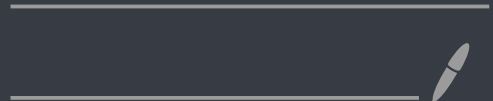


Transition Elements

- Theory +

- Notes from Past Papers.



Transition Elements

• Found between Group 2 & Group 13.

↳ A transition element is a d-block element that forms one or more stable ions with a partially filled d-subshell. first ion

* Scandium And Zinc are NOT transition elements,

because Scandium (Sc) forms only one ion (Sc^{3+}) and this has no electrons in its 3d subshell -

the electronic configuration of Sc^{3+} is $(Ar) 3d^0 4s^0$.

Zinc forms only one ion (Zn^{2+}) and this has a complete 3d-subshell -

the electronic configuration of (Zn^{2+}) is $(Ar) 3d^{10} 4s^0$.

* Electronic Configurations

21 * Scandium (Sc) - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$ or $[Ar] 3d^1 4s^2$ ← Exception

22 Titanium (Ti) - $[Ar] 4s^2 3d^2$

23 Vanadium (V) - $[Ar] 4s^2 3d^3$

24 * Chromium (Cr) - $[Ar] 4s^1 3d^5$ ← Exception

25 Manganese (Mn) - $[Ar] 4s^2 3d^5$

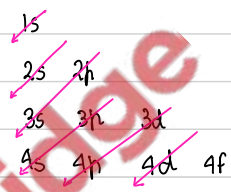
26 Iron (Fe) - $[Ar] 4s^2 3d^6$

27 Cobalt (Co) - $[Ar] 4s^2 3d^7$

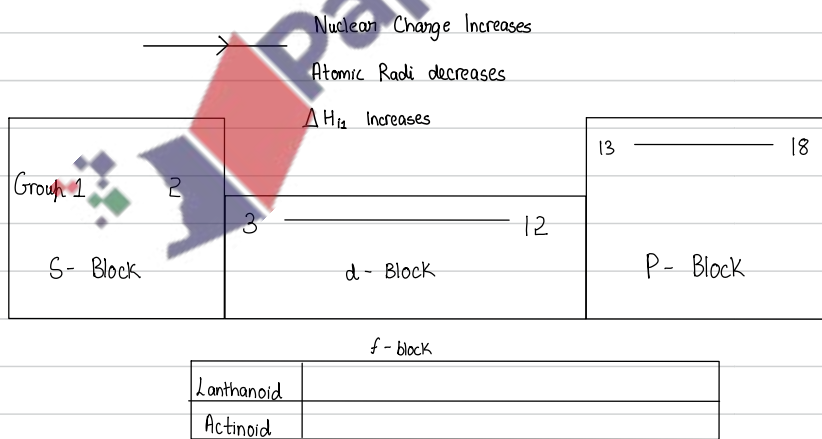
28 Nickel (Ni) - $[Ar] 4s^2 3d^8$

29 * Copper (Cu) - $[Ar] 4s^1 3d^{10}$ ← Exception

30 Zinc (Zn) - $[Ar] 4s^2 3d^{10}$



When transition elements form ions, their atoms lose electrons from the 4s sub-shell first, followed by 3d- electrons.



Physical Properties of Transition Elements

→ All transition elements are metals

→ Strong metallic bonds result from small size and close packing of atoms.

→ Higher melting point, boiling point & densities than s-block metals.

→ Smaller atomic radius than s-block metals.

→ Electrical Capacity of s-block elements is higher than that of a transition element (with the exception of Cu.)

→ First ionisation energy of s-block element is lower than that of a transition element.

Variable Oxidation States

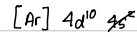
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
				+7					
			+6	+6	+6				
		+5	+5	+5	+5				
	+4	+4	+4	+4	+4	+4			
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
								+1	

→ The most common oxidation state is +2.

Stability of the +2 state increases across the row

3d electrons become increasingly harder to remove

as the nuclear charge increases across the period.



→ The maximum oxidation state at the start of the row involves all the 4s and 3d e's in the atom

→ Higher Oxidation states are found in compounds with "O" or "F".

EXAMPLE: CrO_4^{2-} Chromate (VI) ion

MnO_4^- Manganate (VII) ion

* Co-ordination Compounds

A molecular compound resulting from the combination of two or more stable molecular compounds and retains its identity in the solid state as well as in a solution & the properties are totally different from the constituents present.

EXAMPLE: $K_4[Fe(CN)_6]$, $[Cu(NH_3)_4]SO_4$, $[Co(NH_3)_6]Cl_3$

* Coordination Complex

It is the species enclosed in square bracket.

It contains in it a central metal atom or ion to which a fixed

number of neutral molecules or ions capable of donating

electron pairs are linked with co-ordinate bonds.

These are known as ligands.

For example, in $[Cu(NH_3)_4]^{2+}$ complex ion, four

molecules of NH_3 are linked with Cu^{2+} ion by co-ordinate bonds.

* Coordination Number

The coordination number of a complex is the

total number of co-ordination bonds formed by the

ligands with the metal atom or ion in the complex.

EXAMPLE: $[Ag(CN)_2]^-$ $[Co(CN)_5]^{3-}$ $[Fe(CO)_5]$

Coordination No: 2 5 5

* Nature of Co-ordination Complex

1) Cationic Complex

A complex carrying a net positive charge

example, $[Co(NH_3)_6]^{3+}$, $[Ni(NH_3)_6]^{2+}$

2) Anionic Complex

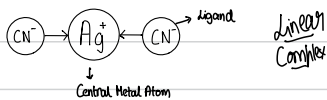
A complex carrying a net negative charge on the square bracket.

example, $[Ag(CN)_2]^-$, $[Fe(CN)_6]^{3-}$

3) Neutral Complex

A complex which has no net charge.

example, $[Ni(CO)_4]$, $[Co(NH_3)_3Cl_3]$



* Ligands (Electron donor species)

They are the electron donor molecules or ions which may be either neutral or anionic and are linked to the central transition metal atom or ion by co-ordinate bonds.

The ligands are also known as dentates.

Ligands have been classified into the following types:-

1. Unidentate or Monodentate ligands -

They have one donor atom with a lone pair of electrons and it may be either neutral or anionic.

Neutral : H_2O , NH_3

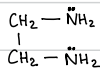
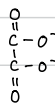
Anionic : OH^- , CN^- , X^- , CH_3COO^- , NO_3^- , NO_2^- , ONO^- , NO_2^- , SCN^- , NCS^- .

2. Bidentate ligands -

These are the ligands which have two donor atoms and have the ability to link with central atom/ion at two positions.

examples,

ethanedioate ion / oxalate ion (ox) 1,2 - diaminoethane (en)



Naming:-

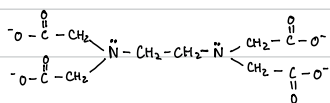
Ligand	Formula	Name of ligand
chloride	Cl^-	chloro
cyanide	CN^-	ciano
hydroxide	OH^-	hydroxo
water	H_2O	aqua
ammonia	NH_3	ammine
Oxide	O^{2-}	oxo

3. Polydentate ligands

A ligand with more than two donor atoms.

examples,

Ethylenediamine tetraacetate ion (EDTA) / (Hexadentate ligand)



* Calculation of oxidation number of metal atom

example ① $[Fe(CN)_6]^{3-}$

$$x + 6(-1) = -3$$

$$x = +3$$

example ② $[Cu(NH_3)_4]^{2+}$

$$x + 4(0) = 2$$

$$x = +2$$

example ③ $K_4[Fe(CN)_6]$

$$(+1 \times 4) + x + 6(-1) = 0$$

$$x = +2$$

example ④ $[Co(NH_3)_6]Cl_3$

$$x + 6(0) + 3(-1) = 0$$

$$x - 3 = 0$$

$$x = +3$$

* Calculation of charge on the complex ion

$[Ag(NH_3)_2]^x$

$$+1 + 2(0) = x$$

$$x = +1$$

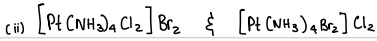
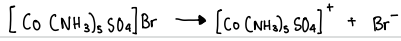
$\therefore [Ag(NH_3)_2]^{+1}$

ISOMERISM IN CO-ORDINATION COMPOUNDS

1. Structural Isomerism

a) Ionisation isomerism

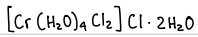
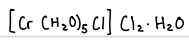
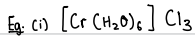
Example (Compounds which have different ions in solution although they have the same composition)



b) Hydrate Isomerism or solvate isomerism

(Compounds which have the same molecular composition but differ

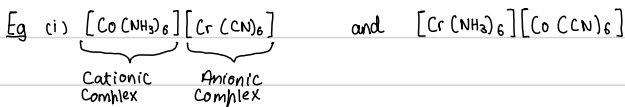
in the number of water molecules present as ligands.)



c) Co-ordination Isomerism

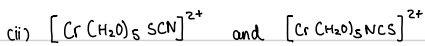
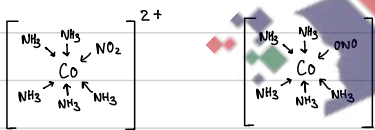
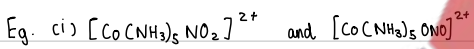
Occurs in those complex compounds which contain both cationic & anionic complexes

and isomers differ with respect to the distribution of ligands in these complexes.



d) Linkage Isomerism

This type of isomerism occurs when more than one atom in a monodentate ligand may function as a donor atom. (i.e. ambidentate ligand)



2. Stereoisomers

a) Geometrical Isomers (cis-trans)

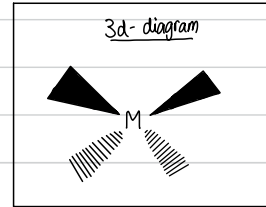
The isomer in which similar ligands occupy adjacent positions is referred to as cis isomer and the isomer in which similar ligands occupy opposite positions is referred to as trans isomer.

Example (i) cis-platin & trans-platin



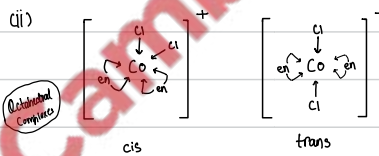
cis-platin

trans-platin



The properties of these geometrical isomers are slightly different.

- Cis-platin has been used as an anti-cancer drug. It acts by binding to sections of DNA in cancer cells, preventing cell division.



en - ethane-1,2-diamine

ox - oxalate

(b) Optical Isomerism

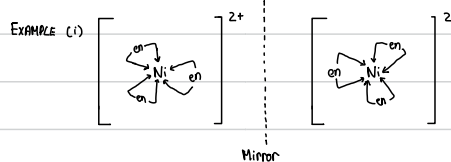
It is shown by those complex compounds whose molecules are not superimposable on their mirror images. These isomers can rotate the plane of polarised light. (to the right - clockwise or to the left anticlockwise)

These optical isomers have identical physical and chemical properties except their behaviour

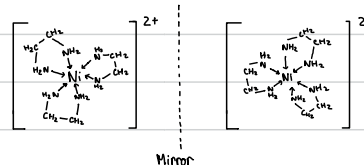
towards the plane of polarised light.

These mirror images are also termed as enantiomers.

Octahedral Complexes that are bi-dentate ligands show optical isomerism



(ii) 1,2-diaminoethane



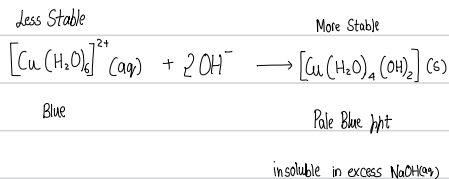
Substitution of Ligands

The ligands in a complex ion can be exchanged wholly or partially, for other ligands. This is called a substitution reaction. This happens if the new complex is more stable than the original complex.

Examples: (i) Copper

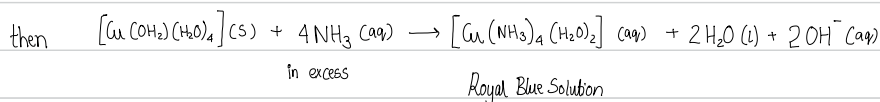
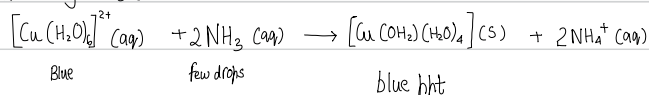
$\text{Cu}^{2+}(\text{aq})$ is blue, octahedral hexaqua copper(II) ion i.e. $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$

→ On Adding $\text{NaOH}(\text{aq})$

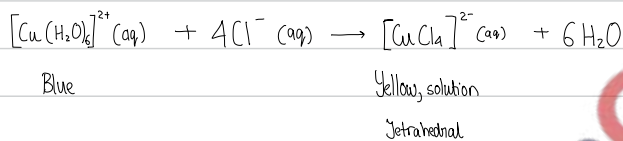


See table on last page for summary of reactions.

→ On Adding $\text{NH}_3(\text{aq})$



→ On Adding Concentrated HCl drop by drop.

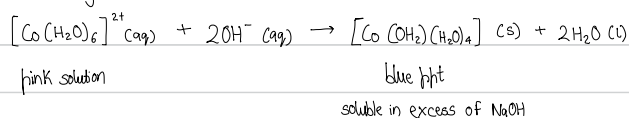


- Cl^- ligands are larger than H_2O and are charged.
- The complex is more stable if the shape changes to tetrahedral from octahedral.
- Adding excess water reverses the reaction.

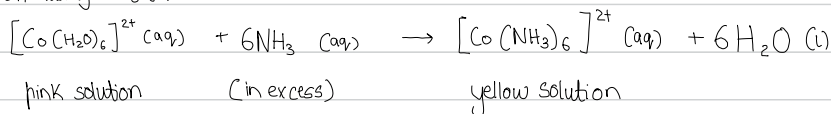
(ii) Cobalt

Co^{2+} aqueous solution is pink, octahedral hexaqua cobalt(II) ion i.e. $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ pink.

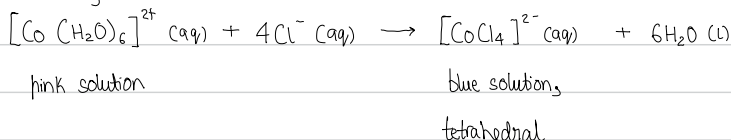
→ On Adding $\text{NaOH}(\text{aq})$



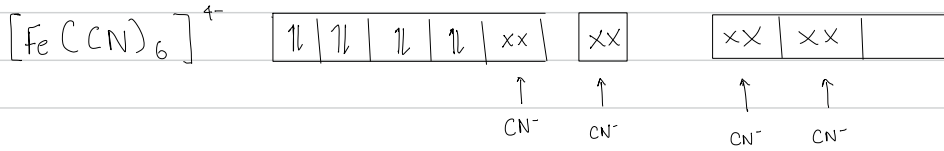
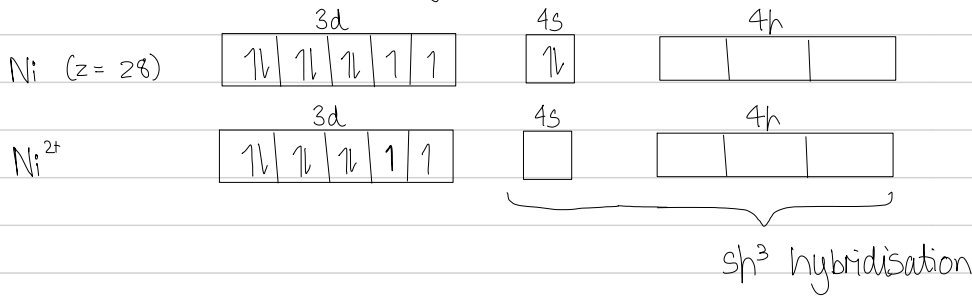
→ On Adding $\text{NH}_3(\text{aq})$



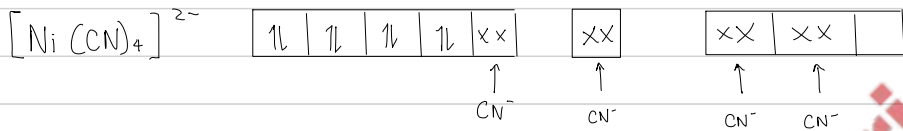
→ On Adding Concentrated HCl



cii) $[\text{NiCl}_4]^{2-}$ Tetrahedral sp^3 hybridisation

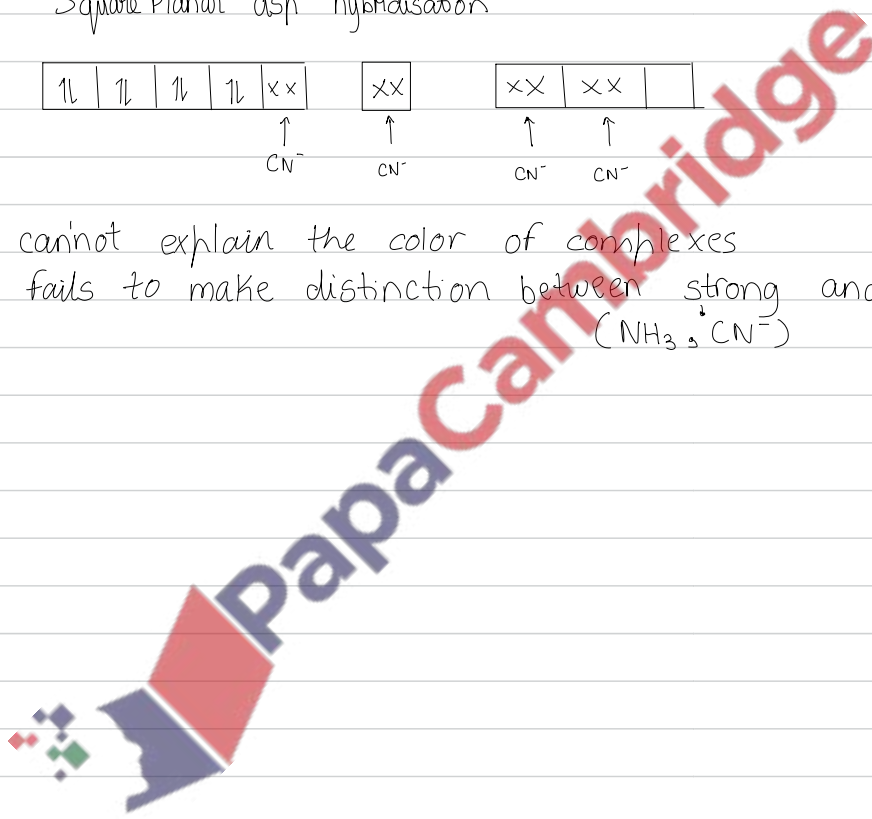


civ) $[\text{Ni}(\text{CN})_4]^{2-}$ Square Planar dsp^2 hybridisation



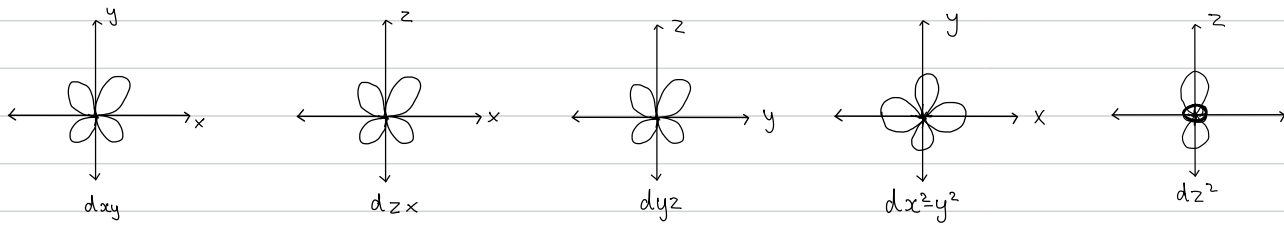
Limitations:

- 1) It cannot explain the color of complexes
- 2) It fails to make distinction between strong and weak ligands.
 (NH₃, CN⁻) (Cl⁻ ions)



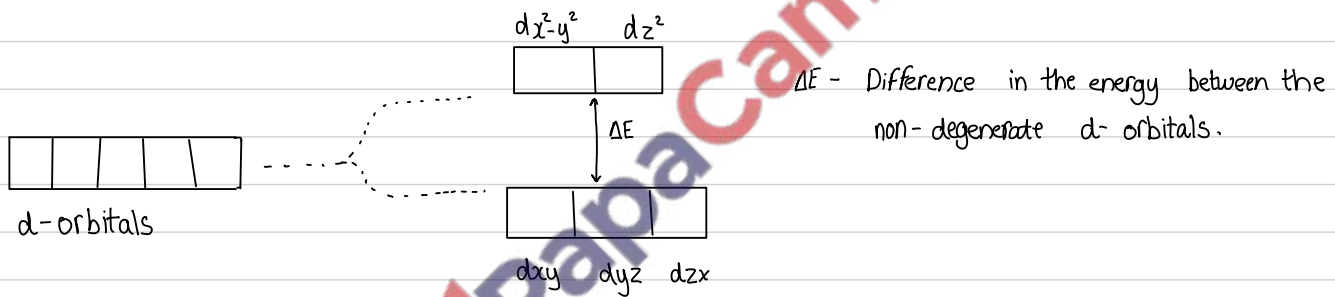
Crystal Field Theory

In a transition metal atom or ion, all the five d-orbitals have the same energy which means that d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$, d_{z^2} orbitals are degenerate orbitals.

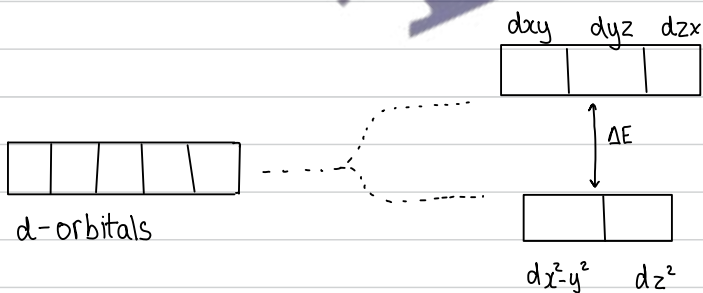


When ligands approach the metal atom/ion, repulsion will arise between the electrons present in d-orbitals and lone pairs on the ligands. The shapes of different orbitals reveal that $d_{x^2-y^2}$ and d_{z^2} orbitals have lobes along the axes and will point in the same direction along which the ligands approach. However, the other 3 d-orbitals (d_{xy} , d_{yz} , d_{zx}) have lobes in between the axes. Consequently, these lobes do not face the ligands so effectively. As a result, the repulsive force interactions between the ligands and orbitals $d_{x^2-y^2}$ & d_{z^2} will be higher than the repulsion in other 3 d-orbitals. Therefore, the orbitals are split into different sets on the basis of energy.

Splitting of d-orbitals in octahedral complexes



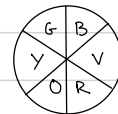
Splitting of d-orbitals in Tetrahedral complexes



Color of Complexes:

• So when light shines on the solution containing $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex, an electron absorbs this ΔE amount of energy. It uses this energy to jump into the higher of the two non degenerate energy levels. The color of the complex which appears is complementary to the color which is absorbed.

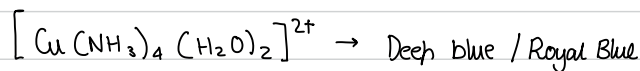
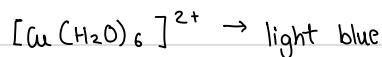
• If the radiation corresponding to orange colour are absorbed, the complex appears to be blue.



• In s-block elements the energy gap is too large (to be able to absorb visible light), therefore they aren't coloured.

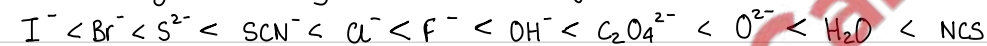
• Eg. A solution of CuSO_4 is blue because red and yellow wavelengths are absorbed.

NOTE: Exact energy difference (ΔE) between the non degenerate d-orbitals in a transition metal ion is affected by many factors, like identity of ligands that surround the transition metal ion.

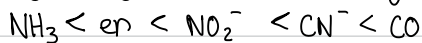


Size of ΔE is different, thus amount of energy being absorbed by electrons jumping into higher orbitals is different. Therefore a different color is absorbed from visible light, so a different colour is seen.

* Weak field ligands (cause only small amount of splitting):

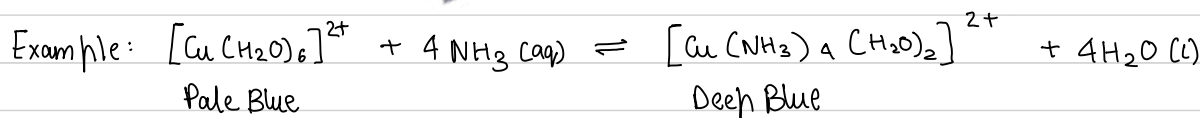


* Strong field ligands (responsible for large splitting)



* Stability Constant - K_{stab}

The stability constant of a complex ion is the equilibrium constant for the formation of the complex ion in a solvent from its constituent ion/molecules.



$$K_{\text{stab}} = \frac{[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}}{[\text{Cu}(\text{H}_2\text{O})_6]^{2+} [\text{NH}_3(\text{aq})]^4}$$

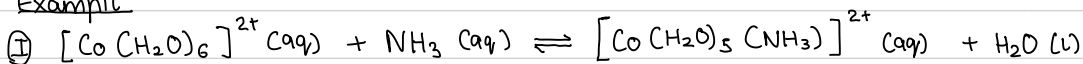
NOTE: Water doesn't appear in the equilibrium expression because it is largely in excess, that is concentration is regarded as being constant.

$$\text{Units of } K_{\text{stab}} = \frac{\text{cmol dm}^{-3}}{\text{cmol dm}^{-3} (\text{mol dm}^{-3})^4} = \text{dm}^3 \text{ mol}^{-4}$$

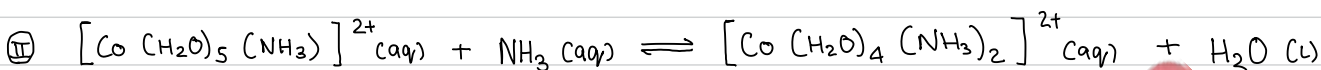
The larger the value of K_{stab} - the more the equilibrium to the right.
 - the more stable the complex ion formed.

Because, the ligand exchange involves a series of equilibria each step in the process has a different stability constant.

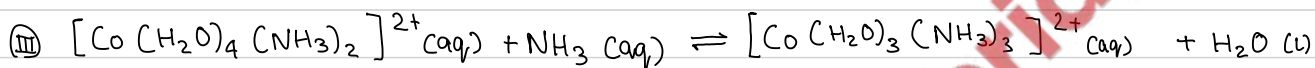
Example



$$K_{stab_1} = 1.02 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$$



$$K_{stab_2} = 3.09 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$$



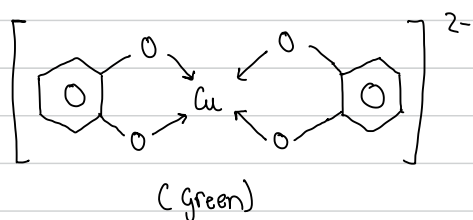
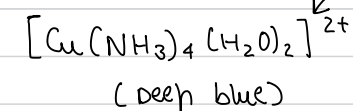
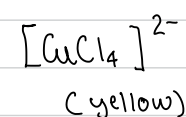
$$K_{stab_3} = 1.17 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1}$$

The Overall Stability Constant: $K_1 \times K_2 \times K_3$

For easier comparison, stability constants are often given on \log_{10} scale.

For Copper (II) Complexes:

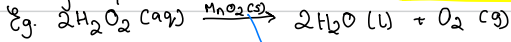
Ligand	$\log_{10} K_{stab}$
Chloride, Cl^-	5.6
Ammonia, NH_3	13.1
2-Hydroxybenzoate (-OOC-C ₆ H ₄ -OH)	16.9
1,2-Hydroxybenzene	25.0



Catalysis

Heterogeneous Catalysis:

Catalyst & Reaction mixture are in **different phases**.



Aqueous state Catalyst in Solid state

- Often involves gaseous molecules reacting at the surface of a solid catalyst

Adsorb vs Absorb

- Adsorb means to bond to the surface of a substance
- Absorb means to move right into the substance. (like sponge & water)

Mechanism

Can be explained by the theory of **Adsorption**

Chemical adsorption (a.k.a. chemisorption) occurs when molecules become bonded to atoms on the surface of a solid.

Eg. Nickel is good at chemisorbing hydrogen gas.

Transition elements in catalytic converters

→ Conversion of harmful nitrogen oxides & carbon monoxide into harmless gases

→ The honeycomb structure inside the catalytic converter contains small beads coated with platinum, Palladium or Rhodium these act as heterogeneous catalysts.

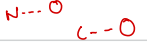
→ Possible steps include:

1) Absorption of nitrogen oxides and carbon monoxide onto the catalyst surface



N-O & C-O

2) Weakening of the covalent bonds within the NO & CO .

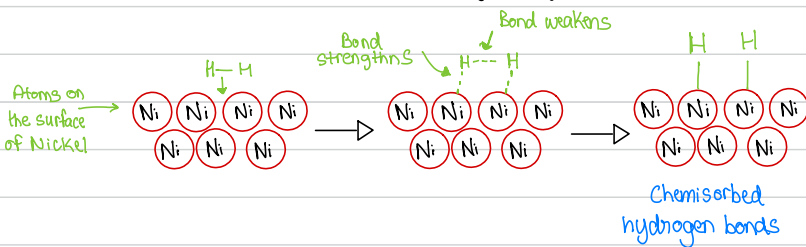


3) Formation of new bonds between

- adjacent nitrogen atoms (to form N_2 molecules)
- CO and O atoms form Carbon dioxide

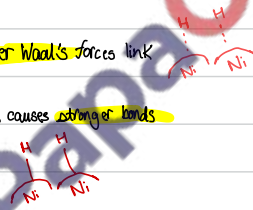


4) desorption of nitrogen molecules and carbon dioxide molecules from the surface of the catalyst.



The Stages in adsorption of hydrogen into Nickel:

- Hydrogen gas diffuses to the surface of nickel
- The hydrogen is physically adsorbed onto the surface - weak van der Waals forces link the hydrogen molecules to the nickel
- The hydrogen becomes chemically adsorbed onto the surface - this causes strong bonds to form between the hydrogen and nickel
- This causes the weakening of the hydrogen-hydrogen covalent bond.



Answers to Past Papers

Explain why transition metals are coloured

When light shines on the solution of a complex compound of a transition metal and electron absorbs the ΔE amount of energy. It uses this energy to jump into the higher of the two non-degenerate d subshell energy levels. The colour of the complex compound noticed is complimentary to that of which light is absorbed.

Explain why the colour of these two complex compounds are different

The size of ΔE is different so the amount of energy being absorbed by electrons jumping up to the higher orbitals is different therefore a different colour is absorbed from visible light so a different colour is seen

Explain why the colour of these two complex compounds are different

The size of ΔE is different so the amount of energy and wavelengths being absorbed by electrons jumping up to the higher orbitals is different therefore a different colour is absorbed from visible light so a different colour is seen

Chemical properties of transition metals

Variable oxidation states

Can act as catalyst

Form complexes

Form coloured ions

Suggest why transition elements show variable oxidation states and their compounds whereas S Block elements like calcium not

This is because electrons of similar energy are in the valence shell orbitals (the 4s and 3d orbitals have similar energies)

Suggest why S Block elements do not have coloured compounds

This is because in the S Block the elements energy gap is too large to be able to absorb visible light

Define complex

A compound formed by central metal ion surrounded by one or more Ligands

Define ligand

A ligand is a species that contains a lone pair of electrons that forms a covalent dative bond with a metal ion

Define bidentate ligand

Bidentate ligands means it donates to 2 pairs of electrons to form 2 dative covalent bond with the central metal ion

Explain why copper (II) is a coloured compound and copper (I) salts are not coloured

In copper (II) the d orbital is split and so an electron is promoted it absorbs light and its complimentary colour is seen
Copper (I) salts are usually white or colourless as there is no gap in the upper orbital (full 3d sub shell)

What is the density of transition metals more than that of S Block elements?

I said has a larger Ar and a smaller atomic radii

Why is the melting point of transition metals more than that of S Block elements?

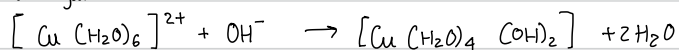
As the Cations are more strongly attracted as there are more delocalised electrons

The higher the K_{stab} value the more the equilibrium is to the right hand side and more of that product will be formed

Ligand	Cu (II)		Co (II)	
H ₂ O	[Cu (H ₂ O) ₆] ²⁺	blue	[Co (H ₂ O) ₆] ²⁺	Pink
NH ₃ (aq) (drops)	[Cu (H ₂ O) ₄ (OH) ₂] (s)	Pale blue	[Co (H ₂ O) ₄ (OH) ₂]	
NH ₃ (aq) (excess)	[Cu (NH ₃) ₄ (H ₂ O) ₂] ²⁺	Royal Blue	[Co (NH ₃) ₆] ²⁺	Yellow Sol ⁿ
OH ⁻ (aq)	[Cu (H ₂ O) ₄ (OH) ₂]	Pale blue	[Co (H ₂ O) ₄ (OH) ₂] (s)	Blue ppt
Cl ⁻	[CuCl ₄] ²⁻	Yellow Sol ⁿ	[CoCl ₄] ²⁻	Blue Sol ⁿ

Copper Chemistry

- Reaction with hydroxide ions.

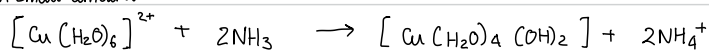


blue solution

pale blue ppt.

- Reaction with Ammonia Solution.

→ In a small amount



blue solution

pale blue ppt

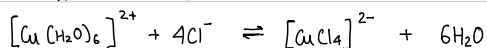
→ Excess ammonia



pale blue solution

deep blue solution

- Reaction with Chloride ions



blue sol.

green sol.

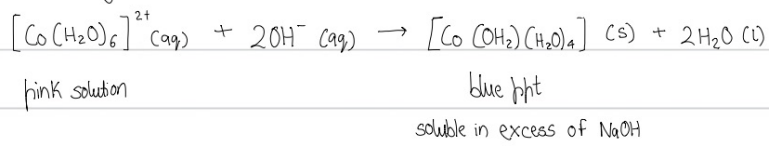


PapaCambridge

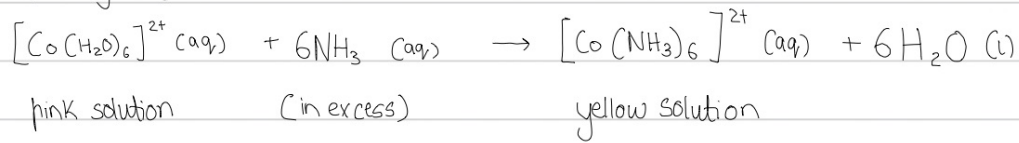
(ii) Cobalt

Co^{2+} aqueous solution is pink, octahedral hexaqua cobalt (II) ion i.e. $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ pink.

→ On Adding NaOH (aq)



→ On Adding NH_3 (aq)



→ On Adding Concentrated HCl

