

Transition Metals Knowledge organiser

1. Keywords

Colorimetry: scientific technique that is used to determine the concentration of coloured compounds using its absorbance

Complex ions: metal ion surrounded by dative covalently bonded ligands.

Coordination number: is the number of dative covalent bonds that are formed with central transition metal ion.

2. Classification

A transition metal is an element that forms at least one stable ion with a partially full d-shell.
 •Transition metals have incomplete d sub-shells. When the fourth period metals form ions the 4s electrons are the first to be lost then 3d electrons.
 •Scandium and Zinc are not considered to be transition metals. Scandium forms only a 3+ ion [Ar] 4s⁰ 3d⁰ •Zinc forms only a 2+ ion [Ar] 4s⁰ 3d¹⁰ •Copper is a transition metal because its +2 ion has an incomplete d orbital. [Ar] 4s⁰ 3d⁹

Chemical properties

•Form coloured ions
 •Form complex ions
 •Act as good catalysts
 •Variable oxidation states.

Physical properties

•Shiny •Strong •Hard • Good conductors

3. Coloured ion formation

Ions with d¹⁰ or d⁰ are colourless, those partly filled tend to be coloured.

Energy is absorbed when an electron is promoted to a higher energy level. The frequency of light is proportional to the energy difference.

Electrons in lower 3d sublevels absorb energy from visible light which promotes them to a higher 3d sublevel. The rest of the frequencies are transmitted hence the complementary colour is observed.

Factors affecting colour

•Size & type of ligand •Oxidation state •Complex shape •Coordination number •Strength of metal-ligand bond

The size of the energy gap can be calculated if we know the frequency (ν) or wavelength (λ) of the light absorbed:

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

ΔE = energy absorbed (J)
 10^8 m s^{-1}

c = speed of light (3.00 x

h = Planck's constant ($6.63 \times 10^{-34} \text{ J s}$) λ = wavelength of light absorbed (m)

ν = frequency of light absorbed (Hz)

Colorimetry: we can then determine the concentration by comparing our sample against known concentrations of the same metal ion / ligand.

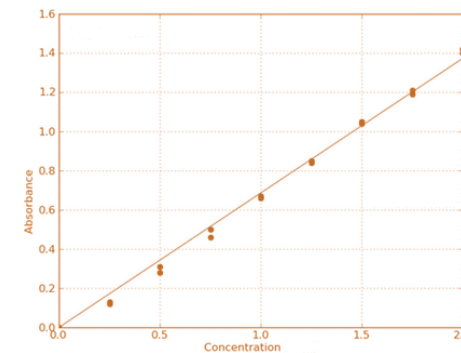
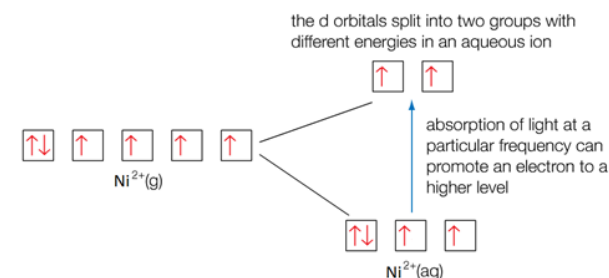
1. Make up solutions of known concentration. 2. Measure absorption of each known solution 3. Plot a graph of absorption vs concentration 4. Measure absorption of unknown and compare on the graph to give a concentration reading

Compounds of Vanadium

Aqueous ion	VO ₂ ⁺	VO ²⁺	V ³⁺	V ²⁺
Oxidation state	+5	+4	+3	+2
Colour	yellow	blue	green	violet

Compounds of Chromium

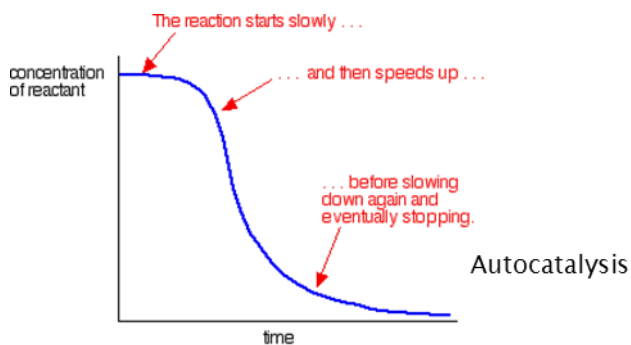
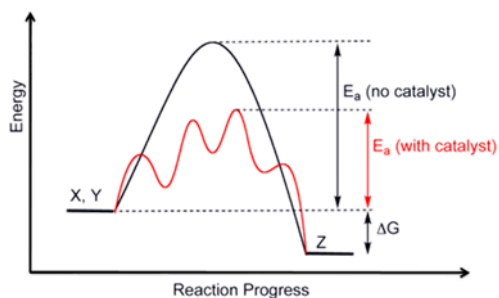
Aqueous ion	Cr ₂ O ₇ ²⁻ (aq)	CrO ₄ ²⁻ (aq)	Cr ³⁺	Cr ²⁺
Oxidation state	+6	+6	+3	+2
Colour	Orange	Yellow	Green	Blue



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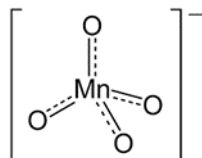
1. Keywords

Catalyst:	is a substance that increases the rate of a chemical reaction by providing an alternative route with a lower activation energy. The catalyst is unchanged by the reaction.
Heterogeneous catalyst:	is in a different phase from the reactants.
Homogeneous catalyst:	is in the same phase as the reactants.
Ligand:	is an atom, ion or molecule that donates a pair of electrons to a central transition metal.
Redox potential (electrode potential):	is a measure of the intensity of its oxidising power, > affinity for electrons = more positive value.



2. Variable oxidation state

The table shows the oxidation states of the transition metals. (red indicates the most common oxidation states found for that element). Not all of them are stable, only the lower oxidation states exist as stable ions (i.e. Mn 7+ exists only when in a covalent bond).



The redox potential for a transition metal ion influenced by pH and by the ligand. In general, oxidation is favoured by alkaline conditions (since there is a higher tendency to form negative ions) and reduction is favoured by acidic conditions.

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

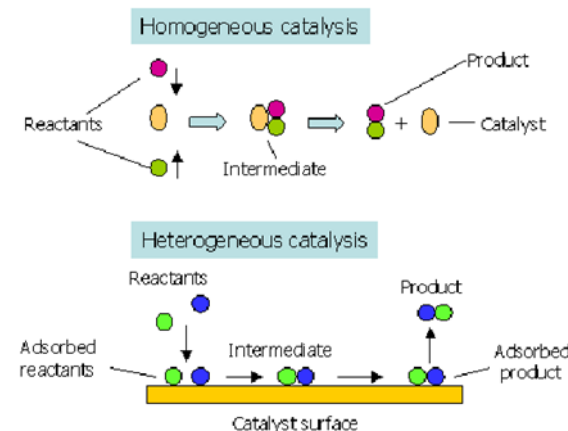
5. Catalytic activity

Transition metals are good as catalysts either due to a change in oxidation state or they adsorb other substances onto the surface. A partially filled d orbital can be used to form bonds with adsorbed reactants.

Types of catalysts:

- Heterogeneous catalyst: The reaction occurs at active sites on the surface.
- Homogeneous catalyst: The reaction proceeds through an intermediate species.
- Autocatalysis: where the catalyst is a product of the reaction. As a result the rate of reaction increases over time as more product, and therefore catalyst, is produced.

Heterogeneous catalysts can become poisoned by impurities blocking the active sites, reducing efficiency. Catalyst can also be lost from the support. This has a cost implication.



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1. Keywords

Chelate:	compound containing a ligand bonded to a central metal atom at two or more points.
Coordinate (dative) bond :	a covalent bond where both electrons in the shared pair come from the same atom
Coordination number:	is the number of dative covalent bonds that are formed with central transition metal ion.
Ligand:	is an atom, ion or molecule that donates a pair of electrons to a central transition metal .
Optical isomerism:	when two or more forms of a compound with the same structure are mirror images of each other and typically differ in optical activity.

2. Complex ion formation

All transition metals form co-ordinate bonds by accepting electron pairs from other ions or molecules generally called ligands.

Different ligands form different strength bonds.

Monodentate ligands (single co-ordinate bond):

- H₂O (Aqua)
- NH₃ (Ammino)
- CN⁻
- OH⁻ (Hydroxi)
- Cl⁻

Bidentate (two co-ordinate bonds):

- H₂NCH₂CH₂NH₂ ethane 1,2 diamine (en)
- C₂O₄²⁻ ethanedioate (oxalate)
- Benzene 1,2 diol

Multidentate (can form many co-ordinate bonds):

- Haem
- EDTA⁴⁻ which can form 6 co-ordinate bonds

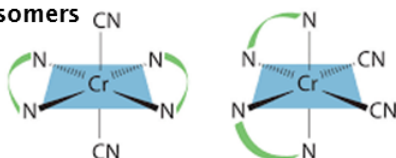
The charge of the complex ion depends on the charge of the transition metal and on the charge and number of the ligands.

3. Complex ion shapes

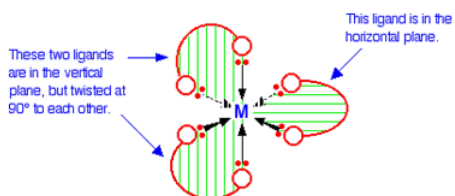
The coordination number dictates the shape of the complex ions.

Coordination number	2	4	6
Shape	Linear	Tetrahedral or square planar	Octahedral

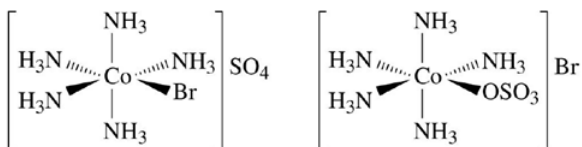
Geometrical isomers



Optical isomers



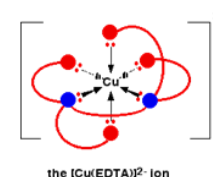
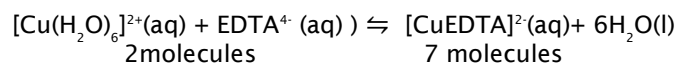
Ionisation isomers



4. Chelate effect

When bidentate or multidentate ligands take the place of monodentate, there are more products than reactants hence entropy of system increases, so products are thermodynamically more stable.

The enthalpy change of these reaction is very small but the increase in entropy makes the reaction possible.



Gibbs free-energy equation

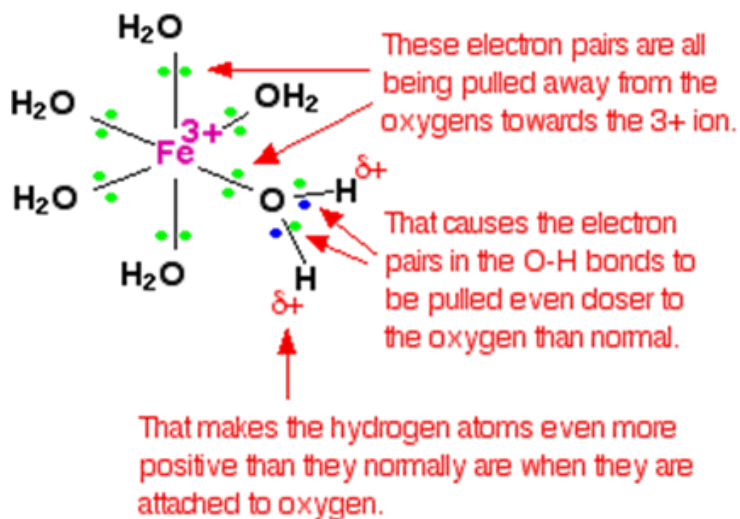
$$\Delta G = \Delta H - T\Delta S$$

Entropy increases = favourable reaction

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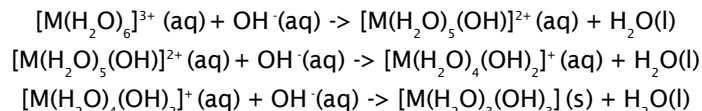
Amphoteric	means can behave as an acid and as a base.
Hydrolysis	the chemical breakdown of a compound due to reaction with water.



2. Acidity of aqua ion

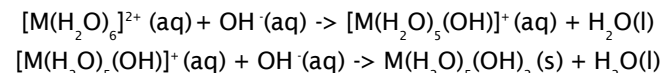
• In general the acidity of M^{3+} will be greater than that of M^{2+} ; i.e. Fe^{3+} has a greater charge density than Fe^{2+} , there are more positive charges on the same ion and the ion is smaller. So the Fe^{3+} aqua ion (pKa 2.2) is more acidic than the Fe^{2+} (pKa 5.9) aqua ion.

Reaction with OH^-
(same with NH_3)



M^{3+} aqua ion

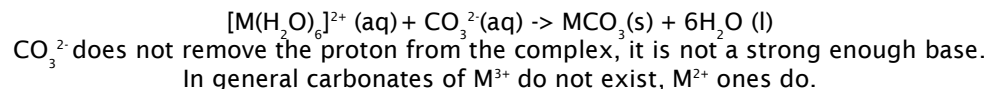
M^{2+} aqua ion



Reaction with CO_3^{2-}
 M^{3+} aqua ion



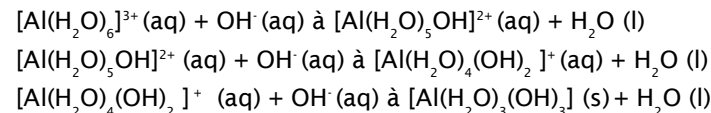
M^{2+} aqua ion



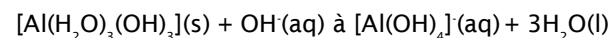
2. Aluminium

Aluminium hydroxide is the most often quoted example of an amphoteric hydroxide.

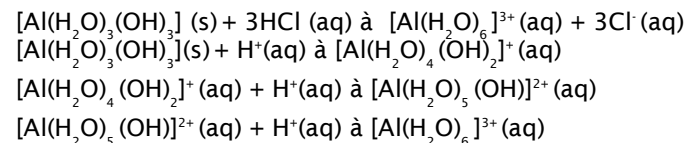
Acting as an acid



This ion will dissolve. What you see occurring is the precipitation of neutral aluminium hydroxide and then the re-dissolving of it. The aluminium hydroxide has acted as an acid.



Acting as a base.



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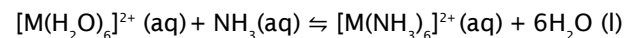
1. Ligand exchange

Ligands can be swapped around, this is called ligand exchange. It usually results in a colour change. This happens when:

- The new ligand can form stronger bonds with the metal ion
- The new ligand is more concentrated

Replacing water as a ligand

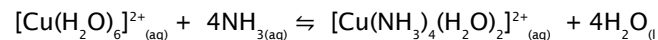
with a neutral ligand



Complete substitution

the coordination number doesn't change and neither does the shape.

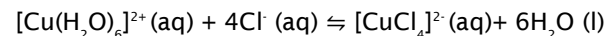
with a neutral ligand



Partial substitution (Cu²⁺)

Ammonia first acts as a base and then as a ligand. the coordination number doesn't change and the shape is still octahedral but it is now a distorted octahedral, this is because water has longer bonds with Cu since it has less affinity.

with other charged ligands (Cu²⁺)



Change in the coordination number and in the shape

with a multidentate ligand

See chelate effect

Change in the coordination number and in the shape forming more stable complex.

Metal aqua-ion	With OH ⁻ or NH ₃ (aq)	With excess OH ⁻ (aq)	With excess NH ₃ (aq)	With Na ₂ CO ₃ (aq)
[Fe(H ₂ O) ₆] ²⁺ (aq)	[Fe(H ₂ O) ₄ (OH) ₂] (s)	No change, precipitate remains	No change, precipitate remains	FeCO ₃ (s)
[Fe(H ₂ O) ₆] ³⁺ (aq) Yellow	[Fe(H ₂ O) ₃ (OH) ₃] (s) Red-Brown	No change, precipitate remains	No change, precipitate remains	[Fe(H ₂ O) ₃ (OH) ₃] (s) Red-Brown
[Cu(H ₂ O) ₆] ²⁺ (aq)	[Cu(H ₂ O) ₄ (OH) ₂] (s)	No change, precipitate remains	[Cu(NH ₃) ₄ (H ₂ O) ₂] ²⁺ (aq) Deep-blue	CuCO ₃ (s) Blue-green
[Al(H ₂ O) ₆] ³⁺ (aq) Colourless	[Al(H ₂ O) ₃ (OH) ₃] (s) White	[Al(OH) ₄] ⁻ (aq)	No change, precipitate remains	[Al(H ₂ O) ₃ (OH) ₃] (s) White

Colours of Vanadium oxidation states

