Inorganic Chemistry – Standard answers

2.1 Periodicity

Atomic radius

a) Across a Period, atomic radius decreases:

- **S**hells: **Same** number of electron shells
- **S**hielding: **Similar** amount of shielding
- **P**rotons: Number of protons **increases**
- **A**ttraction: Attraction is **greater** so shells move in slightly.
- **E**nergy: More energy required.

b) Down a Group, atomic radius increases:

- **S**hells: **More** electron shells
- **S**hielding: **More** shielding
- **P**rotons: Number of protons increases
- **A**ttraction: Attraction is **less** as shells and shielding outweigh number of protons.
- **E**nergy: **Less** energy required.

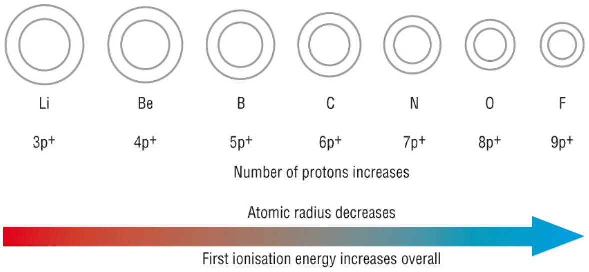
1st ionisation energies

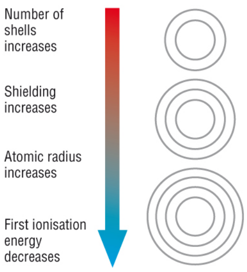
a) Across a Period, 1st ionisation energies increases:

- **S**hells: **Same** number of electron shells
- **S**hielding: **Similar** amount of shielding
- **P**rotons: Number of protons **increases**
- **A**ttraction: Attraction is **greater** so shells move in slightly.
- **E**nergy: **More** energy required.

b) Down a Group, 1st ionisation energies decreases:

- **S**hells: **More** electron shells
- **S**hielding: **More** shielding
- **P**rotons: Number of protons **increases**
- **A**ttraction: Attraction is **less** as shells and shielding outweigh number of protons.
- **E**nergy: **Less** energy required.





Size of ionic radius

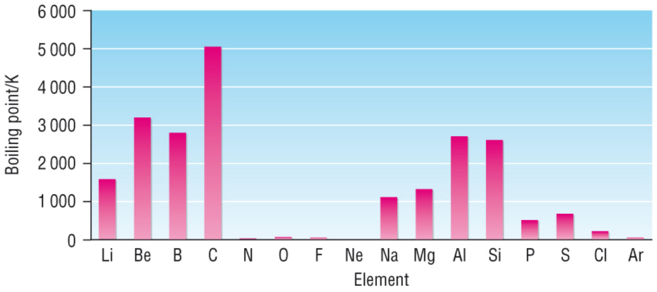
a) Positive ions:

- Are **smaller** due to fewer electrons being attracted by the same number of protons – attraction increases
- With Group 1-3 metals, they also lose their outer shell electrons.

b) Negative ions:

- Are **larger** due to more electrons being attracted by the same number of protons – attraction decreases

Melting and boiling points across a Period

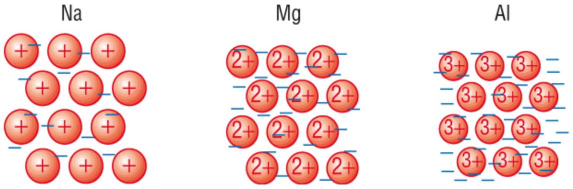


General trends:

a) Increase in Boiling point from Gp 1 - 4.
b) Sharp drop from Gp 4 - 5
c) Low Boiling points for Gp 5 - 0

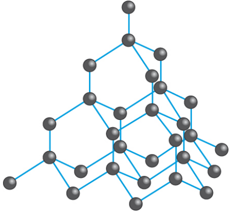
Metallic → Giant Molecular → Molecular → Atomic

a) Metallic bonding - Gp 1 – 3



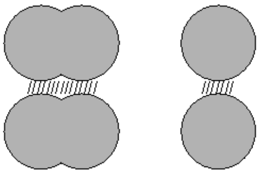
- Increase in charge on metal ion
- Increase in the number of delocalised outer electrons
- Increased attraction **between ions and electrons**
- More energy required

b) Giant covalent structures - Gp 4



- Many strong covalent bonds must be broken
- Requires lots of energy to do this

c) Simple molecular / Atomic - Groups 5 – 0 – Van der Waals



- Larger molecule / atom
- Increases number of electrons
- Stronger VDW force of attraction **between molecules / atoms**
- More energy required to overcome

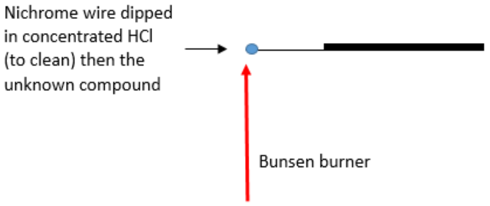
- S_8 is bigger than P_4 which is bigger than Cl_2
- S_8 has more electrons than P_4 which has more electrons than Cl_2
- S_8 has stronger VDW than P_4 which has stronger VDW than Cl_2

Periodicity summary:

Period 2	**Li**	**Be**	**B**	**C**	**N_2**	**O_2**	**F_2**	**He**
Period 3	**Na**	**Mg**	**Al**	**Si**	**P_4**	**S_8**	**Cl_2**	**Ar**
Atomic radius	**Decreases** →							
1st Ionisation energy	**Increases** →							
Electronegativity	**Increases** →							
Structure and bonding	**Giant metallic**			**Giant covalent**	**Simple molecular / atomic structures**			
Forces	**Strong electrostatic forces of attraction between positive ions and negative delocalised electrons**			**Strong covalent bonds between atoms**	**weak VDW forces of attraction between molecules / atoms**			
Melting / Boiling points	**Increases**			**Highest**	**Decreases**			

2.1 Group 2 – The alkaline earth metals

Test for Group 2 metal ions,



Metal ion	*Flame colour*
Calcium, Ca^{2+}	**Brick red**
Strontium, Sr^{2+}	**Red**
Barium, Ba^{2+}	**Pale green**

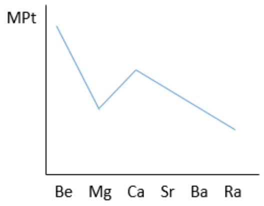
Reactivity of group 2 – Increases down the Group

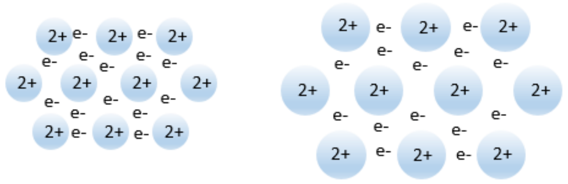
Electrons are lost

- Shells: **More** electron shells
- Shielding: **More** shielding
- Protons: Number of protons **increases**
- Attraction: Attraction is **less** as shells and shielding outweigh number of protons.
- Energy: **Less** energy required.

Electrons are lost more easily:

Melting point – decreases down the group:





- As you go down Group 2 the **ionic radius increases**
- The 2+ charge from the nucleus is **further away** from the delocalised electrons
- **Attraction** between ions and electrons are therefore **weaker**
- **Energy** required is **less**
- Mg's unusually low melting point comes from the different arrangement of the ions in the crystal structure.

Solubility of the Group 2 hydroxides and sulphates:

$Mg(OH)_2$	↓	Least soluble	$MgSO_4$	↑	Most soluble
$Ca(OH)_2$			$CaSO_4$		
$Sr(OH)_2$			$SrSO_4$		
$Ba(OH)_2$		Most soluble	$BaSO_4$		Least soluble

Uses of Group 2 compounds:

a) Barium meals – X – Rays:

- Insoluble barium sulphate, $BaSO_4$, does not allow X – rays to pass through.

b) Extraction of Titanium:

$$TiCl_{4(g)} + 2Mg_{(l)} \rightarrow Ti_{(s)} + 2MgCl_{2(l)}$$

c) Removal of SO_2 from flue gases:

$$CaO_{(s)} + 2H_2O_{(l)} + SO_{2(g)} \rightarrow CaSO_{3(aq)} + 2H_2O_{(l)}$$

$$CaCO_{3(s)} + 2H_2O_{(l)} + SO_{2(g)} \rightarrow CaSO_{3(aq)} + 2H_2O_{(l)} + CO_{2(g)}$$

d) Neutralising acids:

- $Ca(OH)_2$ is used to neutralise acidic soils.
- $Mg(OH)_2$ is used to neutralise excess stomach acids.

2.2 Group 7 – The halogens

Reactivity of halogens – Decreases down the Group:

Electrons are gained

- **S**hells: **More** electron shells
- **S**hielding: **More** shielding
- **P**rotons: Number of protons **increases**
- **A**ttraction: Attraction is **less** as shells and shielding outweigh number of protons.
- **E**nergy: **Less** energy required.

Electrons are gained less easily

Oxidising power of the halogens – Decreases down the Group:

Oxidising agents are themselves reduced – Gains electrons

- **S**hells: **More** electron shells
- **S**hielding: **More** shielding
- **P**rotons: Number of protons **increases**
- **A**ttraction: Attraction is **less** as shells and shielding outweigh number of protons.
- **E**nergy: **Less** energy required.

Electrons are gained less easily

Displacement reactions

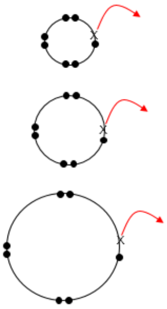
	$Cl^-_{(aq)}$	$Br^-_{(aq)}$	$I^-_{(aq)}$
$Cl_{2(aq)}$ **Add cyclohexane**		**Orange** **Dark orange**	**Brown** **Purple**
$Br_{2(aq)}$ **Add cyclohexane**	**No reaction** Stays orange / dark orange		**Brown** **Purple**
$I_{2(aq)}$ **Add cyclohexane**	**No reaction** Stays brown / purple	**No reaction** Stays Brown / purple	

eg $Cl_{2(aq)} + 2Br^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + Br_{2(aq)}$

Halides as reducing power – increases

Reducing agents are themselves oxidised
Electrons are lost

- **S**hells: **More** electron shells
- **S**hielding: **More** shielding
- **P**rotons: Number of protons **increases**
- **A**ttraction: Attraction **between nucleus and electron to be lost** is **less**
- Energy: **Less** energy required.



Electrons are lost more easily

$$I^-_{(aq)} \rightarrow e^- + \tfrac{1}{2}I_{2(aq)}$$

Reduction products of Sulphuric acid, H_2SO_4:

Name	Sulphuric acid	Sulphur dioxide	Sulphur	Hydrogen sulphate
Formula	H_2SO_4	SO_2	S	H_2S
Oxidation number	+6	+4	0	-2
Test for sulphur product	White fumes with NH_3 gas / Damp blue litmus paper terns red	Dichromate paper turns orange → green	Yellow solid	Lead ethanoate paper turns black
As the power of the Reducing agent increases → H_2SO_4 becomes more reduced - Therefore the halide must be oxidised to the halogen				
How far	F^- and Cl^-			
	→	Br^- and I^-		
	→			I^-

Reactions:

1) **All Halides do the following – H_2SO_4 is not reduced:**

NaX	+	H_2SO_4	→	$NaHSO_4$	+	HX
-1		+6		+6		-1
						White fumes

2) **The HX – Bromide and Iodide will reduce H_2SO_4 to SO_2**

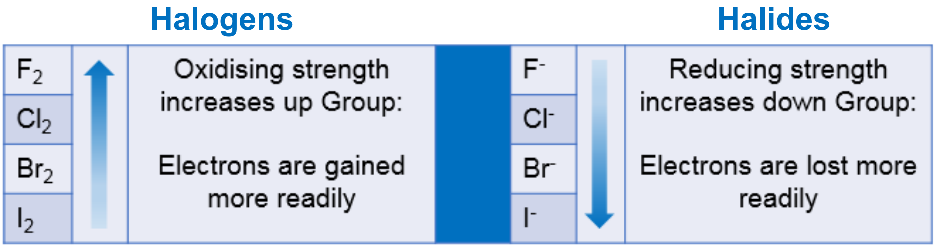
2HX	+	H_2SO_4	→	X_2	+	SO_2	+	$2H_2O$
-1		+6		0		+4		
				Brown / purple fumes				

3) **The HX –Iodide will also reduce H_2SO_4 to H_2S (and S)**

6HX	+	H_2SO_4	→	$3X_2$	+	S	+	$4H_2O$
-1		+6		0		0		
				Purple fumes				

8HX	+	H_2SO_4	→	$4X_2$	+	H_2S	+	$4H_2O$
-1		+6		0		-2		
				Purple fumes				

Summary of Oxidation / Reduction of the Halogens and the Halides



Halogens	Oxidising strength increases up Group: Electrons are gained more readily
F_2	
Cl_2	
Br_2	
I_2	

Halides	Reducing strength increases down Group: Electrons are lost more readily
F^-	
Cl^-	
Br^-	
I^-	

Testing for Halide ions – Using silver nitrate

Halide ion	***Observations***	***With Ammonia***	***Solubility of the precipitate***
Cl^-	White precipitate	Dissolves in dilute NH_3 solution	Most soluble
Br^-	Cream precipitate	Dissolves in concentrated NH_3 solution	
I^-	Yellow precipitate	Insoluble	Least soluble

eg $$Cl^-_{(aq)} + Ag^+_{(aq)} \rightarrow AgCl_{(s)}$$

Disproportionation reactions

a) Chlorine and cold NaOH – Bleach:

$$\underset{0}{Cl_{2(aq)}} + 2NaOH_{(aq)} \rightarrow \underset{-1}{NaCl_{(aq)}} + \underset{+1}{NaClO_{(aq)}} + H_2O_{(l)}$$

b) Chlorine and drinking water:

$$\underset{0}{Cl_{2(aq)}} + H_2O_{(l)} \rightarrow \underset{-1}{HCl_{(aq)}} + \underset{+1}{HClO_{(aq)}}$$

c) Further reactions - In sunlight HClO decomposes further:

$$HClO_{(aq)} \rightarrow HCl_{(aq)} + \tfrac{1}{2}O_{2(aq)}$$

Or

$$\tfrac{1}{2}Cl_{2(aq)} + H_2O_{(l)} \rightarrow HCl_{(aq)} + \tfrac{1}{2}O_{2(aq)}$$

Why does the toxicity not stop chlorine being added to drinking water?

- The benefit of chlorine killing harmful bacteria outweighs the risk of its toxicity

2.4 Period 3

Periodicity:
The repeating trends in physical and chemical properties of elements as you go across the Periodic Table

1) Reactions of Na and Mg with water:

Metal	**+**	**Water**	**→**	**Metal hydroxide**	**+**	**Hydrogen**
$2Na_{(s)}$ 0	+	$2H_2O_{(l)}$	→	$2NaOH_{(aq)}$ +1 *Strong alkali*	+	$H_{2(g)}$
$Mg_{(s)}$ 0	+	$2H_2O_{(l)}$	→	$Mg(OH)_{2(aq)}$ +2 *Weak alkali*	+	$H_{2(g)}$

- Mg reacts with **steam** slightly differently:

$Mg_{(s)}$ 0	+	$H_2O_{(g)}$	→	$MgO_{(s)}$ +2	+	$H_{2(g)}$

2) Reactions with oxygen:

$2Na_{(s)}$ 0	+	$\frac{1}{2}O_{2(g)}$	→	$Na_2O_{(s)}$ +1	Vigorous	Yellow flame / white solid
$Mg_{(s)}$ 0	+	$\frac{1}{2}O_{2(g)}$	→	$MgO_{(s)}$ +2	Vigorous	White flame / white solid
$2Al_{(s)}$ 0	+	$1\frac{1}{2}O_{2(g)}$	→	$Al_2O_{3(s)}$ +3	Slow	
$Si_{(s)}$ 0	+	$O_{2(g)}$	→	$SiO_{2(s)}$ +4	Slow	
$P_{4(s)}$ 0	+	$5O_{2(g)}$	→	$P_4O_{10(s)}$ +5	Spontaneously	White flame
$S_{(s)}$ 0	+	$O_{2(g)}$	→	$SO_{2(g)}$ +4	Steady	Blue flame

- SO_2 can form SO_3 in the presence of **V_2O_5 catalyst** and excess oxygen:

$S_{(s)}$ 0	+	$O_{2(g)}$	→	$SO_{3(g)}$ +6

3) Reactions of the oxides with water:

- **Ionic oxides of metals form alkaline solutions, $OH^-_{(aq)}$**

$Na_2O_{(s)} + H_2O_{(l)} \rightarrow 2NaOH_{(aq)}$ Soluble pH 12 - 14

$MgO_{(s)} + H_2O_{(l)} \rightarrow Mg(OH)_{2(aq)}$ Sparingly Soluble pH 9 - 10

- **Covalent oxides of non - metals form acidic solutions, $H^+_{(aq)}$**

$P_4O_{10(s)} + 6H_2O_{(l)} \rightarrow 4H_3PO_{4(aq)}$ Phosphoric (IV) acid

$SO_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{3(aq)}$ Sulphuric (IV) acid

$SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)}$ Sulphuric (VI) acid

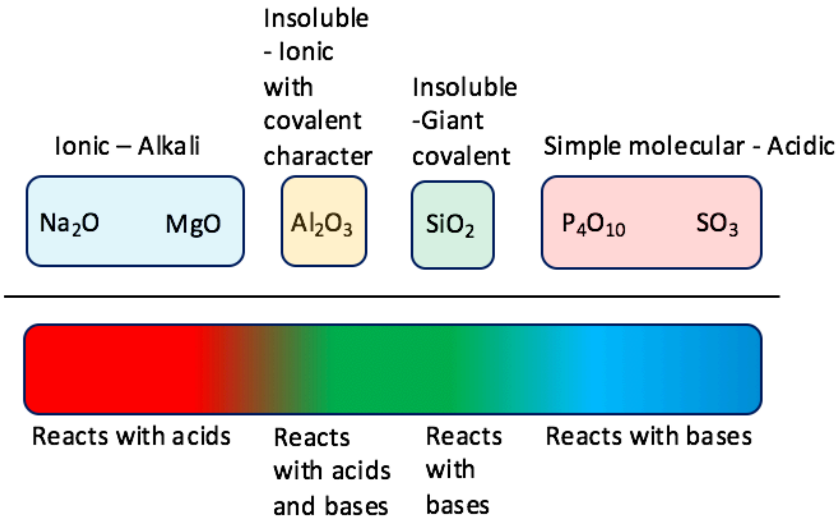
$Al_2O_{3(s)}$ Is insoluble in water - Amphoteric

$SiO_{2(s)}$ Is insoluble in water - Will react with bases, therefore classed as acidic.

Amphoteric

Amphoteric:
A substance that has both acidic and basic properties

Summary of the oxides with water:



4) Reactions of the oxides with acids / bases:

- Alkaline oxides:

$Na_2O_{(s)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O_{(l)}$

$MgO_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_2O_{(l)}$

$Al_2O_{3(s)} + 6HCl_{(aq)} \rightarrow 2AlCl_{3(aq)} + 3H_2O_{(l)}$ *Amphoteric

*Tip:

- Think of the oxides reacting with the water / aq to form the hydroxides.
- The hydroxides then react with the acids forming salt and water.

- Acidic oxides:

$Al_2O_{3(s)} + 2NaOH_{(aq)} + 3H_2O_{(l)} \rightarrow 2NaAl(OH)_{4(aq)}$ *Amphoteric

$SiO_{2(s)} + 2NaOH_{(aq)} \rightarrow Na_2SiO_{3(aq)} + H_2O_{(l)}$

$P_4O_{10(s)} + 12NaOH_{(aq)} \rightarrow 4Na_3PO_{4(aq)} + 6H_2O_{(l)}$

$SO_{2(g)} + 2NaOH_{(aq)} \rightarrow Na_2SO_{3(aq)} + H_2O_{(l)}$

$SO_{3(g)} + 2NaOH_{(aq)} \rightarrow Na_2SO_{4(aq)} + H_2O_{(l)}$

*Tip:

- Think of the oxides reacting with the water / aq to form the acids.
- The acids then react with the metal hydroxides forming salt and water.

*Tip:

- You would be expected to balance these with any acid or base
- It is worth learning the unusual compounds formed and balancing accordingly ie $NaAl(OH)_4$ and Na_2SiO_3.

2.5 Transition metals

Transition element:
A metal that that can form one or more stable ions with an incomplete d sub-level

- Chromium and Copper fills differently
- A half - filled or full d - sub shell offers more stability than a full s - sub shell.
- The 4s subshell fills first but also empties first when forming ions

Complex ion:
A central metal ion surrounded by ligands

Ligand:
A molecule or ion that forms a dative covalent bond with a central metal ion by donating a pair of electrons

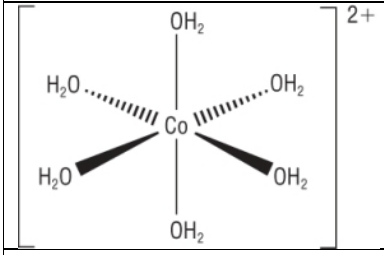
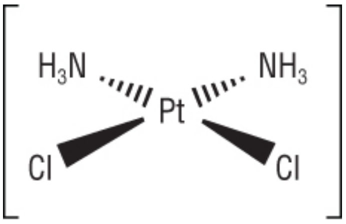
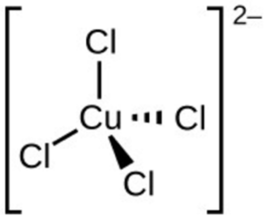
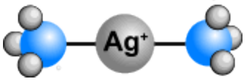
Dative covalent bond (co-ordinate bond)
A covalent bond where the pair of electrons have been donated by the same atom / molecule

Co-ordination number:
Is the number of dative (co-ordinate) bonds to the central metal ion

Bidentate Ligand:
A molecule or ion that forms 2 dative covalent bond with a central metal ion

Multidentate Ligand:
A molecule or ion that forms more than 2 dative covalent bond with a central metal ion

Shapes of complex ions:

6	4	4	2
			
Octahedral	Square planar	Tetrahedral	Linear

Stereoisomerism:
A Molecule with the same structural formula but its atoms are arranged differently in space

Optical isomer:
These are non superimposable mirror images

Coloured ions:

- Absorb specific frequency of light depending on ΔE in the energy levels of the d orbitals
- All other frequencies are transmitted.

$$\Delta E = h\nu$$

$$\nu = c/\lambda$$

$$\Delta E = hc/\lambda$$

ΔE = Energy absorbed (j)

h = Plank's constant (6.63×10^{-34} js)

ν = Frequency of light (Hz)

c = Speed of light (3×10^{8} ms^{-1})

λ = Wavelength of light (m)

- Any changes in the following will alter the size of ΔE between the d orbitals:
  - Oxidation states
  - Co-ordination number
  - Ligands
- Therefore, the frequency of the light required to promote the electron changes.
- As a different frequency is absorbed, the transmitted colours will be different.

Ligand substitution reactions changing shape / coordination number:

- If ligands have a similar size, the co-ordination number remains the same: NH_3 and H_2O.
- With larger ligands, the co-ordination number decreases: Cl^- is larger than NH_3 and H_2O.

Partial substitution: Copper (II) ions and ammonia, NH_3

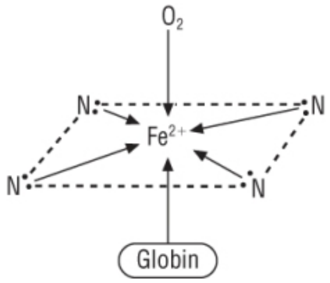
$$[Cu(H_2O)_6]^{2+}{}_{(aq)} \quad + \quad 4NH_{3\,(aq)} \quad \rightleftharpoons \quad [Cu(NH_3)_4(H_2O)_2]^{2+}{}_{(aq)} \quad + \quad 4H_2O_{(l)}$$

Colour: Pale blue — Deep blue

Shape: Octahedral — Octahedral (elongated)

Note: When NH_3 is initially added a precipitate is seen before the ligand substitution reaction.

Haemoglobin and ligand substitution



Lungs:

- In the lungs the $[O_2]$ is high therefore H_2O is substituted for O_2
- The O_2 is exchanged for H_2O and transported back to the lungs.
- Also forms a complex with CO_2, transporting CO_2 to the lungs.

Carbon monoxide - the silent killer

- CO however forms a stronger dative covalent bond.
- The CO cannot be removed.
- That haemoglobin is now useless.
- This reaction is a simple **ligand substitution reaction** where the CO complex is more stable:

Complex ion stability:

- Ligand substitution reactions are mostly easily reversible – Le Chatelier's Principle

1) Enthalpy: Dative covalent bond strength:

$$[Fe(H_2O)_6]^{3+}{}_{(aq)} \quad + \quad 6CN^{-}{}_{(aq)} \quad \rightarrow \quad [Fe(CN)_6]^{3-}{}_{(aq)} \quad + \quad 6H_2O_{(l)}$$

- The CN^- ligand forms a stronger dative covalent bond making it stable and hard to reverse.

2) Multidentate ligand substitution:

$$[Cu(H_2O)_6]^{2+}{}_{(aq)} \quad + \quad 3NH_2CH_2CH_2NH_{2(aq)} \quad \rightarrow \quad [Cu(NH_2CH_2CH_2NH_2)_3]^{2+}{}_{aq)} \quad + \; 6H_2O_{(l)}$$

- Multidentate ligands are more stable than monodentate ligands and are hard to reverse.

The chelate effect:

a) Enthalpy

- Most ligands have similar bond strengths.
- This means it is not down to enthalpy:

b) Entropy

$$[Cu(H_2O)_6]^{2+}{}_{(aq)} \quad + \quad 3NH_2CH_2CH_2NH_{2(aq)} \quad \rightarrow \quad [Cu(NH_2CH_2CH_2NH_2)_3]^{2+}{}_{aq)} \quad + \; 6H_2O_{(l)}$$

4 particles **7 particles**

- Increase in entropy (disorder): 4→ 7 particles.
- As the enthalpy change is minimal, the feasibility of the reaction is down to entropy.

$$\boxed{\Delta G \quad = \quad \Delta H \quad - \quad T\Delta S}$$

Variable oxidation states

Oxidation state	Formula	Colour
+5	$VO_2^{+}{}_{(aq)}$	Yellow
+4	$VO^{2+}{}_{(aq)}$	Blue
+3	$V^{3+}{}_{(aq)}$	Green
+2	$V^{2+}{}_{(aq)}$	Violet

- Vanadium (V) can be reduced all the way to vanadium (II) using acidified zinc:

REDOX potentials (electrode potentials)

The most negative E^{θ} value	**The most positive E^{θ} value**
• Releases electrons the best	• Gains electrons the best
• Oxidised more easily	• **Reduced more easily**
• Reducing agent	• Oxidising agent

Factors affecting REDOX potentials (electrode potentials):

1) Ligands:

- Different ligands will have stronger / weaker bonds with the metal ion.
- This affects its ability to gain / lose electrons and hence its REDOX potential.

2) pH:

$$2VO_2^+{}_{(aq)} + 4H^+{}_{(aq)} + 2e^- \rightleftharpoons 2VO^{2+}{}_{(aq)} + 2H_2O_{(l)}$$

$$CrO_4^{2-}{}_{(aq)} + 4H_2O_{(l)} + 3e^- \rightleftharpoons Cr(OH)_{3(s)} + 5OH^-{}_{(aq)}$$

- Generally, REDOX potentials become more positive in more acidic conditions:
  - Adding more H^+ ions move the equilibrium to the right.
  - This increases the ions ability to accept electrons
  - Increasing its ability to be reduced.

Tollens' Reagent:

- Silver nitrate dissolved in ammonia solvent makes the complex ion: $[Ag(NH_3)]^+$
- When added to aldehydes a silver solid is produced – the silver ions are reduced

$$RCHO_{(aq)} + 2[Ag(NH_3)]^+{}_{(aq)} + 3OH^-{}_{(aq)} \rightarrow RCOO^-{}_{(aq)} + 2Ag_{(s)} + 4NH_{3(aq)} + 2H_2O_{(l)}$$

Redox titrations: Learn

1) MnO_4^- and Fe^{2+}

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$$

$$Fe^{2+}{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + e^-$$

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5Fe^{2+}{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)} + 5Fe^{3+}{}_{(aq)}$$

Purple (MnO₄⁻) → Colourless (Mn²⁺)

2) MnO_4^- and $C_2O_4^{2-}$

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$$

$$C_2O_4^{2-}{}_{(aq)} + 2e^- \rightarrow 2CO_{2(g)}$$

$$2MnO_4^-{}_{(aq)} + 16H^+{}_{(aq)} + 5C_2O_4^{2-}{}_{aq)} \rightarrow 2Mn^{2+}{}_{(aq)} + 8H_2O_{(l)} + 10CO_{2(g)}$$

Purple (2MnO₄⁻) → Colourless (2Mn²⁺)

Transition metals as catalysts

Heterogeneous catalyst:
A catalyst that is in a different phase as the reactants.

The Contact process:

$$SO_{2(g)} \quad + \quad ½O_{2(g)} \quad \xrightarrow{V_2O_{5(s)}} \quad SO_{3(g)}$$

1) The vanadium (V) oxide oxidises the SO_2 while it is itself reduced to vanadium (IV) oxide:

$$SO_2 \quad + \quad \underset{+5}{V_2O_5} \quad \longrightarrow \quad SO_3 \quad + \quad \underset{+4}{V_2O_4}$$

2) The vanadium (IV) oxide is then oxidised back to vanadium (IV) oxide by the oxygen:

$$½O_2 \quad + \quad \underset{+4}{V_2O_4} \quad \longrightarrow \quad \underset{+5}{V_2O_5}$$

- This can only happen because vanadium has variable oxidation states.

Solid supports: are used to increase surface area

Catalytic poisoning:
- Heterogeneous catalysts interact with reactants by **adsorption**:
- Impurities will also be adsorbed
- This blocks that particular site which reduces the area and amount of product made.

Example: Lead poisoning catalytic converters:

- Therefore, catalytic converters only run on unleaded petrol.

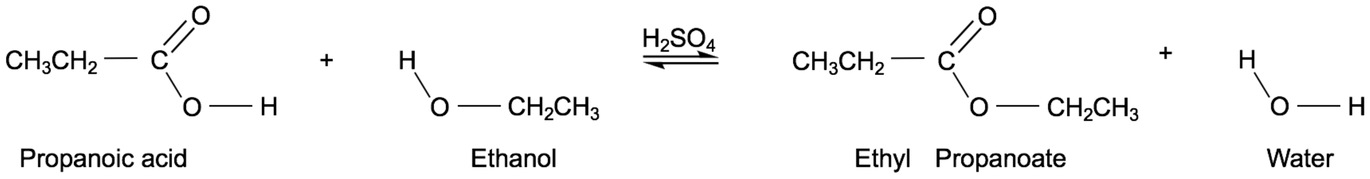
Example: Sulphur poisoning in the Haber process:

- Hydrogen is obtained from natural gas containing sulphur compounds as impurities.
- Sulphur forms iron sulphide and coats the iron catalyst.

❖ Purifying the reactants will increase the life of a catalyst.

Homogeneous catalyst:
A catalyst that is in the same phase as the reactants

Sulphuric acid in esterification



- Transition metals as catalysts in the same phase are usually in the aqueous phase.

Fe^{2+} catalysed reaction between $S_2O_8^{2-}$ and I^-

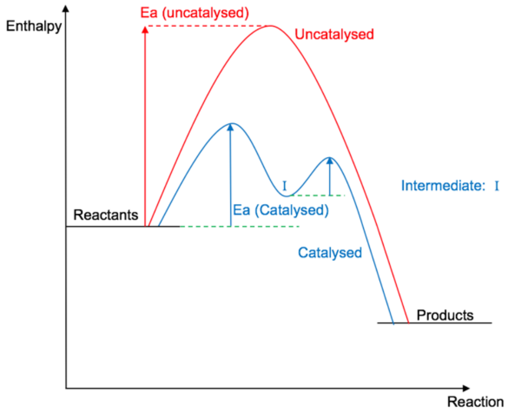
- This reaction occurs very slowly due to 2 negative ions required to collide – repulsion.

$$S_2O_8^{2-}{}_{(aq)} + 2I^-{}_{(aq)} \longrightarrow I_{2(aq)} + 2SO_4^{2-}{}_{(aq)}$$

Catalytic reactions:

$$S_2O_8^{2-}{}_{(aq)} + 2Fe^{2+}{}_{(aq)} \longrightarrow 2Fe^{3+}{}_{(aq)} + 2SO_4^{2-}{}_{(aq)}$$

$$2I^-{}_{(aq)} + 2Fe^{3+}{}_{(aq)} \longrightarrow 2Fe^{2+}{}_{(aq)} + I_{2(aq)}$$



- Each stage now involves a positive and negative ion.
- This can only happen because iron has variable oxidation states.

Mn^{2+} autocatalysis reaction between MnO_4^- and $C_2O_4^{2-}$

- Thi 2 negative ions involved in the reaction – The activation energy is high.
- Mn^{2+} catalyses the reaction when it is made:

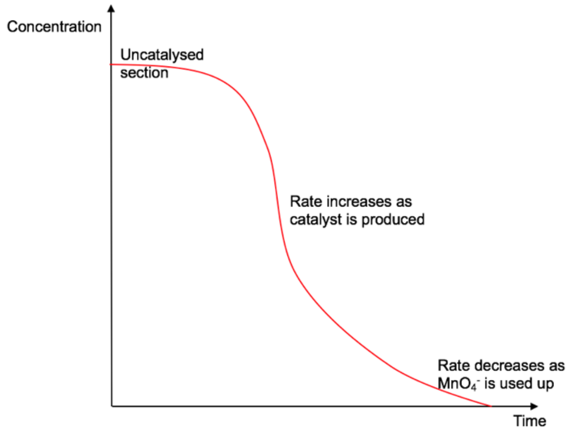
$$2MnO_4^-{}_{(aq)} + 16H^+{}_{(aq)} + 5C_2O_4^{2-}{}_{(aq)} \longrightarrow 2Mn^{2+}{}_{(aq)} + 8H_2O_{(l)} + 10CO_{2(g)}$$

Catalytic reactions:

$$4Mn^{2+}{}_{(aq)} + MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} \longrightarrow 5Mn^{3+}{}_{(aq)} + 4H_2O_{(l)}$$

$$2Mn^{3+}{}_{(aq)} + C_2O_4^{2-}{}_{(aq)} \longrightarrow 2Mn^{2+}{}_{(aq)} + 2CO_{2(g)}$$

How the rate changes:



- Each stage now involves a positive and negative ion.
- This can only happen because manganese has variable oxidation states.

2.6 transition metals:
Coloured solutions / precipitates

Metal ion	Formula of hexa-aqua ion / PPT	Solution / PPT colour
Fe^{2+}	$[Fe(H_2O)_6]^{2+}$ / $[Fe(H_2O)_4(OH)_2]$	Green sol'n / green ppt's
Cu^{2+}	$[Cu(H_2O)_6]^{2+}$ / $[Cu(H_2O)_4(OH)_2]$	Blue sol'n / pale blue ppt's
Fe^{3+}	$[Fe(H_2O)_6]^{3+}$ / $[Fe(H_2O)_3(OH)_3]$	Yellow sol'n / Brown ppt's
Al^{3+}	$[Al(H_2O)_6]^{3+}$ / $[Al(H_2O)_3(OH)_3]$	Colourless sol'n / White ppt's

Bronsted – Lowry acid:

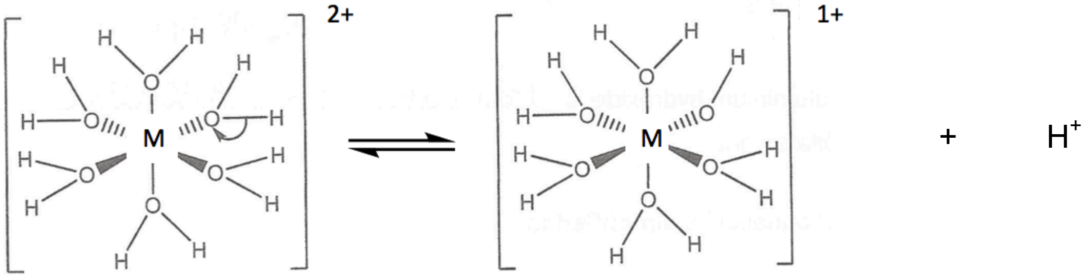
Acids are proton donors

Hydrolysis:

Breaking of a bond with water

Proton donor:

- M^{3+} / M^{2+} is a **small highly charged ion**, M^{2+} therefore has a **high charge density.**
- This **high charge density** will **polarise** the water molecule.
- The O – H bond breaks **donating a proton donor**, making **the complex ion acidic:**



Acidity of the metal aqua 2+ and 3+ ions:

- 3+ ions are smaller and more highly charged ion.
- Polarises water ligand more.
- More protons donated.
- Dissociates more.
- Larger Ka.
- Smaller pKa

Acid base reactions:

1) Reactions with hydroxides, OH^-

M^{3+} ion: Consider the dissolved metal 3+ ion:

$$[M(H_2O)_6]^{3+}_{(aq)} + OH^-_{(aq)} \rightleftharpoons [M(H_2O)_5(OH)]^{2+}_{(aq)} + H_2O_{(l)}$$

$$[M(H_2O)_5(OH)]^{2+}_{(aq)} + OH^-_{(aq)} \rightleftharpoons [M(H_2O)_4(OH)_2]^{+}_{(aq)} + H_2O_{(l)}$$

$$[M(H_2O)_4(OH)_2]^{+}_{(aq)} + OH^-_{(aq)} \rightleftharpoons [M(H_2O)_3(OH)_3]_{(s)} + H_2O_{(l)}$$

Precipitate

- Adding more OH^- shifts the equilibrium to the right
- The product has **neutral charge** and therefore **precipitates** out of solution.

Simplifying to:

$$[M(H_2O)_6]^{3+}_{(aq)} + 3OH^-_{(aq)} \rightleftharpoons [M(H_2O)_3(OH)_3]_{(s)} + 3H_2O_{(l)}$$

Precipitate

$$[M(H_2O)_6]^{2+}_{(aq)} + 2OH^-_{(aq)} \rightleftharpoons [M(H_2O)_4(OH)_2]_{(s)} + 2H_2O_{(l)}$$

Precipitate

- Adding acid will reverse these reactions.

2) Reactions with ammonia, NH_3:

$$[M(H_2O)_6]^{3+}_{(aq)} + 3NH_{3(aq)} \rightleftharpoons [M(H_2O)_3(OH)_3]_{(s)} + 3NH_4^{+}{}_{(aq)}$$

Precipitate

$$[M(H_2O)_6]^{2+}_{(aq)} + 2NH_{3(aq)} \rightleftharpoons [M(H_2O)_4(OH)_2]_{(s)} + 2NH_4^{+}{}_{(aq)}$$

Precipitate

Copper complex with excess NH_3, Ligand substitution follows:

$$[Cu(H_2O)_4(OH)_2]_{(s)} + 4NH_{3(aq)} \rightleftharpoons [Cu(H_2O)_2(NH_3)_4]^{2+}_{(aq)} + 2H_2O_{(l)} + 2OH^-_{(aq)}$$

Pale blue precipitate — Dark blue solution

Overall:

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(H_2O)_2(NH_3)_4]^{2+}_{(aq)} + 4H_2O_{(l)}$$

Blue solution — Dark blue solution

3) Reactions with carbonates, CO_3^{2-}:

M^{3+} ion:

- Reacts in the same way as the hydroxide but, as it is more acidic, it reacts with the carbonate forming CO_2 and H_2O.

$$2[M(H_2O)_6]^{3+}{}_{(aq)} \quad + \quad 3CO_3^{2-}{}_{(aq)} \quad \rightleftharpoons \quad \underset{\text{Precipitate}}{2[M(H_2O)_3(OH)_3]_{(s)}} \quad + \quad 3CO_{2(g)} \quad + \quad 3H_2O_{(l)}$$

M^{2+} ion:

- The M^{2+} is not acidic enough to produce CO_2 with the carbonates.
- They react to from the insoluble metal carbonate:

$$[M(H_2O)_6]^{2+}{}_{(aq)} \quad + \quad CO_3^{2-}{}_{(aq)} \quad \rightarrow \quad \underset{\text{Precipitate}}{MCO_{3(s)}} \quad + \quad 6H_2O_{(l)}$$

- ***Generally: Transition metal carbonates with an oxidation state of 3+ do not exist***

The amphoteric nature of aluminium hydroxide, $Al(OH)_3$:

Amphoteric:

A species that can behave as an acid or a base

With an acid:

$$\underset{\text{White precipitate}}{[Al(H_2O)_3(OH)_3]} \quad + \quad 3H^+ \quad \rightarrow \quad \underset{\text{colourless solution}}{[Al(H_2O)_6]^{3+}}$$

With a base:

$$\underset{\text{White precipitate}}{[Al(H_2O)_3(OH)_3]} \quad + \quad OH^- \quad \rightarrow \quad \underset{\text{colourless solution}}{[Al(H_2O)_2(OH)_4]^-} \quad + \quad H_2O$$