**3.2.6 Reactions of ions in aqueous solution**

**AS & A Level Link:**

**3.1.6 – Equilibria**

**3.1.7 – Redox (oxidation states, oxidation, reduction, redox equations)**

**3.1.10 – Equilibrium constant**

**3.1.12 – Acids & bases**

**3.2.5 – Transition metals**

**Hydration of metal ions**

**Dissolving** a **salt** of a **transition metal** in **water** will result in the water molecules acting as **ligands**. They use a **lone pair of electrons** to form **co-ordinate bonds** with the metal ion and a **complex ion** is formed called a **metal-aqua ion**.

Six water molecules will surround a metal ion forming an octahedral shaped complex.

**Example CGP159**

|  |  |  |
| --- | --- | --- |
| Copper(II)  [Cu(H2O)6]2+ | Iron(II)  [Fe(H2O)6]2+ | Aluminium  [Al(H2O)6]3+ |
| Image result for hexa aqua copper ion |  |  |

**Acidity of metal-aqua ions**

Reminder – Brønsted-Lowry acids and bases:

* Acid – proton donor
* Base – proton acceptor

Another theory developed by Gilbert **Lewis** is also use to describe acids and bases.

***Definition***

**Lewis acid** is an electron pair **acceptor**

**Lewis base** is an electron pair **donor**

The **donor pair** of electrons **forms a co-ordinate** (dative) covalent bond, e.g.

H+ + OH- → H2O

H+ + **-** **˸**O-H → H←O-H

A **water** molecule has **two lone pairs** of electrons and it can use one of them to **accept** a **proton** (acting as a Lewis base and a Brønsted-Lowry base).

H2O + H+ → H3O+

Lewis Lewis

base acid

Another example is the reaction between **boron trifluoride** and **ammonia**:

BF3 + NH3 → [F3B ← NH3]

Lewis Lewis

acid base

In **BF3** there are **3 electrons from boron** plus **3 from the fluorines**, this give a **total**

**of 6**, so it is clearly **electron deficient** and can **accept** a further **2 electrons**. **Ammonia** has a **lone** **pair** of electrons which it can **donate**.

**Boron trifluoride** acts as a **Lewis acid** and **ammonia** as a **Lewis base**. This illustrates that the **Lewis definition is wider** than the Brønsted-Lowry definition. Boron trifluoride contains no protons so cannot be an acid under the Brønsted-Lowry definition. Hydrogen ions have no electrons so they can only form a bond by accepting an electron pair.

In transition metal chemistry:

* **ligands are Lewis bases**
* **metal cations are Lewis acids**.

Hydrolysis or acidity reactions

Consider a hexaaqua ion, **[M(H2O)6]n+**

|  |  |
| --- | --- |
| ***Task: Which bonds could break?***  O-H covalent bond – acidity reaction or hydrolysis  O-M co-ordinate bond – ligand substitution |  |

The only reaction that occurs **without breaking** these bonds is a **redox** reaction, where there is a loss or gain of an electron.

[M(H2O)6]2+ → [M(H2O)6]3+ + e-

In solution metal aqua ion complexes **release hydrogen ions** forming an **acidic solution**.

**Example CGP160**

Metal-aqua 2+ ion:

[Fe(H2O)6]2+(aq) + H2O(l) [Fe(H2O)5(OH)]+(aq) + H3O+(aq)

Metal-aqua 3+ ions react in the same way:

[Al(H2O)6]3+(aq) + H2O(l) [Al(H2O)5(OH)]2+(aq) + H3O+(aq)

An **equilibrium** is set up when a metal aqua ion is placed in water, where a **O-H bond breaks** in a water molecule co-ordinated to the metal ion, forming an **hydronium ion**.

[M(H2O)6]n+ + H2O [M(H2O)5(OH)](n-1)+ + H3O+

acid

This is called **hydrolysis** because a **water** molecule has **split** into **H+** and **OH-**. It’s also called an **acidity reaction** because hydrolysis leads to the **formation** of **H3O+** ions.

**Relative acidity of 2+ and 3+ metal-aqua ions**

With metal-aqua ions the **equilibrium** lies very much to the **LHS**, so it is only **slightly acidic**. The **degree of acidity** is measured by the **magnitude** of the **acid dissociation constant** (Ka). For the above equilibrium, the **acid dissociation** constant or **acid constant** is:

Ka = [M(H2O)5(OH)](n-1)+][H3O+]

[M(H2O)6]n+] [H2O]

For **metal(II)** ions **Ka** valuesarebetween **10-6** and **10-11** showing the **equilibrium** lies **far** to the **left**.

For **metal(III**) ions the **equilibrium** lies **further to the right** giving **Ka** between **10-2** and **10-5,** which is still **weakly acidic** but **stronger than metal(II)** aqua ions.

Two factors decide the **acidity of metal ions**:

* **Charge** on the metal ion **acidity increases with charge**
* **Size** of the metal ion **acidity decreases as size increases**

The **charge-to-size ratio** or **charge density** can be used to predict the **relative acidity** of metal ions. Small **highly charged cations** are the **strongest acids** in aqueous solutions. The ratio reflects the **polarising power** (the ability of a metal ion to attract electron density from a covalent bond).

|  |  |
| --- | --- |
|  | Ions with a **3+** charge are **small** and **highly charged** compared to 2+ metal ions, making them **more strongly polarising**.  They will therefore **attract electrons** from the oxygen atoms in the co-ordinated water molecules making the **O-H bond weaken**.  Hydrogen ions are more likely to be released making a **more acidic solution**. |

|  |  |  |
| --- | --- | --- |
| This can be summarised: | |  |
|  | |
| [M(H2O)6]2+  **smaller charge density**  larger ion  less charge  less polarising  very weak acids  pH ~6 | [M(H2O)6]3+  **greater charge density**  smaller ion  greater charge  strongly polarising  weak acids  pH ~ 3 |
| [Fe(H2O)6]2+  pH ~5 | [Fe(H2O)6]3+  pH ~ 2/3 |  |

***Demo: pH of transition metal solutions***

Further hydrolysis

**Further hydrolysis** can occur with the other co-ordinated water molecules if a **base** (such as OH-) is added; these **react** with the **hydronium ions**.

When **OH- ions** are added, they **attack** the **strongest acid**, which is **H3O+**.

OH- + H3O+ → 2H2O

The equilibrium **opposes** this and **shifts** to the **right**.

[M(H2O)6]n+ + H2O [M(H2O)5(OH)](n-1)+ + H3O+

A new equilibrium is now set up:

[M(H2O)5(OH)](n-1)+ + H2O [M(H2O)4(OH)2](n-2)+ + H3O+

Again hydroxide ions will react with the hydronium ions pushing the equilibrium to the right.

This is illustrated below for the metal(II) and metal(III) aqua ions.

**Metal(II) ions complete hydrolysis:**

The **neutral metal(II) hydroxide**, M(H2O)4(OH)2, is in effect M(OH)2, which is uncharged and **insoluble** so forms a **precipitate**. The overall equation is:

**Metal(III) ions complete hydrolysis:**

The reaction are the same except it occurs three times.

The **neutral metal(III) hydroxide**, M(H2O)3(OH)3, is in effect M(OH)3, which is uncharged and **insoluble** so forms a **precipitate**. The overall equation is:

The final metal hydroxide has **little hydration energy** to **overcome** the **lattice energy** so they always appear as **precipitates**. All **transition metals hydroxides** are **insoluble** in water and are **formed** **when a base** (e.g. NaOH or NH3) is **added** to a solution of metal ions.

**Example**

If **iron(III) nitrate nonahydrate**, Fe(NO3)2.9H2O (pale violet solid) is added to water a **brown solution** forms. It contains the **very pale violet hexaaqua ion** [Fe(H2O)6]3+ but the **colour indicates** that it’s **undergoing hydrolysis**. The brown colour of this ion is more intense than the hexaaqua ion so this is the only colour that is seen. However, the **equilibrium** still lies **far to the left**.

[Fe(H2O)6]3+(aq) + H2O(l) [Fe(H2O)5(OH)]2+(aq) + H3O+(aq)

very pale violet solution brown solution

Adding hydroxide ions produces a brown precipitate of Fe(OH)3:

[Fe(H2O)5(OH)]2+(aq) + H2O(l) [Fe(H2O)4(OH)2]+(aq) + H3O+(aq)

[Fe(H2O)4(OH)2]2+(aq) + H2O(l) **[Fe(H2O)3(OH)3](s)** + H3O+(aq)

brown precipitate

These reactions can be **reversed** with the **addition** of an **acid**.

***Demo: Equilibrium of iron(III) nitrate nonahydrate – addition of NaOH & nitric acid***

|  |  |
| --- | --- |
| **Addition of acid e.g. nitric** | **Addition of base e.g. sodium hydroxide** |
| Brown colour disappears  Almost colourless (very pale violet) solution appears | Solution turns darker brown  Eventually a brown precipitate (Fe(OH)3) appears  (the next stages of hydrolysis occur) |
| Equilibrium moves to the left to remove excess acid | Equilibrium moves to the right as the base reacts with the H3O+ ions |

**Hydrolysis reactions of aqua ions with bases**

* Sodium hydroxide
* Ammonia solution
* Sodium carbonate

Sodium hydroxide - adding sodium hydroxide always gives a **precipitate** ofthe **metal hydroxide**.

***Demo: Reactions of aqua ion with bases – addition of NaOH***

The following reaction with the aqua ions take place as the hydroxide ions react with hydrogen ions from the water ligands:

[M(H2O)6]2+(aq) + **2**OH-(aq) → **[M(H2O)4(OH)2](s)** + **2**H2O(l)

[M(H2O)6]3+(aq) + **3**OH-(aq) → **[M(H2O)3(OH)3](s)** + **3**H2O(l)

**Copper(II) aqua-ion**

Major species: [Cu(H2O)6]2+(aq)

Minor species: [Cu(H2O)5(OH)]+(aq) + H3O+

As **hydroxide ions are added**, further **H3O+ are removed** and **blue** copper(II) hydroxide **precipitates**.

[Cu(H2O)6]2+(aq) + **2**OH-(aq) [Cu(OH)2(H2O)4](s) + **2**H2O(l)

blue soln blue ppt

|  |  |
| --- | --- |
|  | DSCF3832 |

The same sequence of reactions occurs with **other metal ions**.

**Iron(II) aqua-ion**

[Fe(H2O)6]2+(aq) + **2**OH-(aq ) [Fe(H2O)4(OH)2](s) + **2**H2O(l)

green soln green ppt

|  |  |
| --- | --- |
|  | DSCF3847 |

The **green precipitate** of **iron(II)hydroxide** can be **oxidised** by oxygen in the air to give the **brown precipitate** of **iron(III) hydroxide**.

[Fe(H2O)4(OH)2](s) → [Fe(H2O)3(OH)3](s) + e-

Fe2+ → Fe3+ + e-

**Cobalt(II) aqua-ion**

[Co(H2O)6]2+(aq) + **2**OH-(aq) [Co(H2O)4(OH)2](s) + **2**H2O(l)

pink soln blue ppt

|  |  |
| --- | --- |
|  | http://2.bp.blogspot.com/_h9k4A8uEVsU/TP7pJ4GWs4I/AAAAAAAAAVs/6S6dnliH7ic/s1600/transition%2Bion%2Bsolutions.pngImage result for cobalt  hydroxide in test tube |

**Iron(III) aqua-ion**

[Fe(H2O)6]3+(aq) + **3**OH-(aq) [Fe(H2O)3(OH)3](s) + **3**H2O(l)

purple soln brown ppt

(appears yellow-brown due to hydrolysis) (may appear orange-brown)

|  |  |
| --- | --- |
|  | DSCF3855 |

**Aluminium(III) aqua-ion**

[Al(H2O)6]3+(aq) + **3**OH-(aq) [Al(H2O)3(OH)3](s) + **3**H2O(l)

colourless soln white ppt

|  |  |
| --- | --- |
|  | Image result for colourless solution in tets tube |

Aqueous ammonia – adding ammonia solution always gives a **precipitate** of the **metal hydroxide initially**.

If **excess** is added **ammonia** **acts** as a **ligand** and **substitution** reactions occur with some of these metal complexes resulting in a **solution** being produced. See Topic 3.2.5.

The same sequence of reactions takes place with ammonia solution as with sodium hydroxide. When **ammonia** **dissolves** in water it can **accept protons** from the water molecules forming **ammonium ions** and **hydroxide ligands**.

NH3(g) + H2O(l) → NH4+(aq) + OH-(aq)

The following reaction with the aqua ions can then take place:

[M(H2O)6]2+(aq) + **2**NH3(aq) → **[M(H2O)4(OH)2](s)** + **2**NH4+(aq)

[M(H2O)6]3+(aq) + **3**NH3(aq) → **[M(H2O)3(OH)3](s)** + 3NH4+(aq)

**Reactions and colours are the same as with sodium hydroxide:**

***Demo: Reactions of aqua ion with bases – addition of NH3(aq)***

**Copper(II) aqua-ion**

|  |  |
| --- | --- |
|  | DSCF3832 |

**Iron(II) aqua-ion**

|  |  |
| --- | --- |
|  | DSCF3847 |

**Cobalt(II) aqua-ion**

|  |  |
| --- | --- |
|  | http://2.bp.blogspot.com/_h9k4A8uEVsU/TP7pJ4GWs4I/AAAAAAAAAVs/6S6dnliH7ic/s1600/transition%2Bion%2Bsolutions.pngImage result for cobalt  hydroxide in test tube |

**Iron(III) aqua-ion**

|  |  |
| --- | --- |
|  | DSCF3855 |

**Aluminium(III) aqua-ion**

|  |  |
| --- | --- |
|  | Image result for colourless solution in tets tube |

***Starter: 14.2 – Brønsted-Lowry or Lewis base?***

Carbonate ions – addition of sodium carbonate solution always results in a **precipitate** of the **metal(II) carbonate** or the **metal(III) hydroxide** with **carbon dioxide**.

**Metal(II) ions** are **insufficiently acidic** to displace carbonic acid from carbonates, so the ions form **insoluble metal(II) carbonates**, MCO3(s). **No carbon dioxide** is produced.

The following reaction occurs:

[M(H2O)6]2+(aq) + CO32-(aq) → **MCO3(s)** + 6H2O(l)

**The following reactions occur:**

***Demo: Reactions of aqua metal(II) ions with bases – addition of Na2CO3(aq)***

|  |  |
| --- | --- |
| **Copper(II) aqua-ion**    [Cu(H2O)6]2+(aq) + CO32-(aq) → CuCO3(s) + 6H2O(l)  blue soln blue-green ppt | DSCF3835 |

|  |  |
| --- | --- |
| **Iron(II) aqua-ion**  [Fe(H2O)6]2+(aq) + CO32-(aq) → FeCO3(s) + 6H2O(l)  green soln green ppt | DSCF3849 |

|  |  |  |
| --- | --- | --- |
| **Cobalt(II) aqua-ion**  [Co(H2O)6]2+(aq) + CO32-(aq) → CoCO3(s) + 6H2O(l)  pink soln purple ppt | http://2.bp.blogspot.com/_h9k4A8uEVsU/TP7pJ4GWs4I/AAAAAAAAAVs/6S6dnliH7ic/s1600/transition%2Bion%2Bsolutions.png | DSCF3844 |

**Metal(III) ion complexes** are **more acidic** and so carbonate ions react with them to form the **hydrogencarbonate** **ion** then **carbonic acid** (H2CO3), which rapidly becomes **carbon dioxide** and **water**. Effervescence is best observed with solid Na2CO3.

CO32- + H3O+ HCO3- + H2O

HCO3- + H3O+ CO2 + 2H2O

The following reaction occurs resulting in **effervescence** of **carbon dioxide** and **precipitation** of the **metal(III) hydroxide**.

2[M(H2O)6]3+(aq) + 3CO32-(aq) → **2[M(H2O)3(OH)3](s)** + 3CO2(g) + 3H2O(l)

As a result **metal(III) carbonates** **can’t be prepared** in **aqueous solution** and so they **don’t** **exist**, hydroxides form each time. For example, Al2(CO3)3, Fe2(CO3)3, Cr2(CO3)3 can’t be prepared in aqueous solutions and so are unknown.

**The following reactions occur and effervescence is seen.**

***Demo: Reactions of aqua metal(III) ions with bases – addition of Na2CO3(aq) & Na2CO3(s)***

**Iron(III) aqua-ion**

|  |  |
| --- | --- |
| 2[Fe(H2O)6]3+(aq) + 3CO32-(aq) 2[Fe(H2O)3(OH)3](s) + **3CO2**(g) + 3H2O(l)  purple soln brown ppt  (appears yellow-brown due to hydrolysis) (may appear orange-brown) | |
|  | DSCF3858 |

**Aluminium(III) aqua-ion**

|  |  |
| --- | --- |
| 2[Al(H2O)6]3+(aq) + 3CO32-(aq) 2[Al(H2O)3(OH)3](s) + **3CO2**(g) + 3H2O(l)  colourless soln white ppt | |
|  | Image result for colourless solution in tets tube |

***Starter: 14.1 – Acid-base chemistry***

***Starter: 14.4 – Inference from aqueous tests***

**Amphoteric character**

***Definition***

**Amphoteric** means showing **both** **acidic** and **basic** properties.

An amphoteric substance will react with both an acid and a base.

**The general scheme for metal(III) ions is:**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [M(H2O)6]3+(aq) |  | [M(H2O)3(OH)3](s) |  | [M(H2O)2(OH)4]-(aq) |
| in acidic solution |  | in neutral solution |  | in alkaline solution |

***Demo: Amphoteric behaviour aluminium chloride solution with HCl & NaOH***

**Example CGP161**

Aluminium hydroxide is amphoteric. It can act as a Brønsted-Lowry acid and donates hydrogen ions.

[Al(H2O)3(OH)3](s) + OH-(aq) [Al (H2O)2(OH)4]-(aq) + H2O(l)

It can also act as a Brønsted-Lowry base accepting hydrogen ions.

[Al(H2O)3(OH)3] (s) + 3H+(aq) [Al(H2O)6]3+(aq)

Both reactions are summarised:

|  |
| --- |
|  |
| DSCF3851 |

**Summary**

***Sheet: AQA Reactions of metal ions in aqueous solution***

Colours of the transition metal salts in water

Mostly due to the **colours of the aqua ions**.

|  |  |  |  |
| --- | --- | --- | --- |
| **Complex** | **Colour** |  |  |
| [Cu(H2O)6]2+(aq) | **blue solution** |  |
| [Co(H2O)6]2+(aq) | **pink**  **solution** |  |
| [Fe(H2O)6]2+(aq) | **green solution** |  |
| [Fe(H2O)6]3+(aq) | **purple solution\*** | **pale brown**  **(straw)** |
| [Al(H2O)6]3+(aq) | **colourless**  **solution** |  |

\*Hydrolysis occurs and gives a different coloured solution

Metal(II) ions reactions

**[M(H2O)6]2+(aq)**

**OH- / NH3**

**H+**

**[Cu(H2O)6]2+(aq)**

**[Co(H2O)6]2+(aq)**

**[Fe(H2O)6]2+(aq)**

**[Cu(H2O)2(NH3)4]2+(aq)**

**[Co(NH3)6]2+(aq)**

**Cl-**

**CO32-**

**CuCO3 (s)**

**CoCO3 (s)**

**FeCO3 (s)**

**XS NH3**

**ligand**

**substitution**

**acid/base**

**hydrolysis**

**precipitation**

**[M(H2O)4(OH)2](s)**

**[Cu(H2O)6(OH)2](s)**

**[Co(H2O)6 (OH)2](s)**

**[Fe(H2O)6 (OH)2](s)**

**XS OH-**

**no reaction**

**[MCO3](s)**

**[CuCl4]2-(aq)**

**[CoCl4]2- (aq)**

**[MCl4]2-(aq)**

Metal(III) ions reactions

***Sheet: Summary of aqueous metal ion reactions***

**Tests to identify metal ions**

**Test tube reactions** provide a **qualitative** way of working out the **identity** of **unknown metal** **ions** in solution. By adding different reagents to separate samples of a metal ions solution will produce coloured solutions or precipitates. **Recording** these **observations** allows the metal ions to be identified.

**Describing observations- be specific for colour and state:**

* Colour
* States e.g. precipitate (ppt) or solution (aq)
* Describe change e.g. re-dissolving or no visible change or precipitate remains.

***Required practical 11***: Carry out simple test tube reactions to identify the metal ions in aqueous solutions

***Sheet: Reactions of inorganic complex ions exam questions***

***Application: CGP164 PQ1***

***Fact recall: CGP164 Q1-5***

***Exam questions: Oxford p130-131 Q1-4***