

## The aqueous chemistry of cations

- Hydrolysis**
- when salts dissolve in water the ions are **stabilised by polar water molecules**
  - **hydrolysis** can occur and the resulting solution can become acidic
  - the acidity of the resulting solution depends on the cation present
  - the greater the charge density of the cation, the more acidic the solution

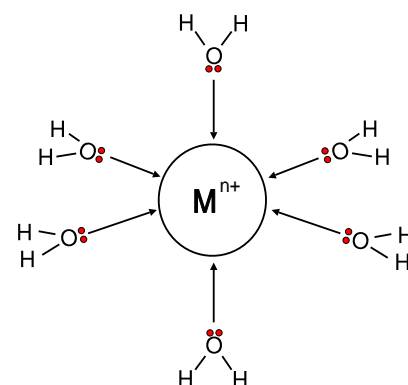
cation	charge	ionic radius	reaction with water and trend in pH of chloride
Na	1+	0.095 nm	
Mg	2+	0.065 nm	
Al	3+	0.050 nm	

**the greater charge density of the cation, the greater the polarising power and the more acidic the solution**

**Q.1** Predict what will happen when  $\text{SiCl}_4$  is added to water.

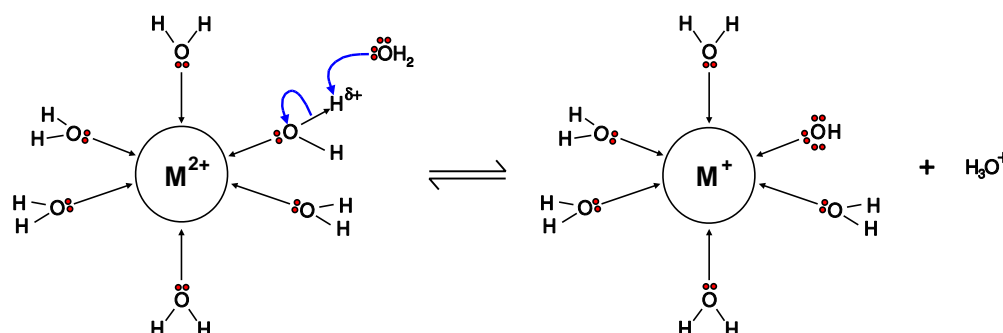
### Theory

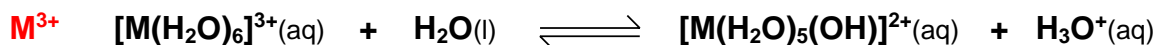
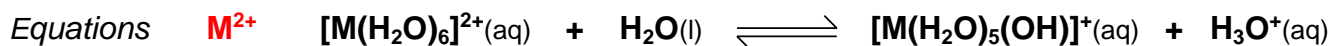
- aqueous metal ions attract water molecules
- many have **six water molecules** surrounding
- these are known as **hexaaqua ions**
- they are **octahedral** in shape
- water acts as a Lewis Base - lone pair donor
- water forms a co-ordinate bond to the metal ion
- metal ions accept the lone pair - Lewis Acids



### Acidity

- as charge density increases, the cation exhibits a greater attraction for water
- the attraction extends to the shared pair of electrons in the O-H bonds of water
- the electron pair is pulled towards the O, making the bond more polar
- this makes the H more acidic (more  $\delta^+$ )
- it can then be removed by solvent water molecules to form  $\text{H}_3\text{O}^+$  (aq).



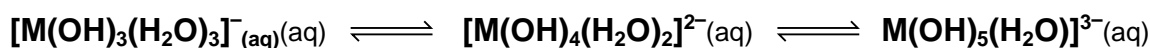
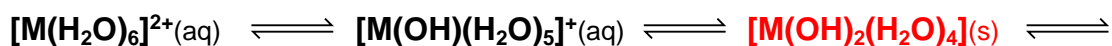


- the **resulting solution is acidic** as there are more protons in the water
- the greater the charge density of the cation, the more the equilibrium lies to RHS
- the reaction is known as **hydrolysis** - the water causes the substance to split up

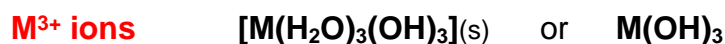
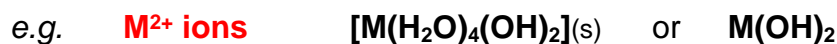
**Stronger bases** (e.g.  $CO_3^{2-}$ ,  $NH_3$  and  $OH^-$ ) **can remove further protons ...**

- Lewis bases can attack the water molecules co-ordinated to metal ions.
- protons can be removed from each water molecule turning the water from a neutral molecule to a negatively charged hydroxide ion.
- this will affect the overall charge on the complex ion.

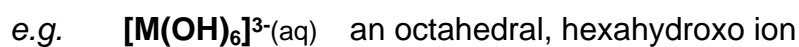
**ADD BASE - EQUILIBRIUM MOVES TO THE RIGHT**  
**ADD ACID - EQUILIBRIUM MOVES TO THE LEFT**



When sufficient protons have been removed the complex becomes **neutral** and precipitation of a hydroxide or carbonate occurs.



In some cases, if the base is strong, further protons are removed and the precipitate dissolves as soluble anionic complexes are formed.



Summary	Very weak bases	$H_2O$	remove few protons
	Weak bases	$NH_3$ , $CO_3^{2-}$	remove protons until precipitation
	Strong bases	$OH^-$	can remove all the protons

## The First Row Transition Elements - an introduction

**Definition** D-block elements **forming one or more stable ions with partially filled (incomplete) d-sub shells**. The first row runs from Sc to Zn filling the 3d orbitals.

**Q.2** Why, in terms of energy levels, are the 4s orbitals filled before the 3d orbitals ?

### Electronic configs.

The filling proceeds according to the usual rules except that chromium and copper change slightly to achieve a more stable configuration.

	4s	3d							
Sc							$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$	or	$[Ar] 3d^1 4s^2$
Ti									
V									
Cr									
Mn									
Fe									
Co									
Ni									
Cu									
Zn									

The characteristic properties arise from an incomplete d sub-shell in atoms or ions

### Metallic properties

- all the transition elements are metals
- **strong metallic bonds** result from **small size** and **close packing** of the atoms
- **higher melting** and **boiling points** and **higher densities** than s-block metals

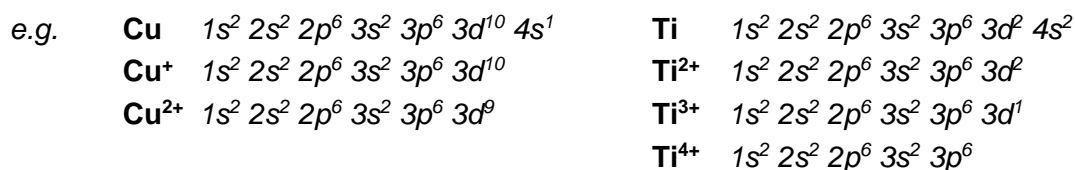
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	etc.
<i>m. pt</i> / °C	63	850	1400	1677	1917	1903	1244	1539	1495	
<i>density</i> / g cm <sup>-3</sup>	0.86	1.55	3	4.5	6.1	7.2	7.4	7.9	8.9	

### Variable oxidation state

- arises from the similar energies required for removal of 4s and 3d electrons.
- maximum oxidation state rises across the group to manganese
- then falls as the energy required to remove more electrons becomes very high
- all (except scandium) have an  $M^{2+}$  ion
- stability of the +2 state increases across the row - marked increase in 3rd I.E.

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	

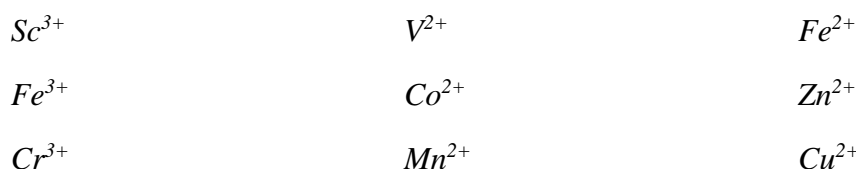
**N.B.** When electrons are removed they come from the 4s orbitals first



### Coloured ions

- ions with a  $d^{10}$  (full) or  $d^0$  (empty) configuration are **colourless**
  - ions with **partially filled d-orbitals** tend to be **coloured**
  - caused by the ease of transition of electrons between energy levels
  - energy is absorbed when an electron is promoted to a higher level
  - the frequency of light is proportional to the energy difference
- colour depends on ...
    - transition element
    - oxidation state
    - ligand
    - coordination number

**Q.3** Find out the colours of the following ions in aqueous solution



**Splitting of d orbitals**

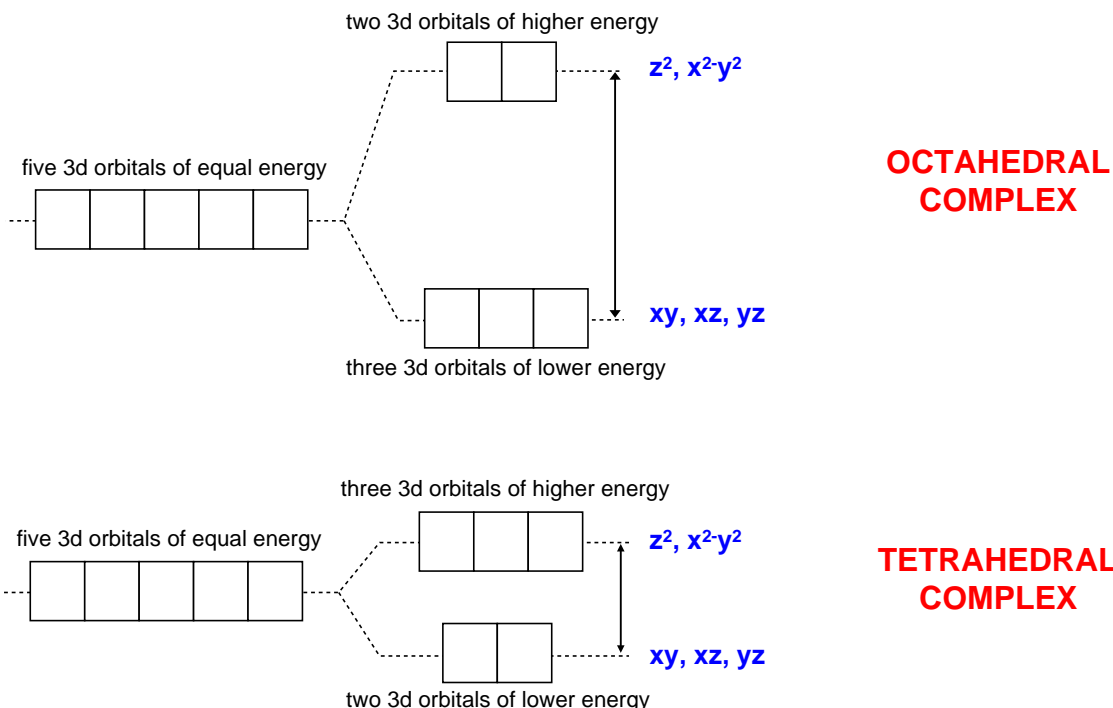
Placing ligands around a central metal ion changes the energies of the d orbitals. Some of the d orbitals gain energy and some lose energy

The amount of splitting depends on the

- central ion
- ligand

The difference in energy between the new levels affects how much energy will be absorbed when an electron is promoted to a higher level.

The amount of energy will govern the colour of light which will be absorbed.



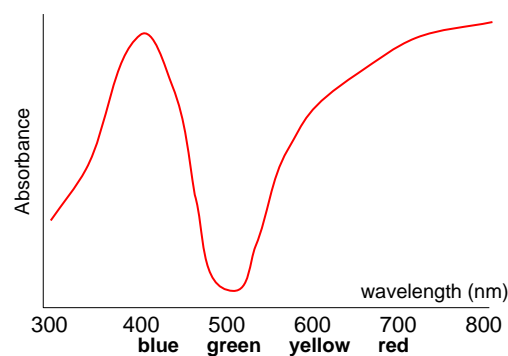
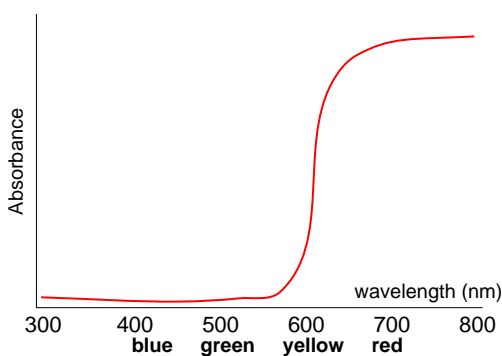
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Absorbed colour	$\lambda$ nm	Observed colour	$\lambda$ nm
VIOLET	400	GREEN-YELLOW	560
BLUE	450	YELLOW	600
BLUE-GREEN	490	RED	620
YELLOW-GREEN	570	VIOLET	410
YELLOW	580	DARK BLUE	430
ORANGE	600	BLUE	450
RED	650	GREEN	520

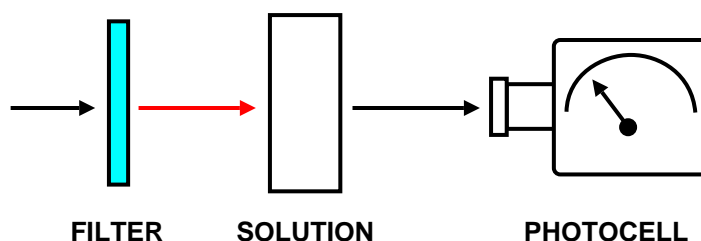
*a solution of copper(II)sulphate is blue because red and yellow wavelengths are absorbed*

*What colour is this hexaaqua complex?*



## FINDING COMPLEX ION FORMULAE USING COLORIMETRY

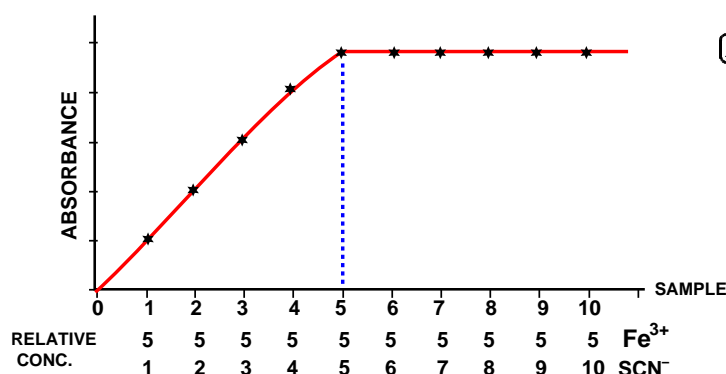
- Colorimetry**
- a change of ligand can change the colour of a complex
  - this property can be used to find the formula of a complex ion
  - light of a certain wavelength is passed through a solution
  - the greater the colour intensity, the greater the absorbance
  - the concentration of each species in the complex is altered
  - the mixture which gives the greatest absorbance identifies ligands / ion ratio



- Examples**
- finding the formula of the iron(III) complex  $\text{Fe}[(\text{H}_2\text{O})_5\text{SCN}]^{2+}$
  - the complex formed between nickel(II) and edta

**Fe(III)** White light is passed through a **blue filter**. The resulting **red light** is passed through various mixtures of an aqueous solution of iron(III) and potassium thiocyanate solution.

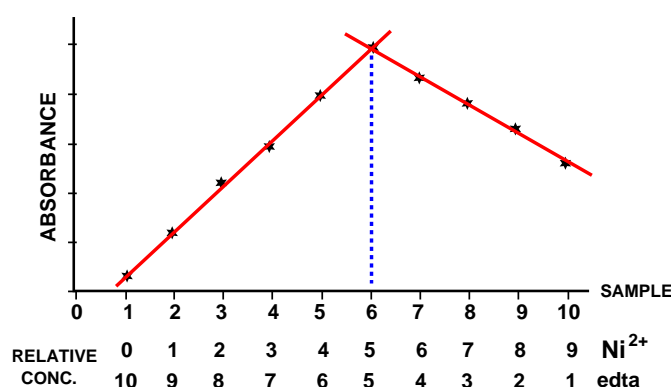
The **maximum absorbance occurs first** when the ratio of  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  is 1:1.



This shows the complex has the formula  $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$

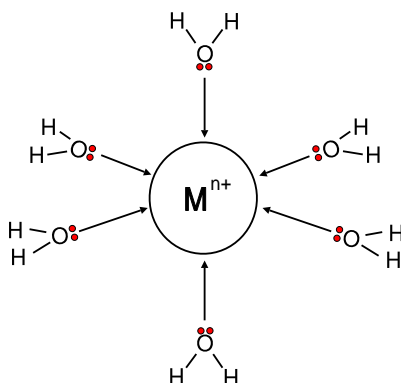
**Ni(II)** Filtered light is passed through various mixtures of an aqueous solution of nickel(II) sulphate and edta solution.

The **maximum absorbance occurs** when the ratio of  $\text{Ni}^{2+}$  and edta is 1:1.



**COMPLEX IONS**

Formed when species called **ligands** form **co-ordinate bonds** to a central species such as a transition metal ion.



The six  $\text{H}_2\text{O}$  molecules are acting as **ligands**

**Ligands**

- atoms, or ions, which possess **lone pairs** of electrons
- form **co-ordinate bonds** to the central ion
- donate a lone pair of electrons into vacant orbitals on the central species

<i>Ligand</i>	<i>Formula</i>	<i>Name of ligand</i>
chloride	$\text{Cl}^-$	chloro
cyanide	$\text{NC}^-$	cyano
hydroxide	$\text{HO}^-$	hydroxo
oxide	$\text{O}^{2-}$	oxo
water	$\text{H}_2\text{O}$	aqua
ammonia	$\text{NH}_3$	ammine

- some ligands attach themselves using two or more lone pairs
- classified by the **number of lone pairs they use**, not the number they have
- multidentate and bidentate ligands lead to more stable complexes

<b>Unidentate</b>	form one co-ordinate bond	$\text{H}_2\text{O}$ , $\text{NH}_3$ , $\text{Cl}^-$ and $\text{OH}^-$
<b>Bidentate</b>	form two co-ordinate bonds	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ , $\text{C}_2\text{O}_4^{2-}$
<b>Multidentate</b>	form several co-ordinate bonds	EDTA , Haem

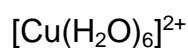
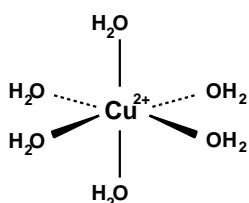
**Q.4** Draw structures for some bidentate and multidentate ligands

- SHAPES**
- the shape is **governed by the number of ligands** around the central ion
  - shapes are based on electron pair repulsion theory
  - **a change of ligand can affect the shape**

**COORDINATION NUMBER**

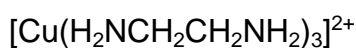
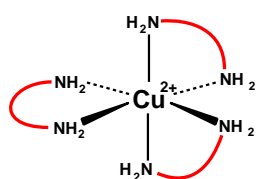
- the **number of co-ordinate bonds formed to the central ion**
- if monodentate ligands are present it will equal the number of ligands
- **a change of ligand can affect the co-ordination number**

<i>Co-ordination No.</i>	<i>Shape</i>	<i>Example(s)</i>
<b>6</b> (sixfold)	Octahedral	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
<b>4</b> (fourfold)	Tetrahedral Square planar	$[\text{CuCl}_4]^{2-}$ $[\text{NiCl}_4]^{2-}$
<b>2</b> (twofold)	Linear	$[\text{Ag}(\text{NH}_3)_2]^+$



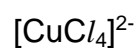
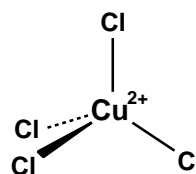
**octahedral**

**CN = 6**



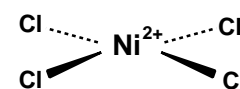
**octahedral**

**CN = 6**



**tetrahedral**

**CN = 4**



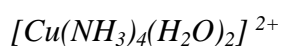
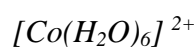
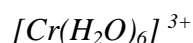
**square planar**

**CN = 4**

**Q.5** What is the co-ordination number and shape of the following complex ions?

*Coordination No.*

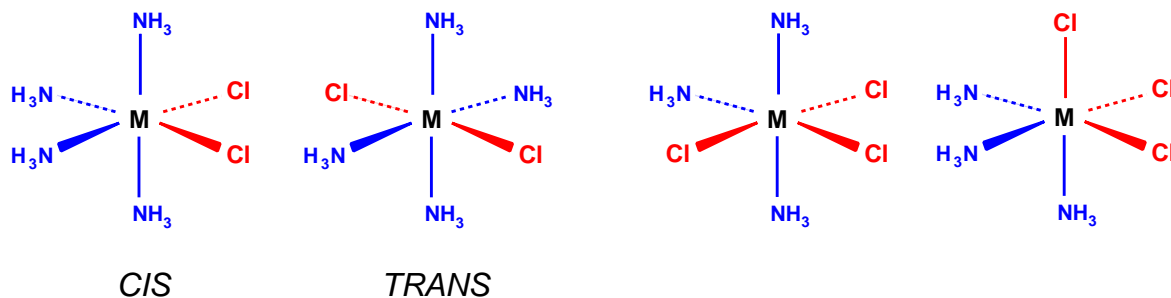
*Shape*





## ISOMERISM IN COMPLEXES

**Octahedral** Some complexes; e.g.  $[\text{MA}_4\text{B}_2]^{n+}$  or  $[\text{MA}_3\text{B}_3]^{n+}$  can exist in more than one form.



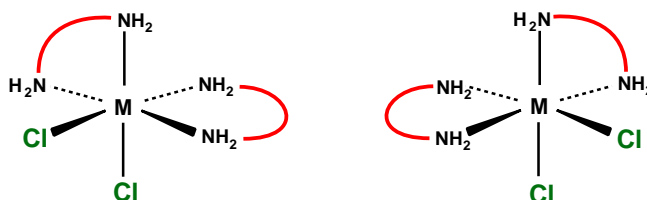
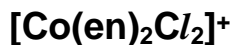
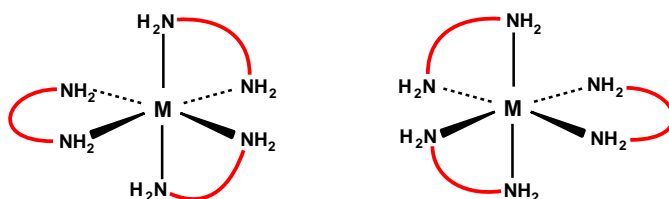
**Cis-trans** Square planar complexes of the form  $[\text{MA}_2\text{B}_2]^{n+}$  exist in two forms



**Q.6** Why is the cis isomer more effective than the trans?

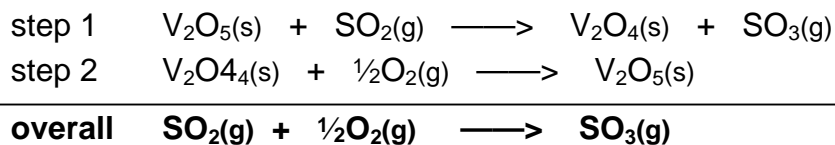
**Optical** Octahedral complexes with bidentate ligands can exist as a pair of enantiomers (optical isomers).  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$

**Example** With cobalt(III)



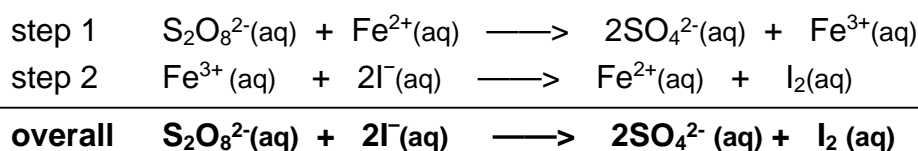
- CATALYSIS**
- transition metals and their compounds show great catalytic activity...
  - partly filled d-orbitals can be used to **form bonds with adsorbed reactants**
  - activity is due to their ability to exist in **more than one oxidation state**

*Example 1* Oxidation of  $\text{SO}_2$  in the Contact Process is catalysed by vanadium(V) oxide



*Example 2* Reaction between  $\text{I}^-$  and  $\text{S}_2\text{O}_8^{2-}$  (peroxodisulfate ion)

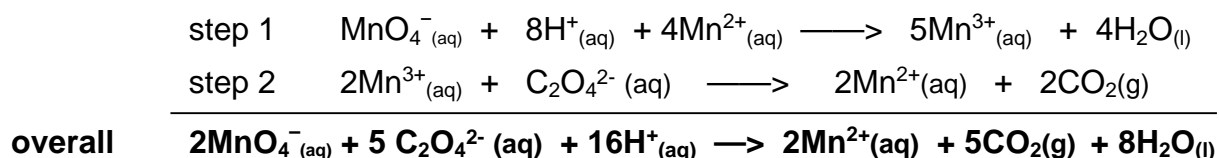
- a **slow** reaction because **reactants are both negative ions**  $\therefore$  REPULSION
- addition of iron(II) catalyses the reaction



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*Example 3* Autocatalysis by  $\text{Mn}^{2+}$  (**Autocatalysis** - where a product catalyses the reaction)

- the titration is carried out at c.  $60^\circ\text{C}$  as the reaction is slow at room temperature
- once some  $\text{Mn}^{2+}$  is formed, the reaction is much quicker



**Q.7** In which industrial processes are the following catalysts used ?

*Fe*

*Ni*

*Pt/Rh*

**Q.8** Give details of reactions where the following laboratory catalysts are used ?

*MnO<sub>2</sub>*

*Cu*

## Reactions of the first row transition elements

### An introduction

The examples aim to show typical properties of transition metals and their compounds.

- Variable oxidation states
- Formation of complex ions
- The importance of variable oxidation state in catalysis
- Definitions of Lewis Acids and Bases

One typical properties of transition elements is their ability to **form complex ions**. Complex ions consist of a **central metal ion surrounded by** co-ordinated ions or molecules known as **ligands**.

Ligand substitution can lead to changes in ...

- colour
- co-ordination number
- shape
- stability to oxidation or reduction

**Reactions** When investigating the reactions of selected transition metal ions, look for...

- **substitution** reactions of complex ions
- variation in **oxidation state** of transition metals
- the effect of ligands on **co-ordination number** and **shape**
- the increased acidity of  $M^{3+}$  over  $M^{2+}$  due to the increased charge density
- any difference in reactivity of  $M^{3+}$  and  $M^{2+}$  ions in reactions with  $OH^-$  and  $NH_3$
- the reason why  $M^{3+}$  ions don't form carbonates
- **amphoteric character** in some metal hydroxides e.g.  $Al^{3+}$  and  $Cr^{3+}$
- the effect a ligand has on the **stability of an oxidation state**

#### **Amphoteric character**

Metal ions of 3+ charge have a **high charge density** and their hydroxides can dissolve in both acid and alkali.