

1. Chemistry of The *d*-Block Elements

Introduction

- d -block elements
 - ➔ locate between the s -block and p -block
 - ➔ known as transition elements
 - ➔ occur in the fourth and subsequent periods of the Periodic Table

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Ac	Unq	Unp	Unh	Uns	Uno	Une			

A 10x10 grid with various colored squares and a grey triangle. The grid is composed of 10 columns and 10 rows. The colors of the squares are as follows:

- Column 1: Red (rows 1-10)
- Column 2: Orange (rows 1-10)
- Column 3: Light blue (rows 1-10)
- Column 4: Light blue (rows 1-10)
- Column 5: Light blue (rows 1-10)
- Column 6: Light blue (rows 1-10)
- Column 7: Light blue (rows 1-10)
- Column 8: Light blue (rows 1-10)
- Column 9: White (rows 1-10)
- Column 10: White (rows 1-10)

A grey triangle is located in the top right corner of the grid, with its hypotenuse running from the top left to the bottom right. The triangle is shaded grey and has a black outline. The hypotenuse is defined by the following coordinates (row, column): (1, 9), (2, 8), (3, 7), (4, 6), (5, 5), (6, 4), (7, 3), (8, 2), (9, 1), (10, 0).

Transition elements are elements that contain an incomplete d sub-shell (i.e. d^1 to d^9) in at least one of the oxidation states of their compounds.

Sc^{3+}

[Ar]



3d



4s

$3d^0$

Zn^{2+}

[Ar]



3d

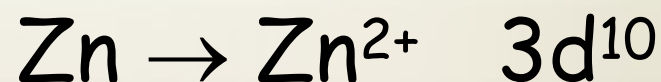


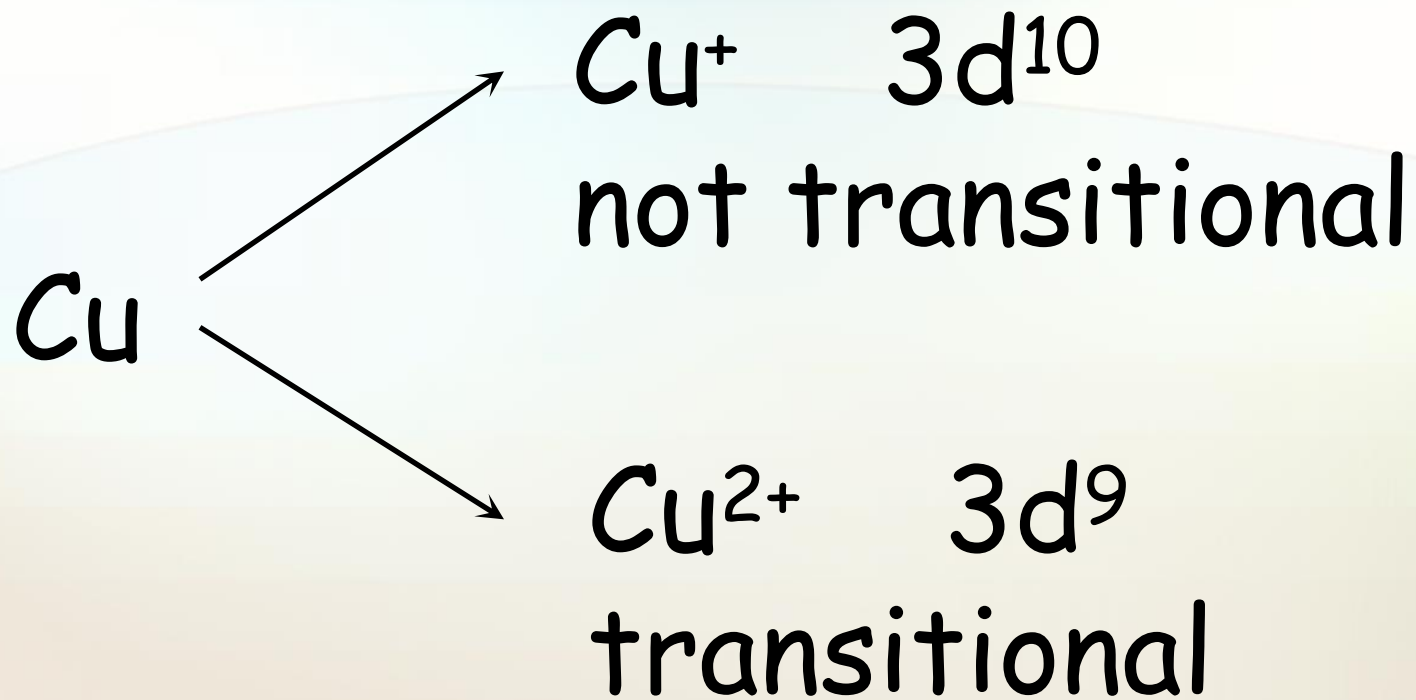
4s

$3d^{10}$

Sc and Zn are not transition elements because

They form compounds with only one oxidation state in which the d sub-shell are NOT incomplete.





General Characteristics of transition elements

(d-block metals vs s-block metals)

1. Physical properties vary slightly with atomic number across the series (cf. s-block and p-block elements)
2. Higher m.p./b.p./density/hardness than s-block elements of the same periods.
3. Variable oxidation states
(cf. fixed oxidation states of s-block metals)

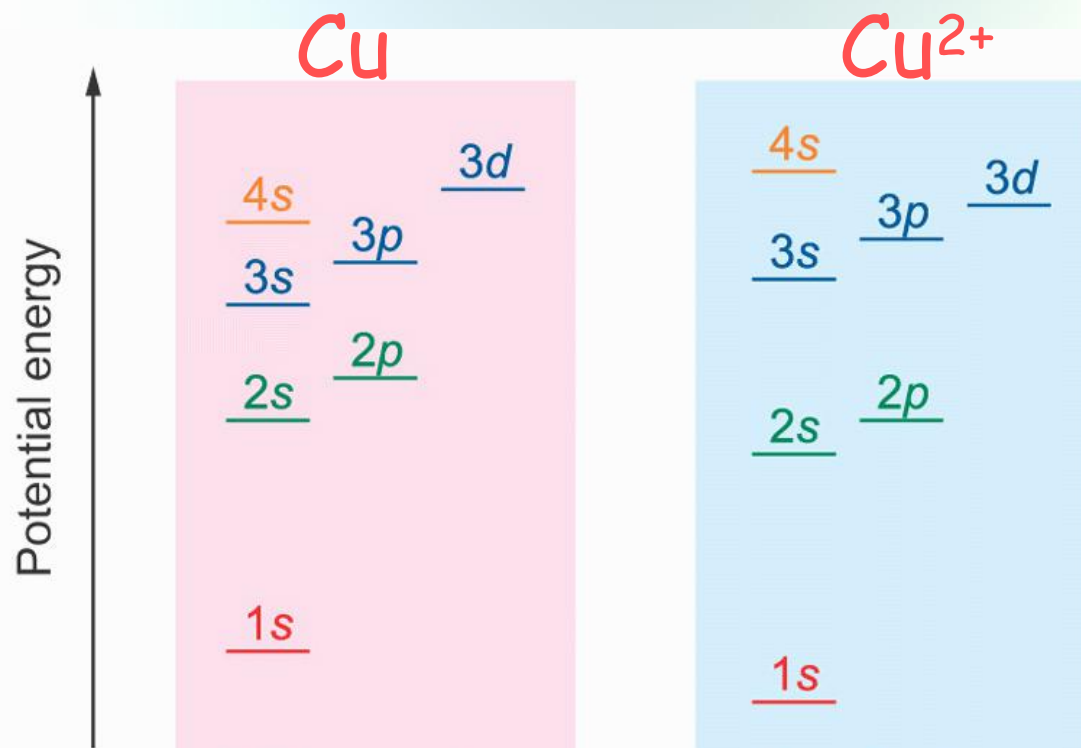
- 4. Formation of coloured compounds/ions
(cf. colourless ions of s-block elements)**
- 5. Formation of complexes**
- 6. Catalytic properties**

Electronic Configurations

The building up of electronic configurations of elements follow:

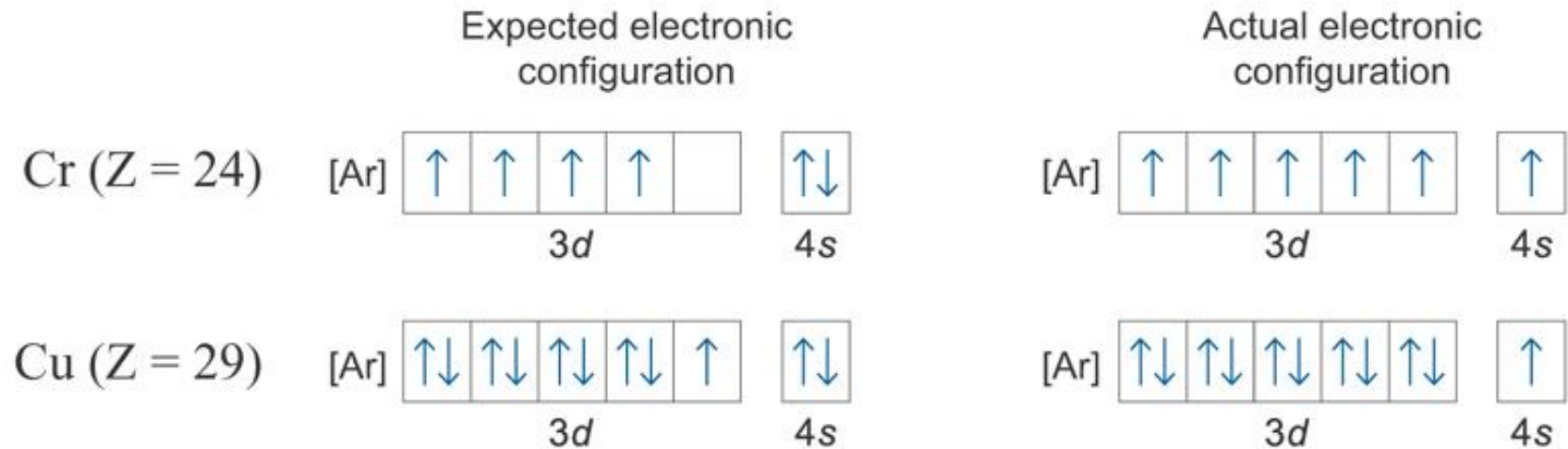
- Aufbau principle
- Pauli exclusion principle
- Hund's rule

- 3d and 4s sub-shells are very close to each other in energy.
- Relative energy of electrons in sub-shells depends on the effective nuclear charge they experience.
- Electrons enter 4s sub-shell first
- Electrons leave 4s sub-shell first



Relative energy levels of orbitals
in atom and in ion

- Valence electrons in the inner 3d orbitals
- Examples:
 - ➔ The electronic configuration of scandium: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
 - ➔ The electronic configuration of zinc: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$



- A half-filled or fully-filled d sub-shell has extra stability

1.1.general physical properties

1.1.1.Density,melting and boiling points

1. Density

s-block element

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										

d-block element

Densities (in g cm^{-3}) of the s-block elements and the first series of the d-block elements at 20°C

- d -block $>$ s -block
 - \therefore the atoms of the d -block elements
 1. are generally smaller in size
 2. are more closely packed
 3. have higher relative atomic masses

- The densities
 - ➔ generally increase across the first series of the d-block elements
 - ∴
 1. general decrease in atomic radius across the series
 2. general increase in atomic mass across the series

2. Melting and boiling point

d-block >> s-block

∴ 1. both 4s and 3d e⁻ are involved in the formation of metal bonds

2. d-block atoms are smaller

s-block element

Li 180.5	Be 1278
Na 97.8	Mg 648.8
K 63.7	Ca 839
Rb 39.1	Sr 769
Cs 28.4	Ba 729

d-block element

Sc 1541	Ti 1668	V 1910	Cr 1907	Mn 1246	Fe 1538	Co 1495	Ni 1455	Cu 1084	Zn 419

- The hardness of a metal depends on
→ the strength of the metallic bonds
- The metallic bonds of the d-block elements are stronger than those of the s-block elements
∴ much harder than the s-block elements

→ high melting points and boiling points

- Exceptions : Mercury

→ low melting point

→ liquid at room temperature and pressure

1.1.2. Trends in the periodic table

Atomic Radii and Ionic Radii

- Two features can be observed:
 1. The *d*-block elements have smaller atomic radii than the *s*-block elements
 2. The atomic radii of the *d*-block elements do not show much variation across the series

- At the beginning of the series
 - atomic number \uparrow
 - effective nuclear charge \uparrow
 - the electron clouds are pulled closer to the nucleus
 - atomic size \downarrow

- In the middle of the series
 - ➔ more electrons enter the inner 3d sub-shell
 - ➔ The inner 3d electrons shield the outer 4s electrons effectively
 - ➔ the effective nuclear charge experienced by 4s electrons increases very slowly
 - ➔ only a slow decrease in atomic radius in this region

- At the end of the series
 - ➔ the screening and repulsive effects of the electrons in the 3d sub-shell become even stronger
 - ➔ Atomic size ↑

1.2.General chemical properties

Variable Oxidation States

- One of the most striking properties
 - ➔ variable oxidation states
- The 3d and 4s electrons are
 - ➔ in similar energy levels
 - ➔ available for bonding

- Elements of the first transition series
 - ➔ form ions of roughly the same stability by losing different numbers of the 3d and 4s electrons

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

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

1. Scandium and zinc do not exhibit variable oxidation states

- Scandium of the oxidation state +3
 - the stable electronic configuration of argon (i.e. $1s^2 2s^2 2p^6 3s^2 3p^6$)
- Zinc of the oxidation state +2
 - the stable electronic configuration of $[Ar] 3d^{10}$

2. (a) All elements of the first transition series (except Sc) can show an oxidation state of +2

(b) All elements of the first transition series (except Zn) can show an oxidation state of +3

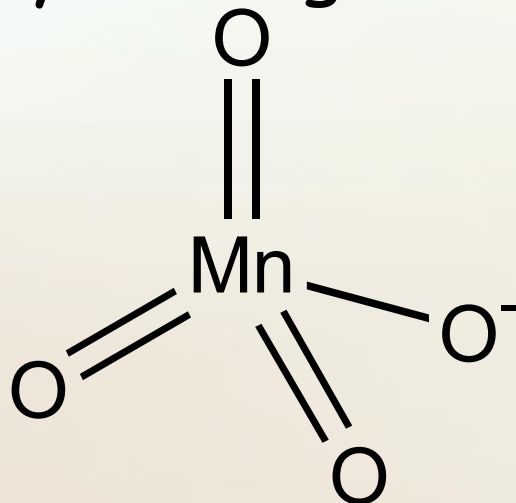
3. Manganese has the highest oxidation state +7

E.g. MnO_4^- , Mn_2O_7

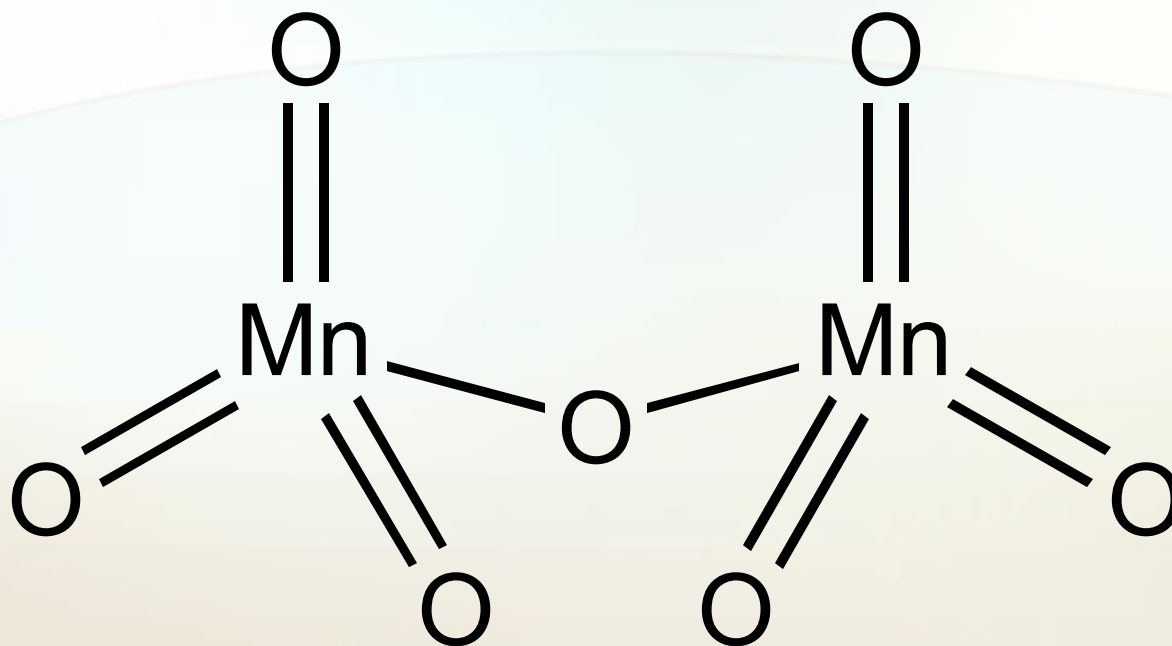
Mn^{7+} ions do not exist.

The +7 state of Mn does not mean that all 3d and 4s electrons are removed from Mn to give Mn^{7+} .

Instead, Mn forms covalent bonds with oxygen atoms by making use of its half filled orbitals



Draw the structure of Mn_2O_7



3. Manganese has the highest oxidation state +7

- The highest possible oxidation state
= the total no. of the 3d and 4s electrons
∴ inner electrons (3s, 3p...) are not
involved in covalent bond formation

4. For elements after manganese, there is a reduction in the number of possible oxidation states

- The 3d electrons are held more firmly
 - ∴ the decrease in the number of unpaired electrons
 - ∴ the increase in nuclear charge

5. The relative stability of various oxidation states is correlated with the stability of electronic configurations

Stability : - $\text{Mn}^{2+}(\text{aq}) > \text{Mn}^{3+}(\text{aq})$

$[\text{Ar}] 3d^5$

$[\text{Ar}] 3d^4$

$\text{Fe}^{3+}(\text{aq}) > \text{Fe}^{2+}(\text{aq})$

$[\text{Ar}] 3d^5$

$[\text{Ar}] 3d^6$

Formation of Complexes

- Another striking feature of the d -block elements is the formation of complexes

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 donate lone pairs of electrons to form the dative covalent bonds are called ligands.

Formation of Complexes

- A ligand
 - ➔ can be an ion or a molecule having at least one lone pair of electrons that can be donated to the central metal atom or ion to form a dative covalent bond

Formation of Complexes

→ Complexes can be

electrically neutral Ni(CO)_4

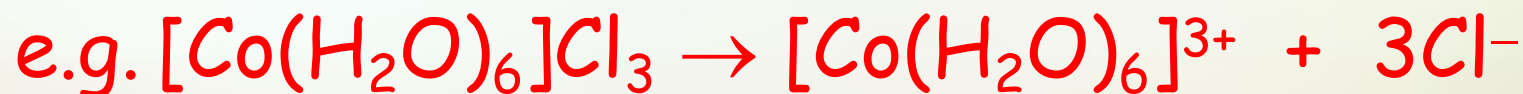
positively charged $[\text{Co(H}_2\text{O)}_6]^{3+}$

negatively charged $[\text{Fe(CN)}_6]^{3-}$

→ A co-ordination compound is either
a neutral complex e.g. $\text{Ni}(\text{CO})_4$

or made of

a complex ion and another ion



Criteria for complex formation

1. Presence of vacant and low-energy 3d, 4s, 4p and 4d orbitals in the metal atoms or ions to accept lone pairs from ligands.
2. High charge density of the central metal ions.
3. Smaller size

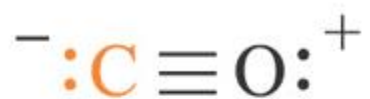
1. Complexes with Monodentate Ligands

A ligand that forms one dative covalent bond only is called a monodentate ligand.

- Examples:

neutral → $\text{CO}, \text{H}_2\text{O}, \text{NH}_3$

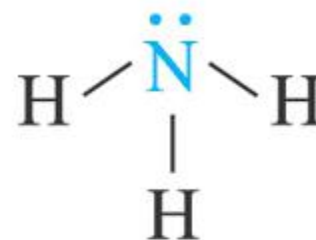
anionic → $\text{Cl}^-, \text{CN}^-, \text{OH}^-$



carbon monoxide



water



ammonia



chloride ion



cyanide ion



hydroxide ion

In the formation of complexes, classify the transition metal ion and the ligand as a Lewis acid or base. Explain your answer briefly.

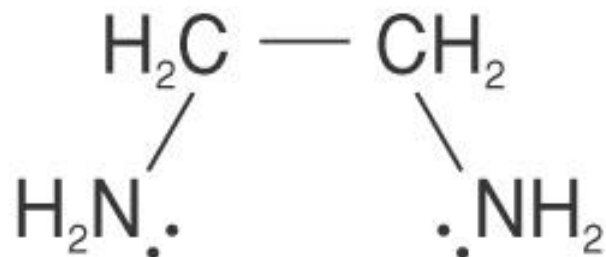
The transition metal ion is the Lewis acid since it accepts lone pairs of electrons from the ligands in forming dative covalent bonds.

The ligand is the Lewis base since it donates a lone pair of electrons to the transition metal ion in forming dative covalent bonds.

2. Complexes with Bidentate Ligands

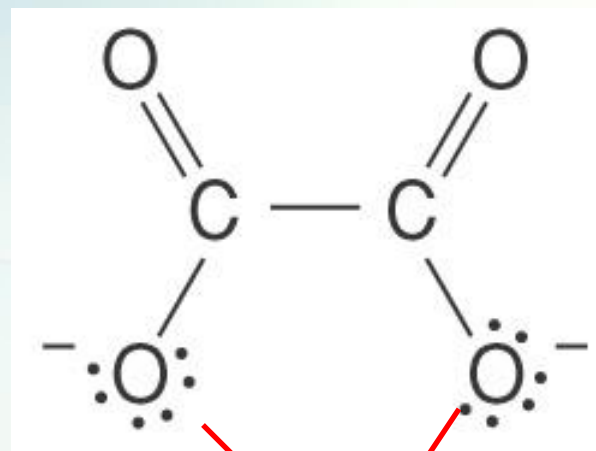
A ligand that can form two dative covalent bonds with a metal atom or ion is called a bidentate ligand.

A ligand that can form more than one dative covalent bond with a central metal atom or ion is called a chelating ligand.



Ethylenediamine
($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$)

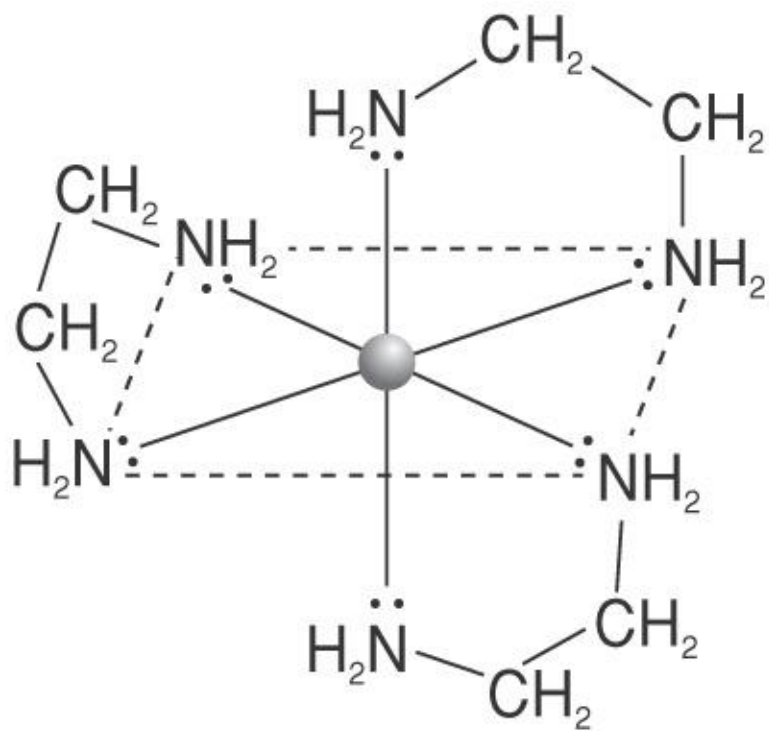
ethylenediamine



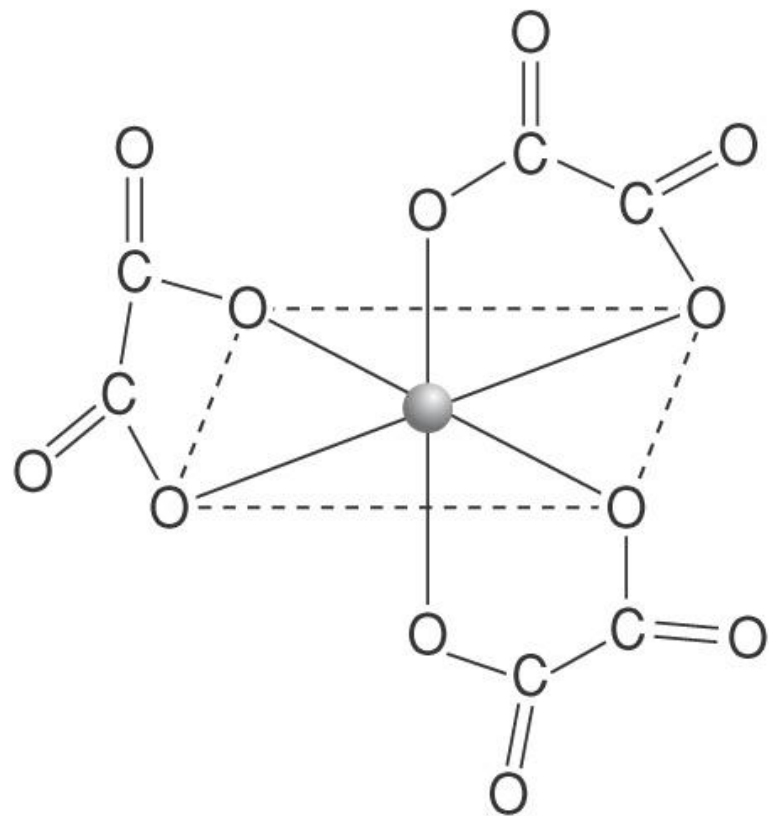
Oxalate ($\text{C}_2\text{O}_4^{2-}$)

oxalate ion

The term chelate is derived from Greek, meaning 'claw'.
The ligand binds with the metal like the great claw of the lobster.



ethylenediamine



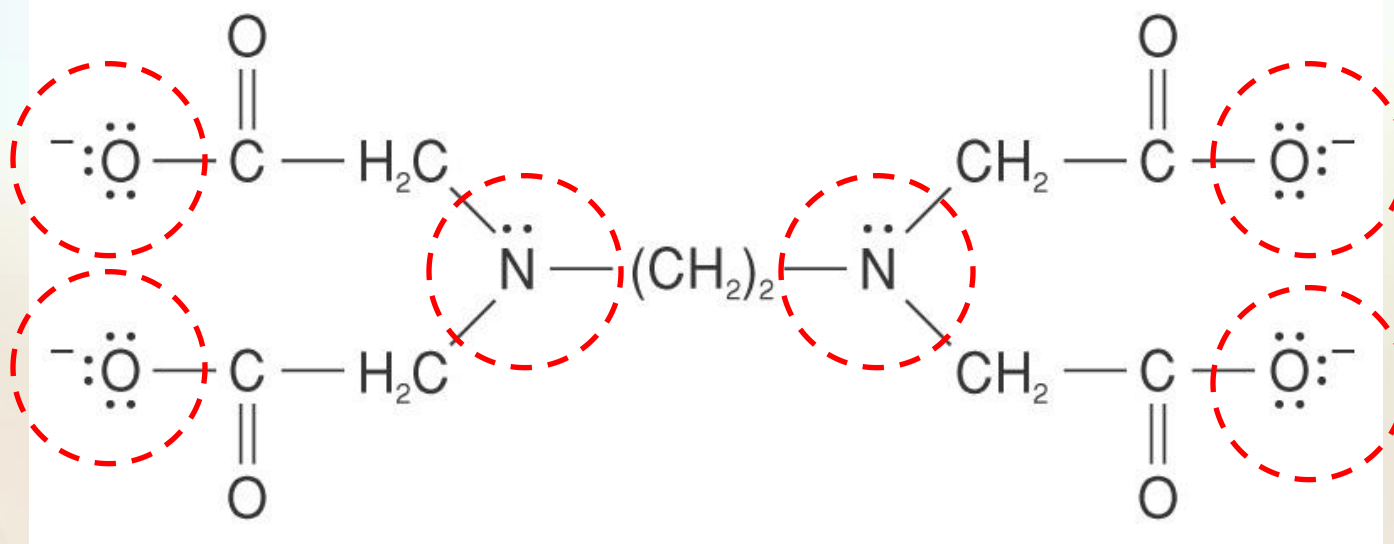
oxalate ion

3. Complexes formed by Multidentate Ligands

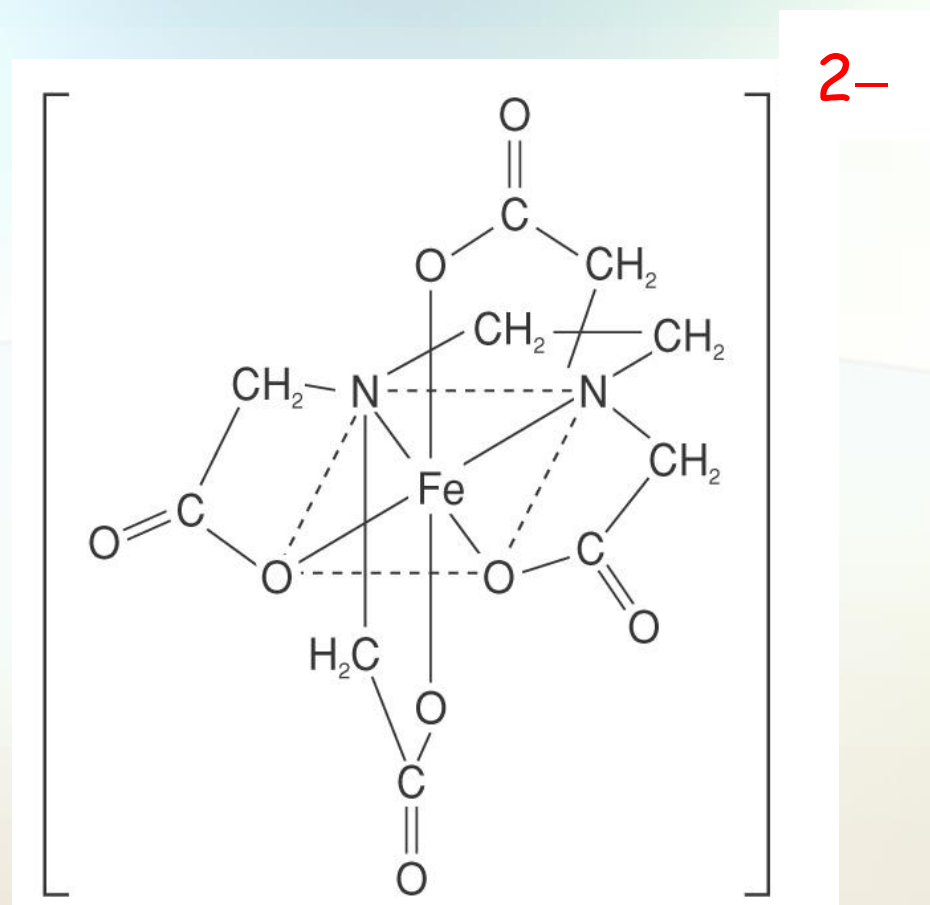
Ligands that can form more than two dative covalent bonds to a metal atom or ion are called multidentate ligands. Some ligands can form as many as six bonds to a metal atom or ion.

- Example:
 - ➔ ethylenediaminetetraacetic acid
(abbreviated as EDTA)

- EDTA forms six dative covalent bonds with the metal ion through six atoms giving a very stable complex.
- hexadentate ligand



ethylenediaminetetraacetate ion



Structure of the complex ion formed by
iron(II) ions and EDTA

Non-stoichiometric compounds

Transition metals some times form

- ✓ Non-stoichiometric compounds

Compounds of indefinite structure and proportion

- ✓ The ratio between the number of atoms of one kind to the number of atoms of another kind does not Correspond to the ideal whole number, suggested by the molecular formula.

✓ Do not obey the law constant composition

Iron (II)sulphide is non stoichiometric compound



The ratio of Fe and O atom is not exactly 1:1

-analysis show that $\text{Fe}_{0.94}\text{O}$ and $\text{Fe}_{0.84}\text{O}$

$VSe(VSe_{0.98} - VSe_{1.2})$

$V_2Se_3(VSe_{1.2} - VSe_{1.6})$

$V_2Se_4(VSe_{1.6} - VSe_2)$

Shown particularly among transition
metal compounds of **G-VIA elements**

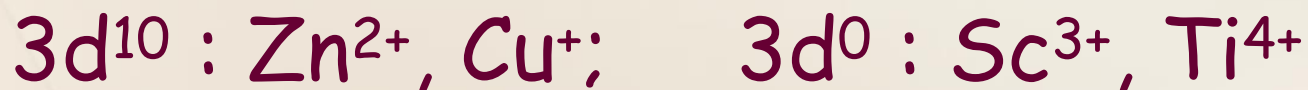
-mostly due to

✓ **Variable valancy** of transition elements

Coloured Ions

- Most of the d-block metals
 - form coloured compounds
 - due to the presence of the incompletely filled d orbitals in the d-block metal ions

Which aqueous transition metal ion(s) is/are not coloured ?



A substance absorbs visible light of a certain wavelength

→ reflects or transmits visible light of other wavelengths (complimentary colour)

→ appears coloured

Coloured ion	Light absorbed	Light reflected or transmitted
$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}(\text{aq})$	Yellow	Blue
$[\text{CuCl}_4]^{2-}(\text{aq})$	Blue	Yellow

Coloured Ions

- The absorption of visible light is due to the d-d electronic transition



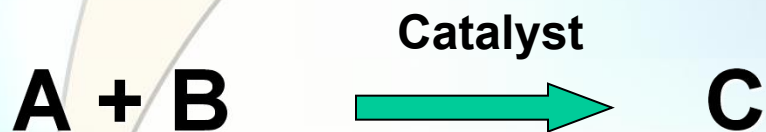
i.e. an electron jumping from a lower 3d orbital to a higher 3d orbital

1.3. Catalytic Properties of Transition Metals and their Compounds

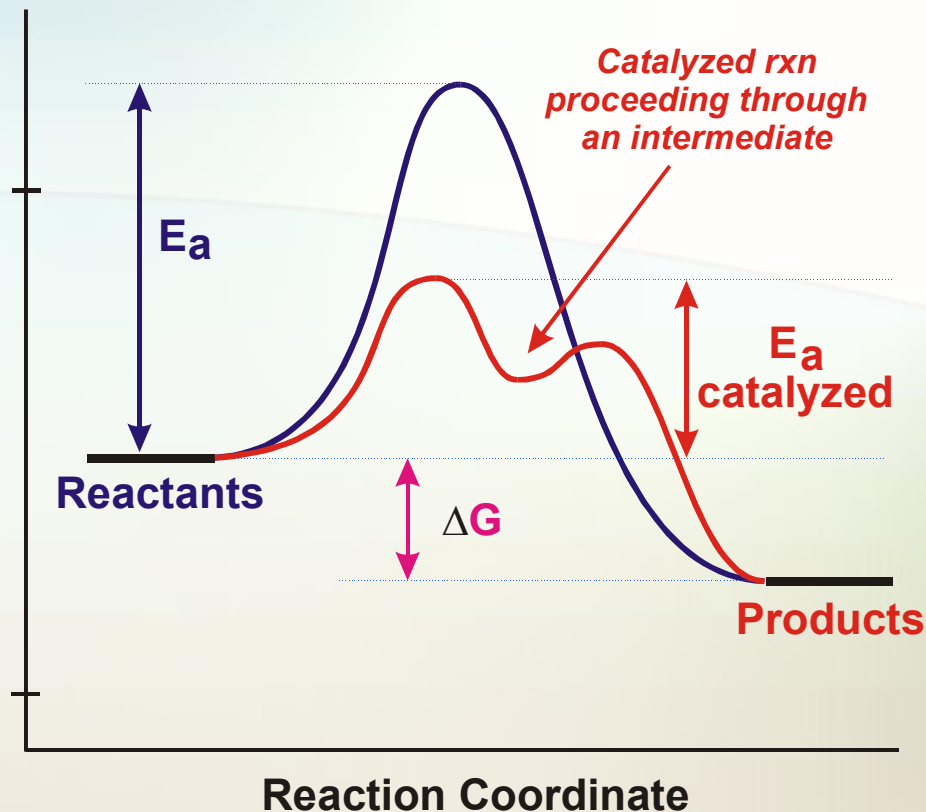
- The *d*-block metals and their compounds
 - ➔ important **catalysts** in industry and biological systems

- A *catalyst* is a substance that increases the rate of a reaction but it is not itself consumed
- *Catalysis* plays a vital role in the production of
Fuels
commodity chemicals
fine chemicals and
pharmaceuticals as
providing the means for experimental
safeguards all over the world
- More than 60% of all chemical products and 90% of all chemical processes are based on catalysis.

Catalysis



A catalyst lowers the activation barrier for a transformation, by introducing a new reaction pathway.



It does not change the thermodynamics!!

Heterogeneous

Homogeneous

The use of some *d*-block metals and their compounds as catalysts in industry

<i>d</i>-Block metal	Catalyst	Reaction catalyzed
V	V ₂ O ₅ or vanadate(V) (VO ₃ ⁻)	Contact process $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
Fe	Fe	Haber process $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

The use of some *d*-block metals and their compounds as catalysts in industry

<i>d</i>-Block metal	Catalyst	Reaction catalyzed
Ni	Ni	Hardening of vegetable oil (Manufacture of margarine) $\text{RCH} = \text{CH}_2 + \text{H}_2 \longrightarrow \text{RCH}_2\text{CH}_3$
Pt	Pt	Catalytic oxidation of ammonia (Manufacture of nitric(V) acid) $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{l})$

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

- Generally speaking, the function of a catalyst
 - ➔ provides an **alternative reaction pathway** of **lower activation energy**
 - ➔ enables the reaction to proceed **faster** than the uncatalyzed one

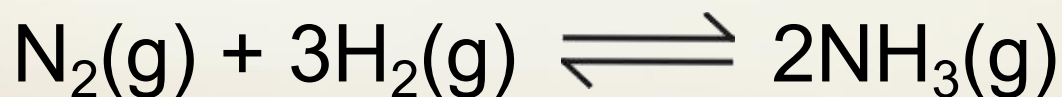
1. Heterogeneous Catalysis

- The catalyst and reactants
→ exist in different states
- The most common heterogeneous catalysts
→ finely divided solids for gaseous reactions

A **heterogeneous catalyst** provides a suitable reaction surface for the reactants to come close together and react.

- Example:

The synthesis of gaseous ammonia from nitrogen and hydrogen (i.e. **Haber process**)



- 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** (i.e. one nitrogen and three hydrogen molecules)
 - ➔ **very small**

2. Homogeneous Catalysis

- A homogeneous catalyst
 - ➔ the **same state** as the reactants and products
 - ➔ the catalyst forms an **intermediate** with the reactants in the reaction
 - ➔ changes the reaction mechanism to an another one with a **lower activation energy**

In **homogeneous catalysis**, the ability of the d-block metals to exhibit variable oxidation states enables the formation of the reaction intermediates.

- Example:

The reaction between
peroxodisulphate(VI) ions ($\text{S}_2\text{O}_8^{2-}$) and
iodide ions (I^-)

- Peroxodisulphate(VI) ions
 - ➔ oxidize **iodide ions** to **iodine** in an aqueous solution
 - ➔ themselves being reduced to **sulphate(VI) ions**

