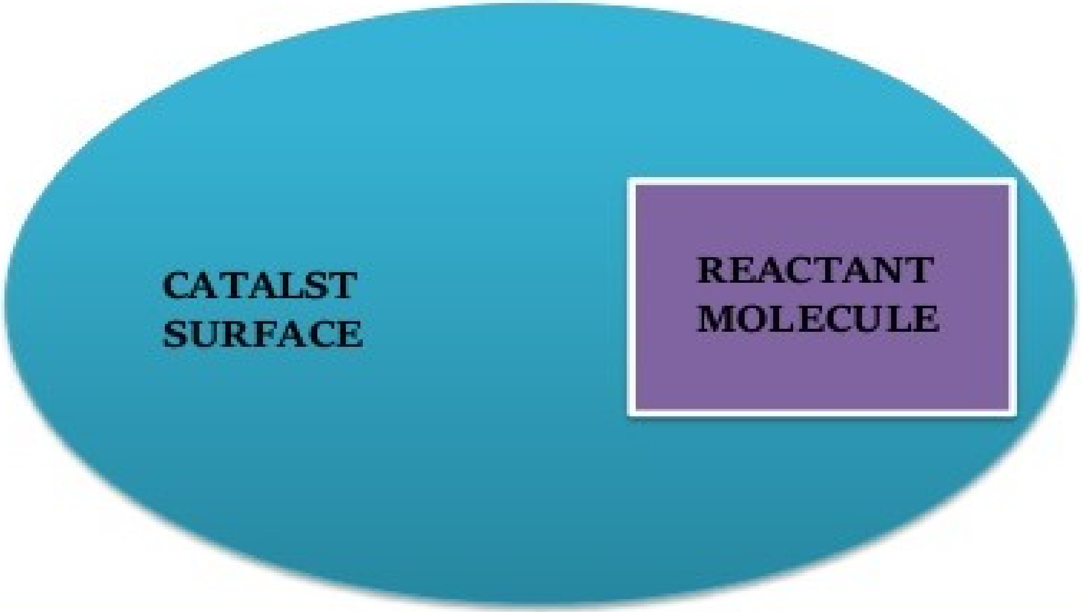


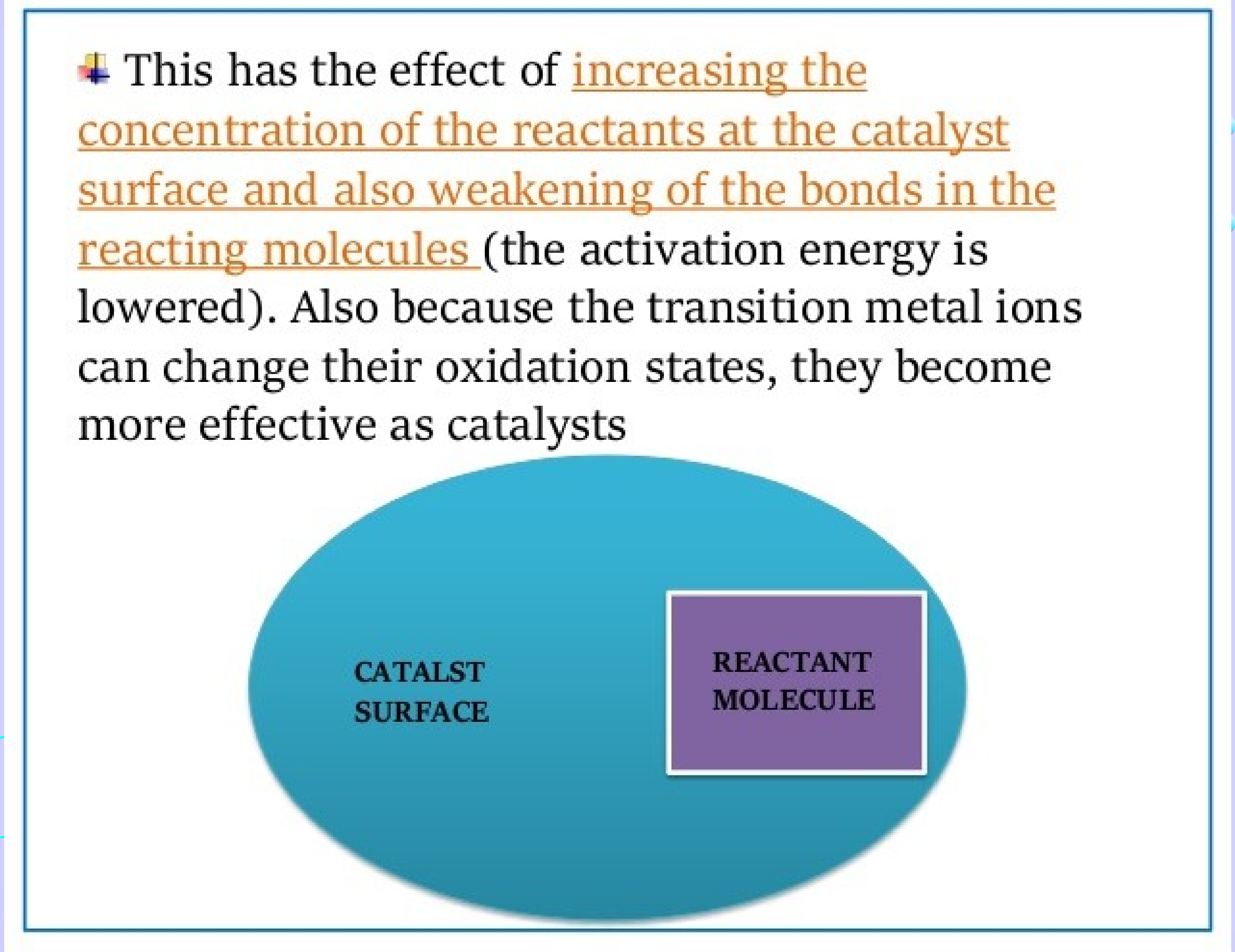
Catalytic Properties

- The catalyst itself is not consumed.
- **As the activation energy is lowered, there will be a greater proportion of particles present at a given temperature with sufficient kinetic energy to overcome the activation energy.**

- **d-block metals and their compounds exert their catalytic actions in either heterogeneous catalysis or homogeneous catalysis**

- Catalysts at a solid surface (nanomaterial-based catalysts) involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilize 3d and 4s electrons for bonding).





- This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowered). Also because the transition metal ions can change their oxidation states, they become more effective as catalysts

45.3 Characteristic Properties of the *d*-Block Elements and their Compounds (SB p.199)

e.g.: Synthesis of gaseous ammonia from N_2 and H_2

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

- In the **absence of a catalyst**, the formation of gaseous ammonia proceeds at an **extremely low rate**

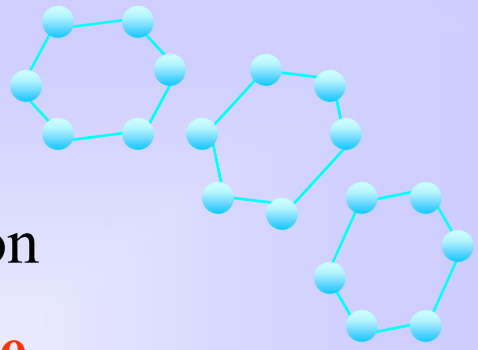
∵ the **probability of collision** of four gaseous molecules is very **small**

⇒ the **four** reactant molecules have to **collide** in a **proper orientation** in order to give products

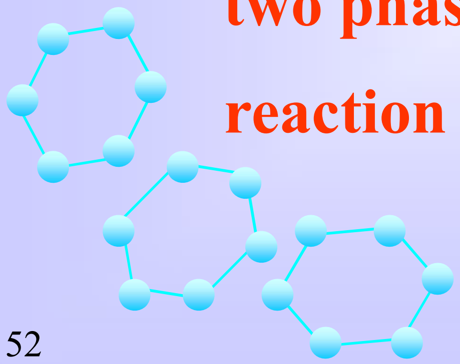
⇒ the **bond enthalpy** of $N \equiv N$ is **very large**

⇒ the reaction has a **high activation energy**

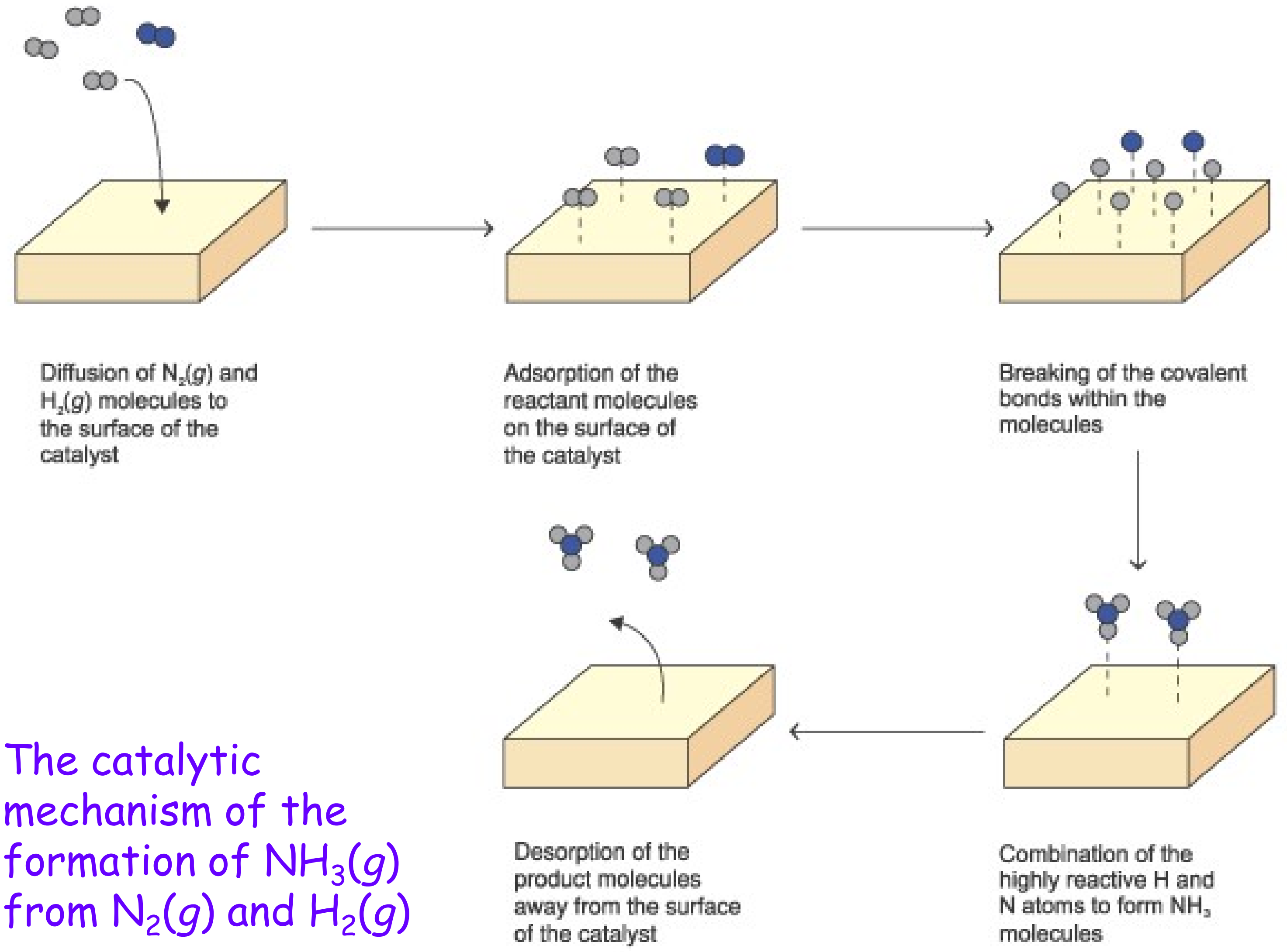
45.3 Characteristic Properties of the *d*-Block Elements and their Compounds (SB p.199)



- In the **presence of iron catalyst**, the reaction proceeds **faster** as it provides an **alternative reaction pathway**
- The catalyst exists in a **different phase** from that of both reactant and products
- The catalytic action **occurs at the interface between two phases**, and the metal provides an **active reaction surface** for the reaction to occur

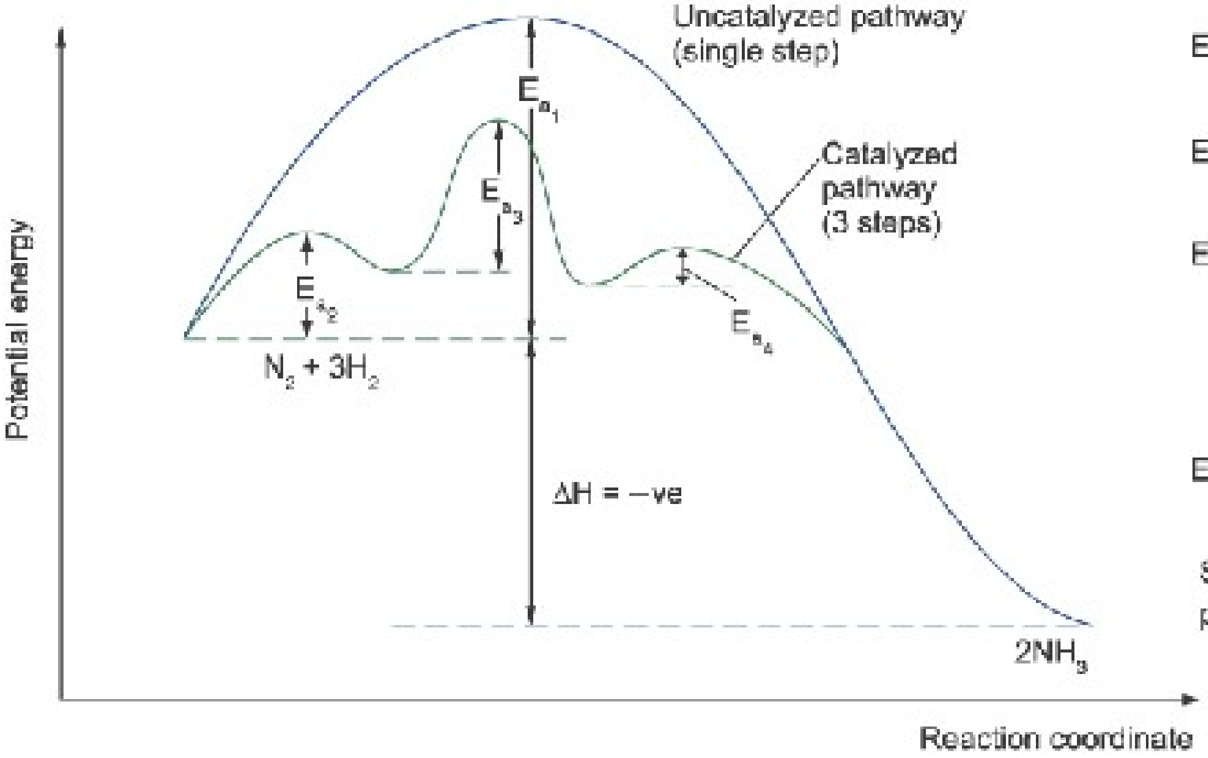


45.3 Characteristic Properties of the *d*-Block Elements and their Compounds (SB p.200)



The catalytic mechanism of the formation of $NH_3(g)$ from $N_2(g)$ and $H_2(g)$

45.3 Characteristic Properties of the *d*-Block Elements and their Compounds (SB p.200)



E_{a_1} : Activation energy for the uncatalyzed pathway

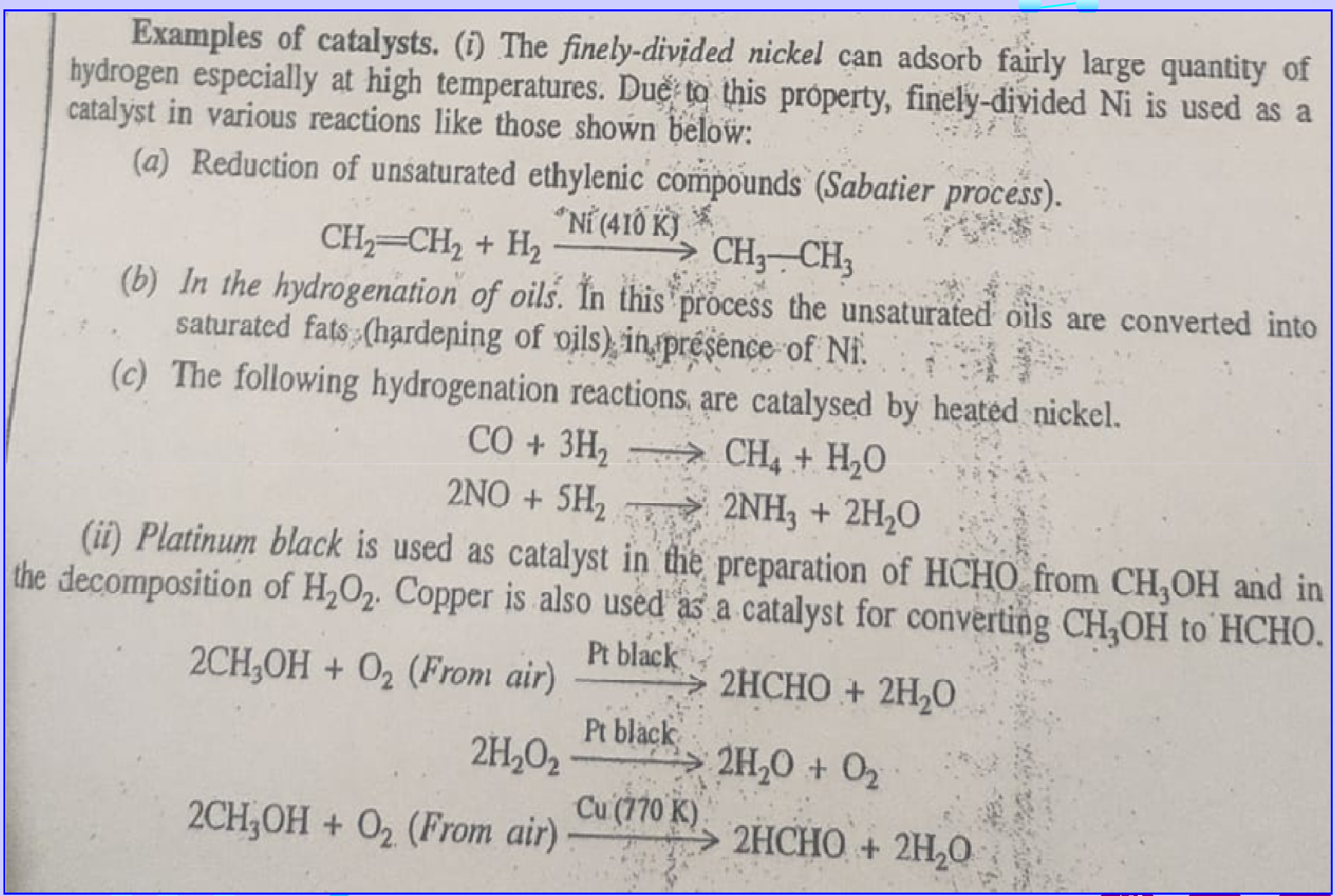
E_{a_2} : Activation energy for the first step of the catalyzed pathway

E_{a_3} : Activation energy for the second step of the catalyzed pathway; since it is the highest for the catalyzed reaction, the second step is the rate-determining step

E_{a_4} : Activation energy for the third step of the catalyzed pathway

Since $E_{a_3} << E_{a_1}$, the catalyzed pathway proceeds at a much faster rate.

Energy profiles of the reaction pathways in the presence and absence of a heterogeneous catalyst



Examples of catalysts. (*i*) The *finely-divided nickel* can adsorb fairly large quantity of hydrogen especially at high temperatures. Due to this property, finely-divided Ni is used as a catalyst in various reactions like those shown below:

(*a*) Reduction of unsaturated ethylenic compounds (*Sabatier process*).

$$CH_2{=}CH_2 + H_2 \xrightarrow{\text{Ni (410 K)}} CH_3{-}CH_3$$

(*b*) *In the hydrogenation of oils.* In this process the unsaturated oils are converted into saturated fats (hardening of oils) in presence of Ni.

(*c*) The following hydrogenation reactions are catalysed by heated nickel.

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

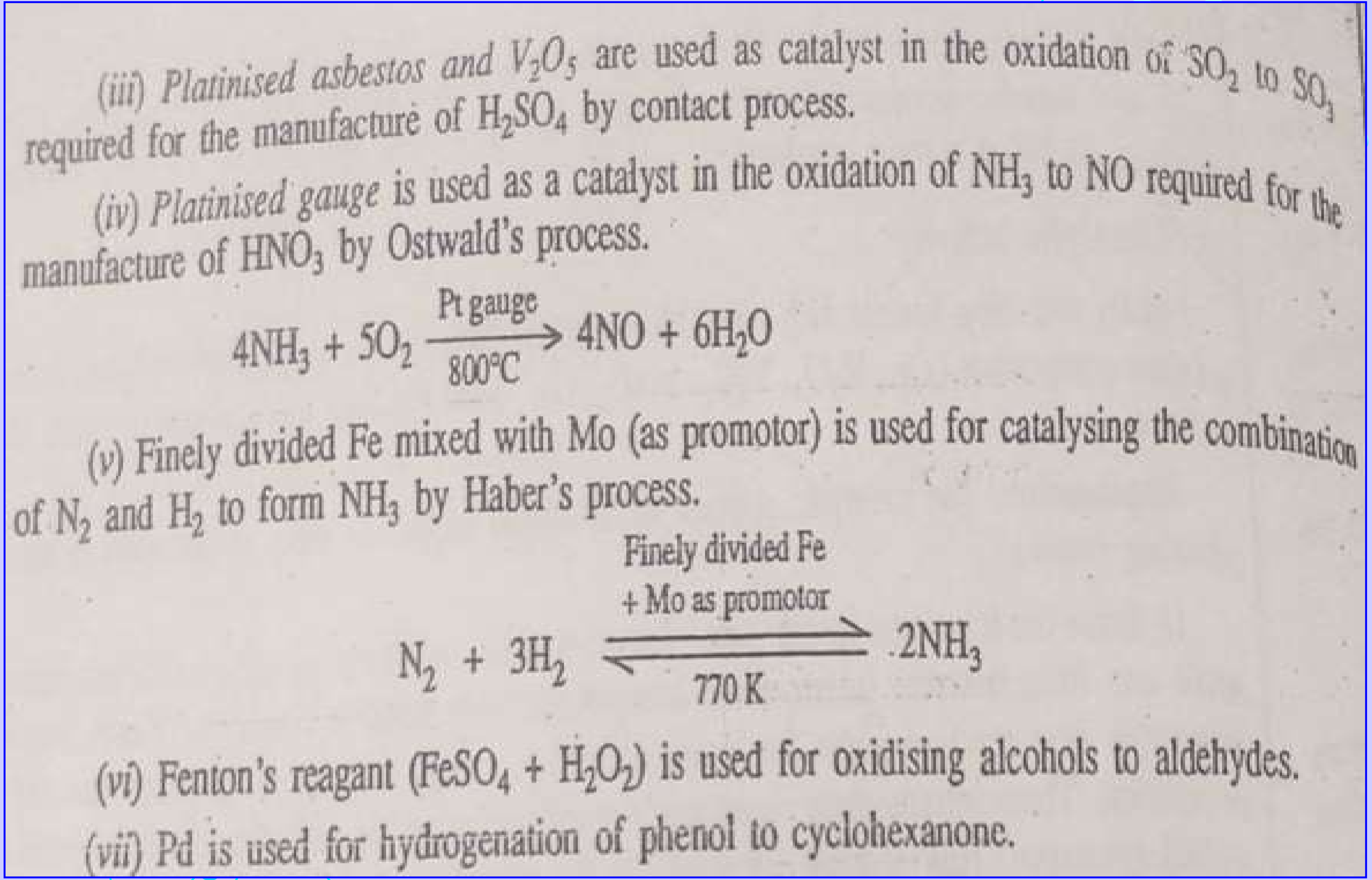
$$2NO + 5H_2 \longrightarrow 2NH_3 + 2H_2O$$

(*ii*) *Platinum black* is used as catalyst in the preparation of HCHO from CH_3OH and in the decomposition of H_2O_2. Copper is also used as a catalyst for converting CH_3OH to HCHO.

$$2CH_3OH + O_2\ (\textit{From air}) \xrightarrow{\text{Pt black}} 2HCHO + 2H_2O$$

$$2H_2O_2 \xrightarrow{\text{Pt black}} 2H_2O + O_2$$

$$2CH_3OH + O_2\ (\textit{From air}) \xrightarrow{\text{Cu (770 K)}} 2HCHO + 2H_2O$$



(*iii*) *Platinised asbestos and V_2O_5* are used as catalyst in the oxidation of SO_2 to SO_3 required for the manufacture of H_2SO_4 by contact process.

(*iv*) *Platinised gauge* is used as a catalyst in the oxidation of NH_3 to NO required for the manufacture of HNO_3 by Ostwald's process.

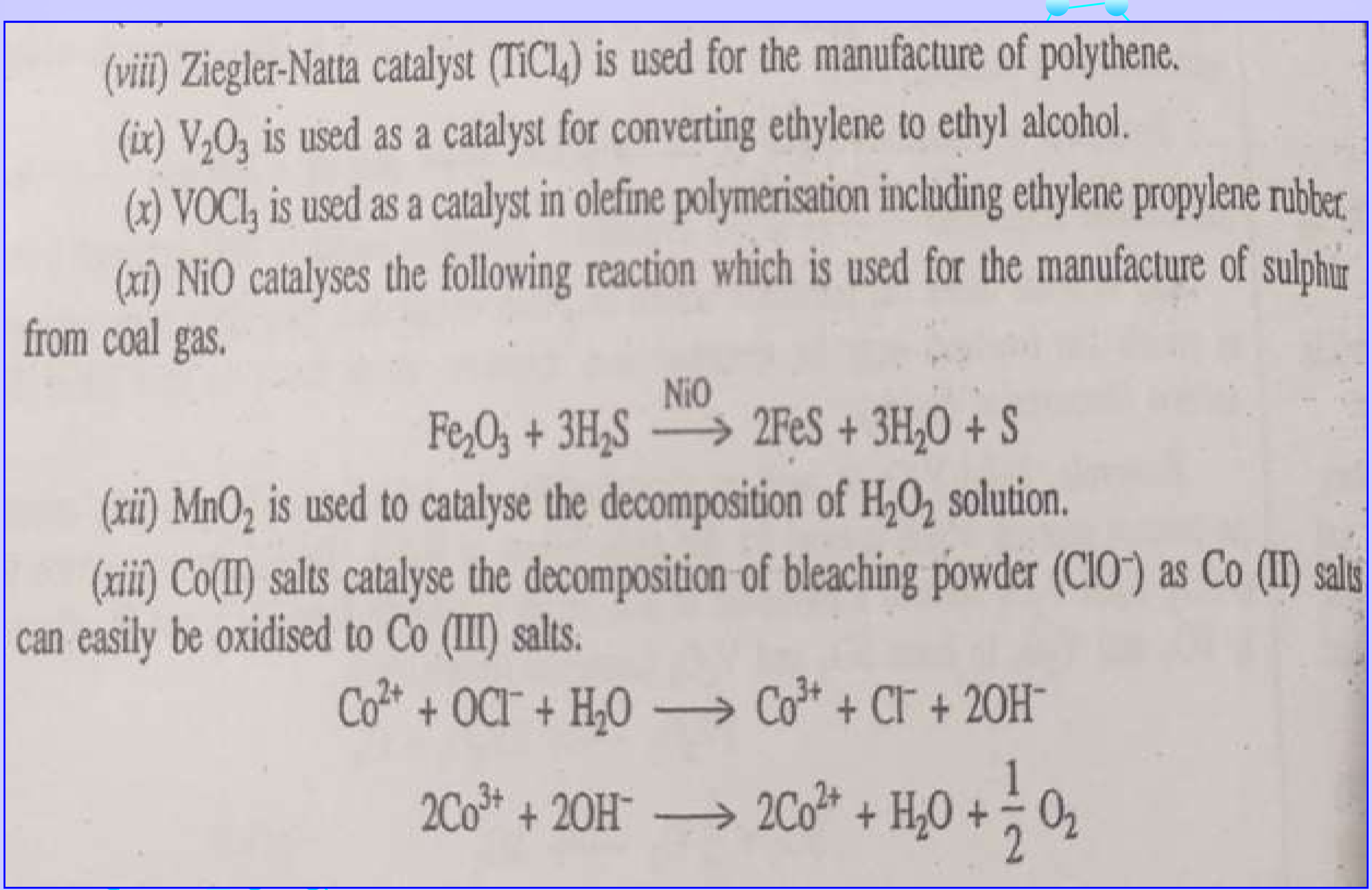
$$4NH_3 + 5O_2 \xrightarrow[800°C]{\text{Pt gauge}} 4NO + 6H_2O$$

(*v*) Finely divided Fe mixed with Mo (as promotor) is used for catalysing the combination of N_2 and H_2 to form NH_3 by Haber's process.

$$N_2 + 3H_2 \xrightleftharpoons[770\text{ K}]{\text{Finely divided Fe + Mo as promotor}} 2NH_3$$

(*vi*) Fenton's reagant ($FeSO_4 + H_2O_2$) is used for oxidising alcohols to aldehydes.

(*vii*) Pd is used for hydrogenation of phenol to cyclohexanone.



(*viii*) Ziegler-Natta catalyst ($TiCl_4$) is used for the manufacture of polythene.

(*ix*) V_2O_3 is used as a catalyst for converting ethylene to ethyl alcohol.

(*x*) $VOCl_3$ is used as a catalyst in olefine polymerisation including ethylene propylene rubber.

(*xi*) NiO catalyses the following reaction which is used for the manufacture of sulphur from coal gas.

$$Fe_2O_3 + 3H_2S \xrightarrow{NiO} 2FeS + 3H_2O + S$$

(*xii*) MnO_2 is used to catalyse the decomposition of H_2O_2 solution.

(*xiii*) Co(II) salts catalyse the decomposition of bleaching powder (ClO^-) as Co (II) salts can easily be oxidised to Co (III) salts.

$$Co^{2+} + OCl^- + H_2O \longrightarrow Co^{3+} + Cl^- + 2OH^-$$

$$2Co^{3+} + 2OH^- \longrightarrow 2Co^{2+} + H_2O + \frac{1}{2}O_2$$

FORMATION OF COMPLEX COMPOUNDS

- Complex compounds are those in which the metal ions bind a number of anions or neutral molecules giving complex species with characteristic properties.

- The transition metals form a large number of complex compounds.

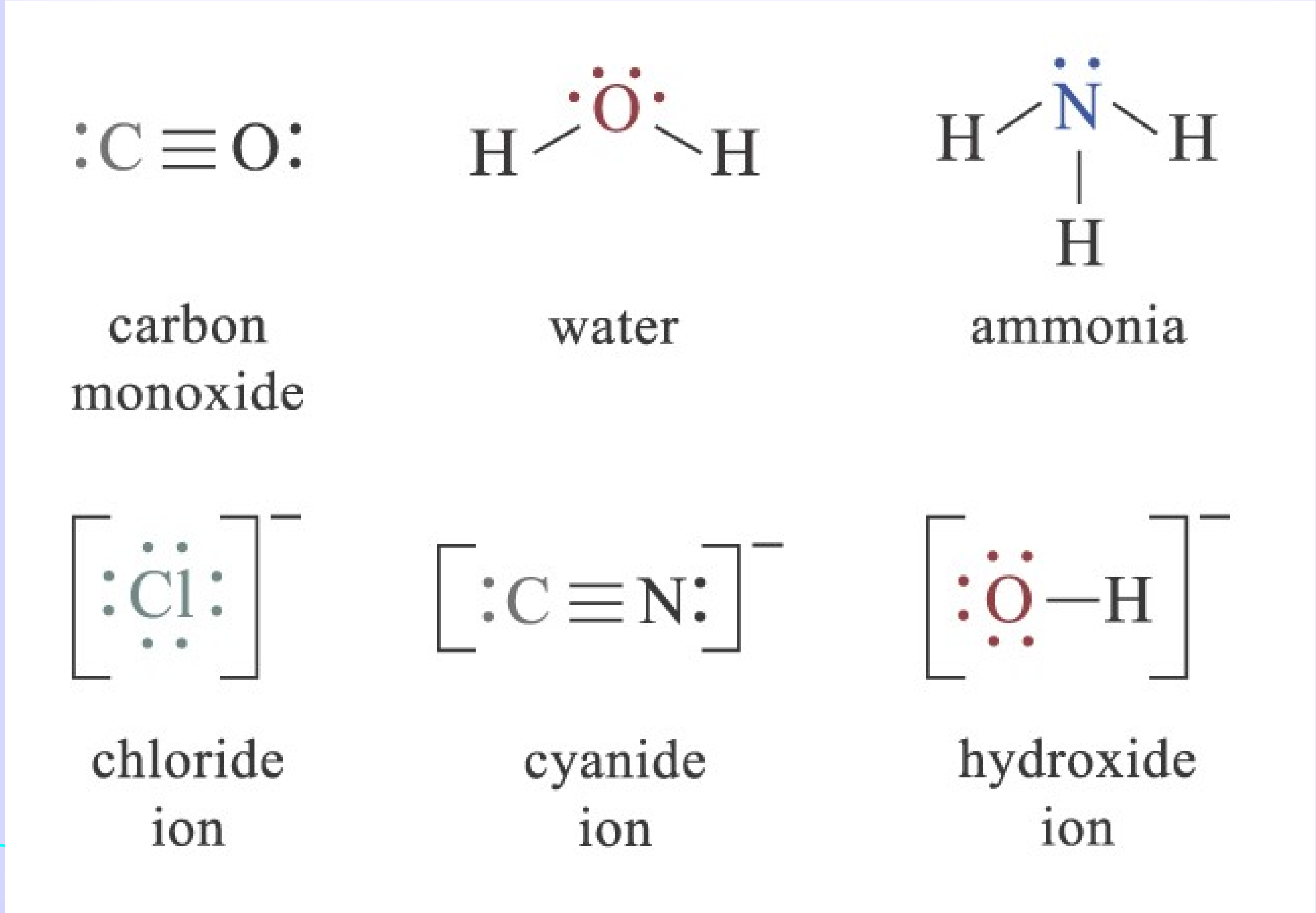
- A few examples are: $[Fe(CN)6]^{3-}$, $[Fe(CN)6]^{4-}$, $[Cu(NH3)4]^{2+}$ and $[PtCl4]^{2-}$.

Formation of Complexes

A **complex** is formed when a central metal atom or ion is surrounded by other molecules or ions which form **dative covalent bonds** with the central metal atom or ion.

- The molecules or ions that form the dative covalent bonds are called **ligands**
- In a ligand, there is at least one atom having **a lone pair of electrons** which can be donated to the central metal atom or ion to form a dative covalent bond

Examples of ligands:



carbon monoxide

water

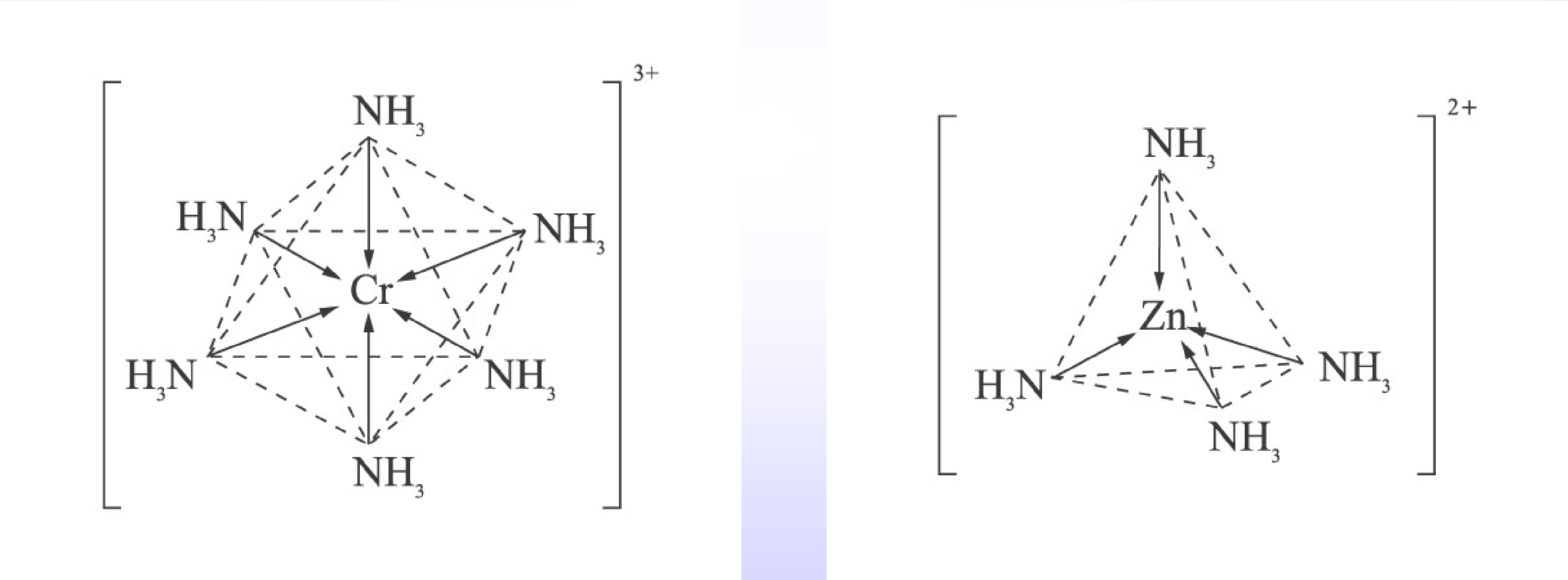
ammonia

chloride ion

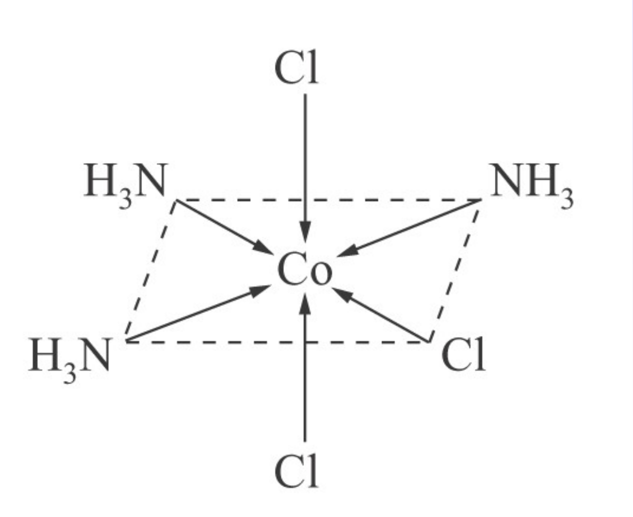
cyanide ion

hydroxide ion

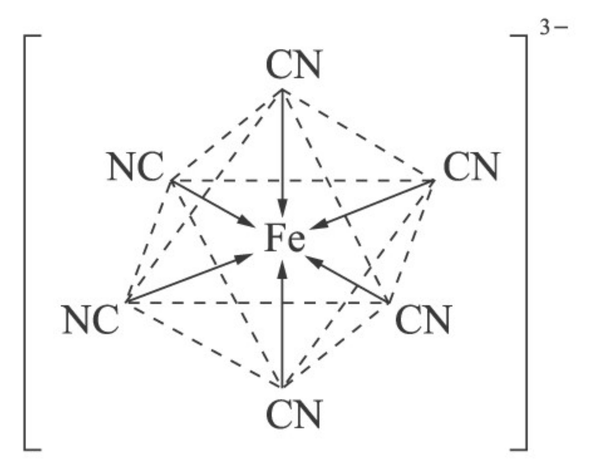
- Depending on the overall charge of the complex formed, complexes are classified into 3 main types: **cationic**, **neutral** and **anionic complex**

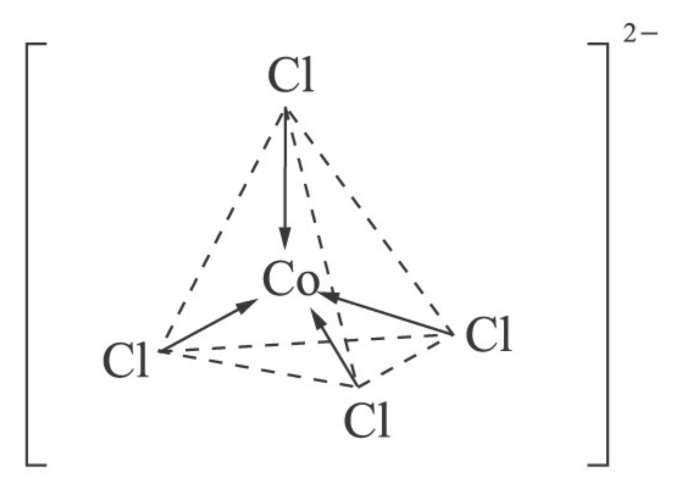


Cationic complex ions



Neutral complex





Anionic complex ions

- The **coordination number** of the central metal atom or ion in a complex is the **number of ligands bonded to this metal atom or ion**

  e.g. in $[Cu(NH_3)_4]^{2+}(aq)$, there are 4 ligands are bonded to the central Cu^{2+} ion, so the coordination number is 4

- The most common coordination numbers are **4** and **6**

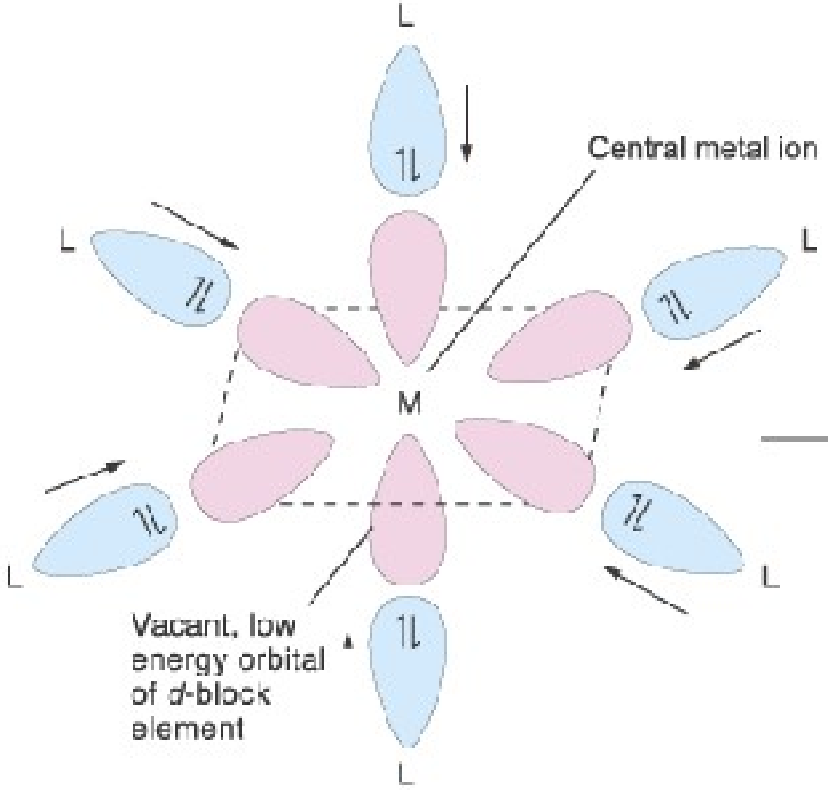
- For the first series of *d*-block metals, complexes are formed using the **3*d*, 4*s*, 4*p* and 4*d* orbitals** present in the metal atoms or ions

- Due to the presence of **vacant, low energy orbitals**, *d*-block metals can interact with the orbitals of the surrounding ligands

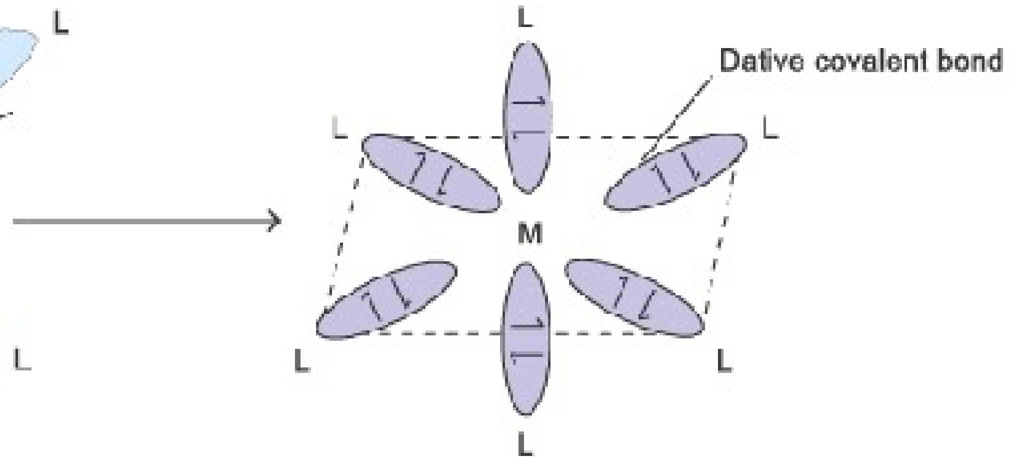
- Due to the the relatively **small sizes and high charge** of *d*-block metal ions, they introduce **strong polarization** on the ligands. This **favours** the formation of bonds of **high covalent character**

This property is due to the-

- comparatively smaller sizes of the metal ions
- their high ionic charges and the
- availability *of d orbitals for bond formation*.
- **high effective nuclear charge**
- **ability to form sigma as well as pi bonds**
- **weak electropositive character**
- **ability to undergo oxidation-reduction reactions easily.**



The ligands donate their lone pairs of electrons to the vacant, low energy orbitals of the central metal ion.



Dative covalent bonds are formed.

Diagrammatic representation of the formation of a complex

Explanation of lability and inertness according to VBT

- VBT classifies octahedral complexes into two types.
- Inner orbital complexes – d^2sp^3
- Outer orbital complex – sp^3d^2
- The two d-orbitals involved in the hybridization are the e_g set of orbitals.

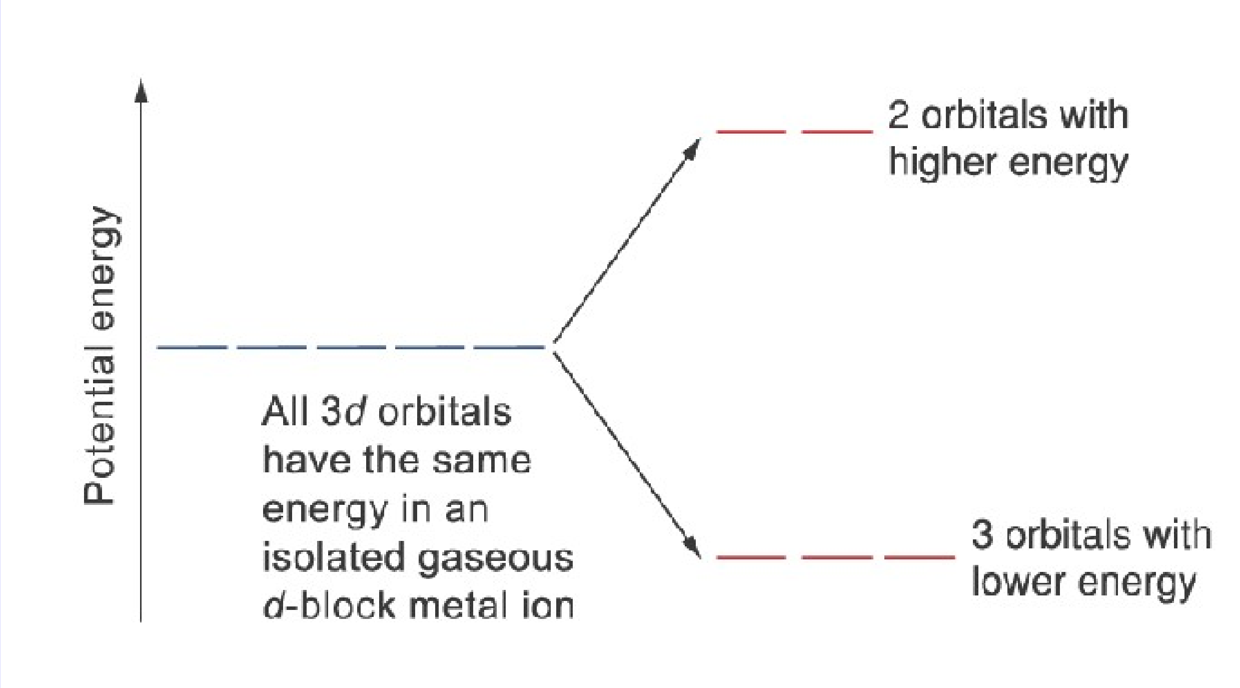
Outer orbital complexes

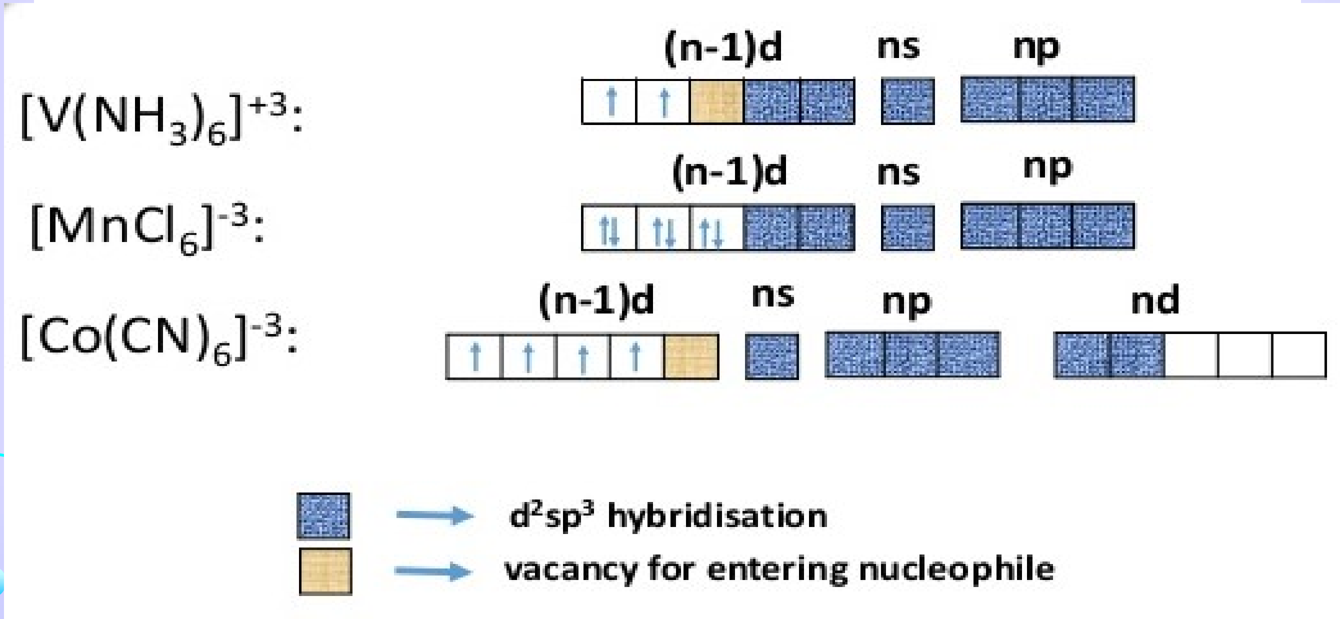
- The complexes having sp^3d^2 hybridization are called outer orbital complexes.
- In terms of VBT these bonds are weaker.
- They are generally labile.
- Mn(II), Fe(II),Fe(III),Co(II),Ni(II),Cu(II) and Cr(II) are labile.

Inner orbital complexes

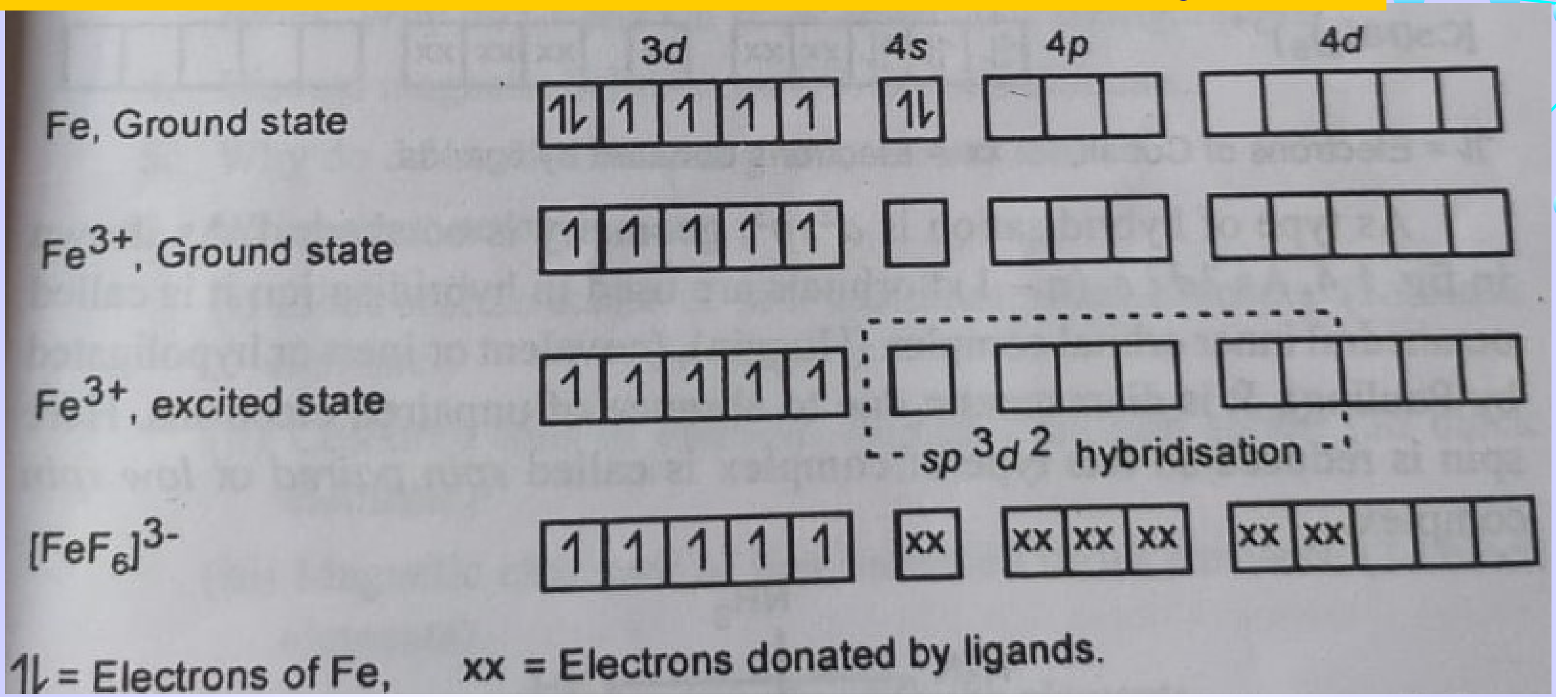
- These complexes generally have d^2sp^3 hybridization.
- The hybrid orbitals are filled with the ligand electrons.
- The t_{2g} orbitals of metal accommodate the d electrons of the metal.

- If the t_{2g} levels are left vacant then the complex can associate with an incoming ligand and the complex is labile
- If all the t2g levels are occupied then the complex becomes inert.


Potential energy
2 orbitals with higher energy
All 3*d* orbitals have the same energy in an isolated gaseous *d*-block metal ion
3 orbitals with lower energy


$[V(NH_3)_6]^{+3}$:
(n-1)d
ns
np
$[MnCl_6]^{-3}$:
(n-1)d
ns
np
$[Co(CN)_6]^{-3}$:
(n-1)d
ns
np
nd
d^2sp^3 hybridisation
vacancy for entering nucleophile

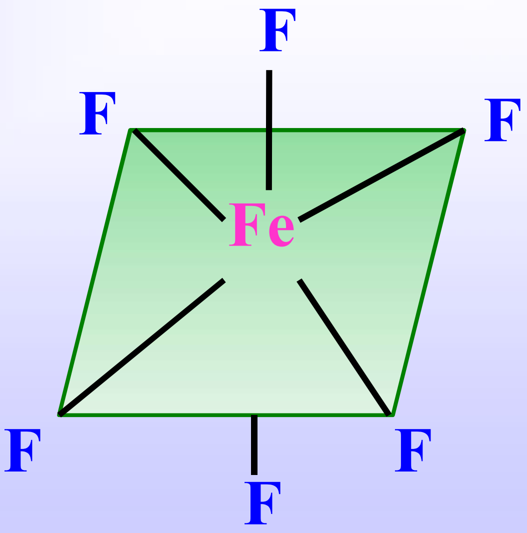
Formation of Hexafluoro ferrate (III) ion $[FeF_6]^{3-}$



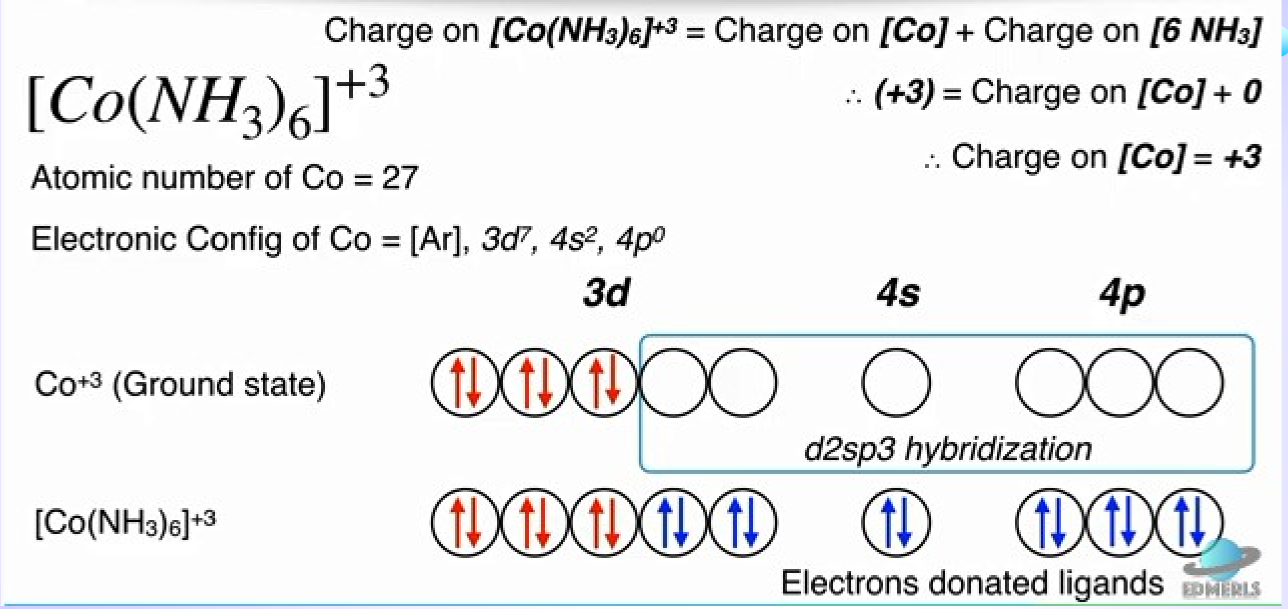
	3d					4s	4p			4d				
Fe, Ground state	↿⇂	↿	↿	↿	↿	↿⇂								
Fe^{3+}, Ground state	↿	↿	↿	↿	↿									
Fe^{3+}, excited state	↿	↿	↿	↿	↿									
$[FeF_6]^{3-}$	↿	↿	↿	↿	↿	xx	xx	xx	xx	xx	xx			

sp^3d^2 hybridisation

↿⇂ = Electrons of Fe, xx = Electrons donated by ligands.



Formation of Hexaammine cobalt (III) ion $[Co(NH_3)_6]^{3+}$



Charge on $[Co(NH_3)_6]^{+3}$ = Charge on [Co] + Charge on [6 NH_3]

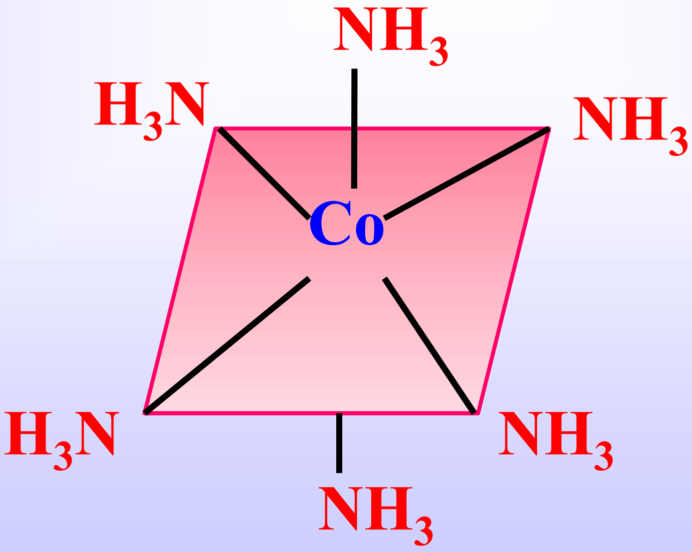
$[Co(NH_3)_6]^{+3}$

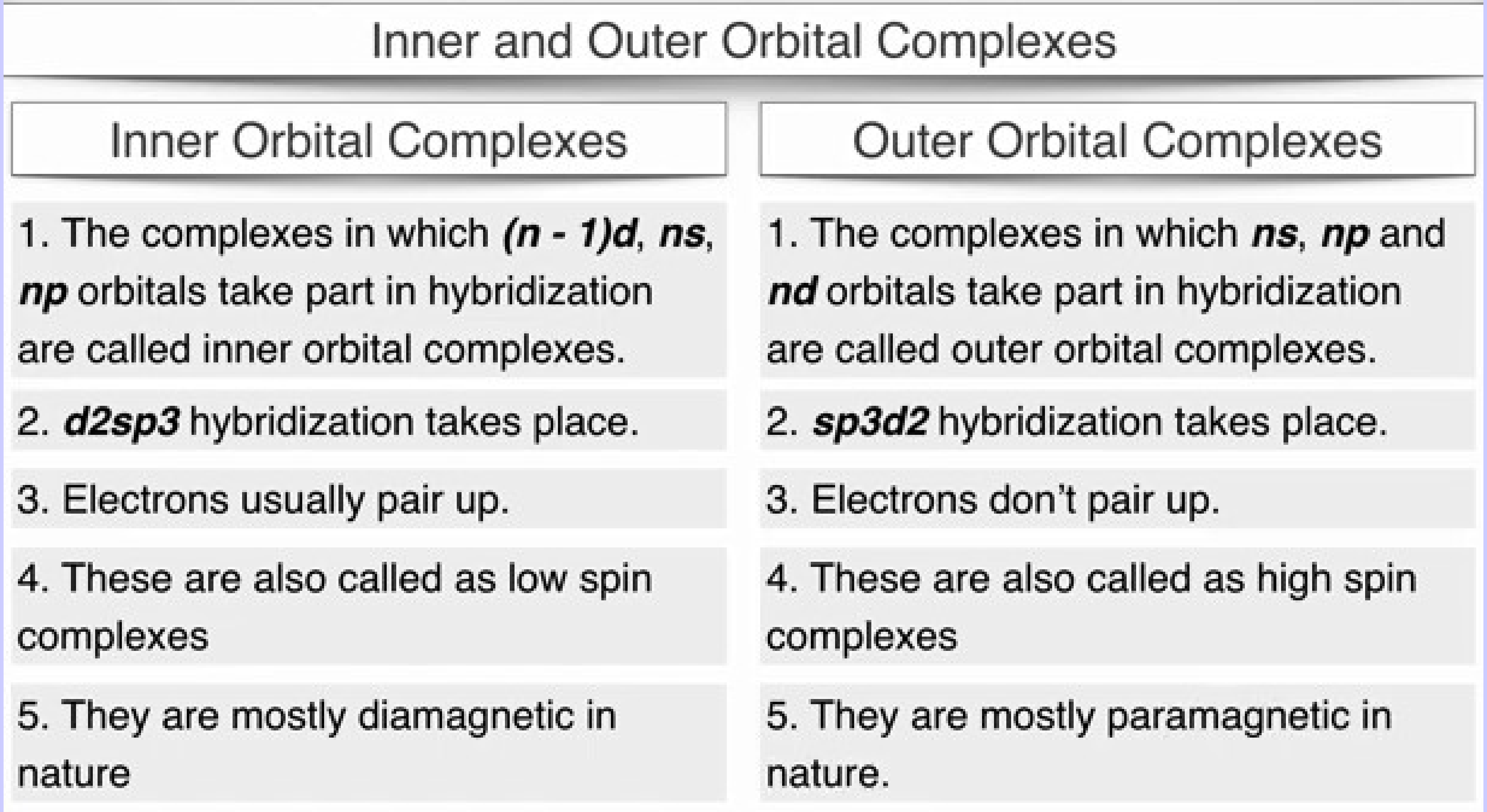
∴ (+3) = Charge on [Co] + 0

∴ Charge on [Co] = +3

Atomic number of Co = 27

Electronic Config of Co = [Ar], $3d^7$, $4s^2$, $4p^0$





Inner and Outer Orbital Complexes

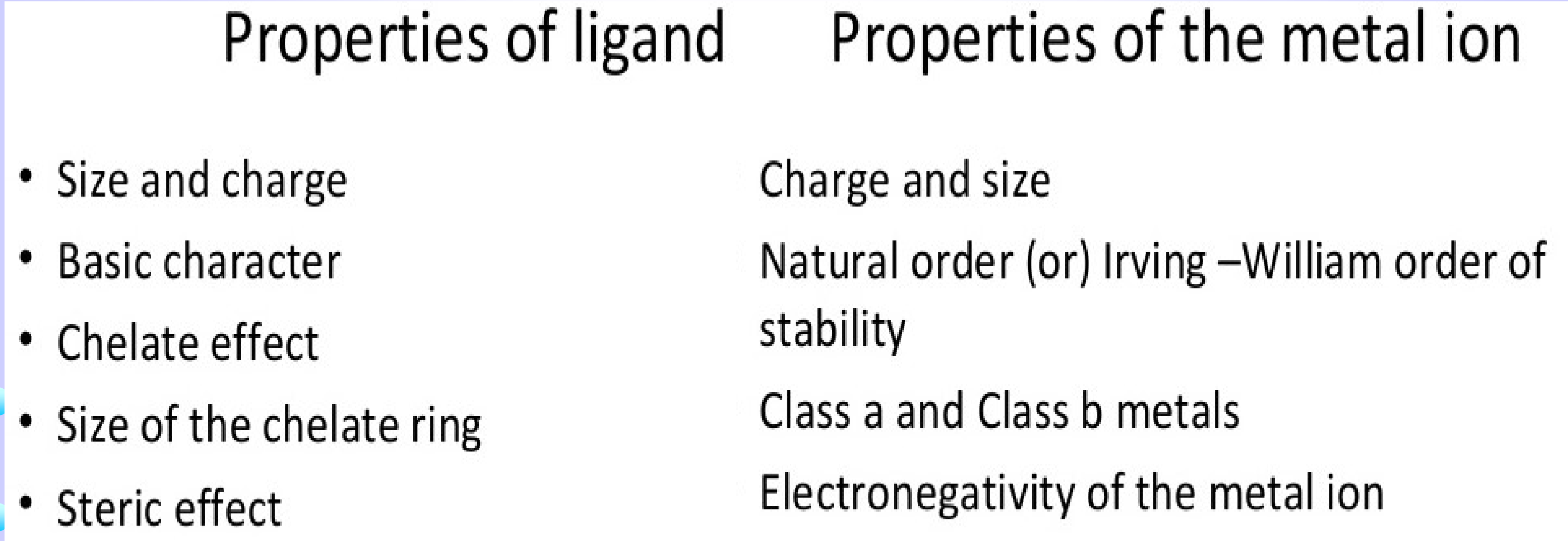
Inner Orbital Complexes	Outer Orbital Complexes
1. The complexes in which ***(n - 1)d***, ***ns***, ***np*** orbitals take part in hybridization are called inner orbital complexes.	1. The complexes in which ***ns***, ***np*** and ***nd*** orbitals take part in hybridization are called outer orbital complexes.
2. ***d2sp3*** hybridization takes place.	2. ***sp3d2*** hybridization takes place.
3. Electrons usually pair up.	3. Electrons don't pair up.
4. These are also called as low spin complexes	4. These are also called as high spin complexes
5. They are mostly diamagnetic in nature	5. They are mostly paramagnetic in nature.

Geometry of complexes: Co-ordination number and hybridisation

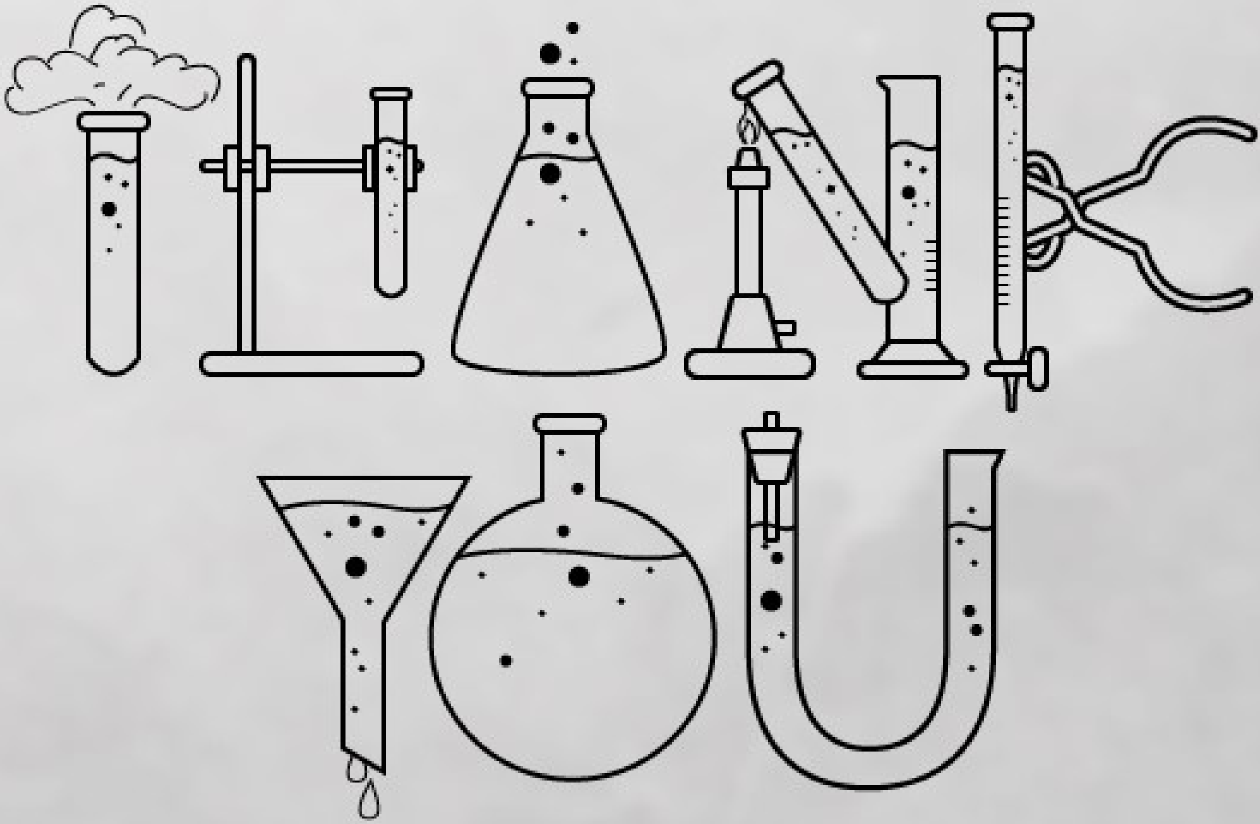
Trends in first transition series for complex formation:

- Stability of complexes increases with increase in atomic number
- Higher oxidation state cations form more stable complexes

Stability of complexes:



Properties of ligand	Properties of the metal ion
• Size and charge	Charge and size
• Basic character	Natural order (or) Irving –William order of stability
• Chelate effect	Class a and Class b metals
• Size of the chelate ring	Electronegativity of the metal ion
• Steric effect	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