



Salt Hydrolysis

To succeed in this topic you need to understand:

- bonding (covered in Factsheet 5);
- the Brønsted-Lowry theory of acids and bases (covered in Factsheet 25);
- the pH scale of acidity and alkalinity (covered in Factsheet 25);
- complex ion formation (covered in Factsheet 38).

After working through this Factsheet you will:

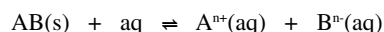
- know that there are two ways in which ions can become hydrated;
- understand why salts derived from a weak acid and a strong base are alkaline in solution;
- understand why salts derived from a strong acid and a weak base are acidic in solution;
- understand why salts derived from a strong acid and a strong base are neutral in solution;
- understand why salts derived from a weak acid and a weak base are approximately neutral in solution.

Hydration of ions

Before you can understand the topic of salt hydrolysis, you need to know about the hydration of ions in aqueous solution.

Remember - Hydration is defined as 'combination with water'.

When a salt dissolves in water, it *dissociates*, i.e. its ions break away from their regular arrangement in the crystal and become free to move about in the water. For a salt $A^{n+} B^n$, this is represented by the equation:



The equation is written with two half-arrows because the change is reversible. The reverse change, i.e. the joining together of ions from solution to give the crystalline solid, occurs during crystallisation.

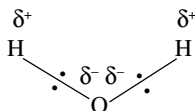
Exam Hint - Do not refer to dissociation in this context as 'ionisation'. **Ionisation** means, literally, 'ion formation', but all that happens here is the separation of ions which are already present in the crystal.

Ions exist in solution, not as simple ions, but as *hydrated ions*, i.e. surrounded by shells of water molecules: hence the symbols $A^{n+}(aq)$ and $B^n(aq)$ in the above equation.

Why do ions become hydrated?

There are two causes.

1. Common to *all* ions is an effect known as *ion-dipole attraction*. The water molecule is a *dipole*; literally, one with two electrical poles. Because oxygen is more electronegative than hydrogen, the electron pair of each O-H bond is drawn towards the oxygen atom. Consequently, it acquires a slight negative charge, while each hydrogen atom has a slight positive charge:

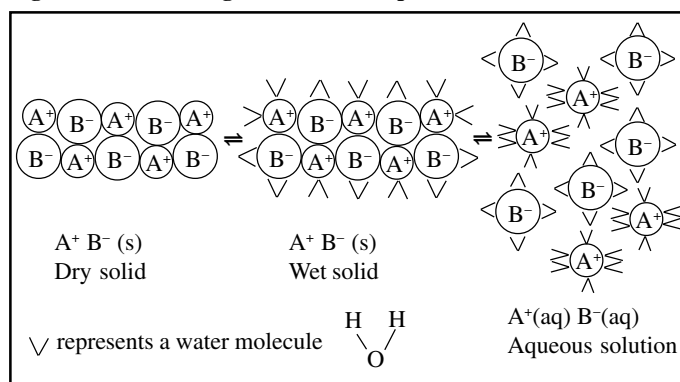


Remember

- δ^- represents a small amount of negative charge which is unspecified but less than the charge on an electron. (Conversely for δ^+ .)
- The molecule as a whole is electrically neutral.

Negatively charged oxygen atoms are attracted to cations, and positively charged hydrogen atoms to anions (Fig 1). There are approximately six water molecules in the primary (i.e. first) hydration shell.

Fig 1. The dissolving of an ionic compound $A^+ B^-$ in water



Anions, such as CO_3^{2-} , Cl^- , SO_4^{2-} and NO_3^- , are hydrated by ion-dipole attraction only. The same applies to all cations of the s-block elements, except for Be^{2+} .

2. For all other cations, notably Al^{3+} and cations of the transition elements, ion-dipole attraction is reinforced by coordination, i.e. the formation of coordinate bonds (dative covalent bonds) between H_2O molecules and the cation. The reason is that these cations are relatively small and have a charge of at least $2+$. They therefore have a high *surface charge density*, i.e. high density of positive charge on the surface. (Some people say that they have a high charge:radius ratio.)

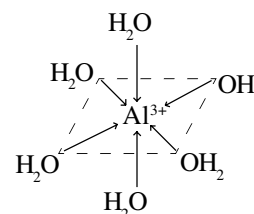
Exam Hint - The term 'surface charge density' refers only to ions. Never apply it to atoms or molecules, because such particles are uncharged and cannot possibly have a charge density.

Any cation with a high surface charge density attracts a lone pair of electrons from the outer shell of the oxygen atom of a water molecule so strongly that the lone pair can be donated from one to the other so that a coordinate bond is formed.


Remember - A coordinate bond is a special kind of covalent bond, in which both electrons of the bond originate from one atom. Once formed, a coordinate bond is identical with a covalent bond.

Generally, as for Al^{3+} , six H_2O molecules are coordinated to a cation so that an octahedral complex is formed.

The hydrated Al^{3+} ion

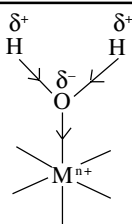


Because cations that are hydrated by coordination are complex ions, they can be given formulae and names on the IUPAC system: indeed, to understand the chemistry of salt hydrolysis, this is vital. The hydrated aluminium ion, for example, often represented by the symbol $\text{Al}^{3+}(\text{aq})$, has the formula $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ and is named systematically as the hexaaquaaluminium(III) ion.

 An important difference between ions that are hydrated by ion-dipole attraction only, and those where the attraction is reinforced by coordination, is that the latter are acids on the Brønsted-Lowry theory, i.e. they are proton donors.

The high surface charge density on the cation causes the electrons of the metal-oxygen bond to be drawn towards the metal. This in turn increases polarisation of the O-H bonds (Fig 2).

Fig 2. Electron shifts in a complex aqua-cation




This causes weakening of the O-H bonds. You can argue that H atoms become more like protons and hence more easily lost as protons in the presence of a base, i.e. a proton acceptor.

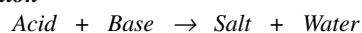
Remember - On the Brønsted-Lowry theory:

- an acid is a species (molecule or ion) that can donate protons.
- a base is a species that can accept protons.
- neutralisation is a process of proton transfer from acid to base.
- every acid is related to a conjugate base, i.e. the species formed from it by loss of a proton. For most acids, this is the anion produced on ionisation.
- every base is related to a conjugate acid, i.e. the species formed from it by gain of a proton.

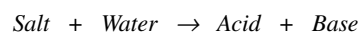
Salt hydrolysis

 Salt hydrolysis is essentially the reverse of neutralisation.

Neutralisation



Salt hydrolysis



Both acids and bases can be classed as strong or weak, depending upon their degree of dissociation in water. Salts can therefore be divided into four broad categories.

Salts derived from a weak acid and a strong base

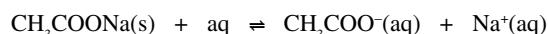
Such salts undergo partial hydrolysis to give an alkaline solution. An example is sodium ethanoate, which is derived from ethanoic acid (a weak acid) and sodium hydroxide (a strong base).

Practical 1 - Hydrolysis of sodium ethanoate

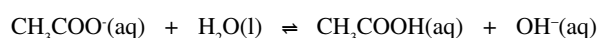
Dissolve a few crystals of sodium ethanoate in water at room temperature and measure the pH of the solution with a pH meter, pH paper or universal indicator.

Note In all Practicals in the Factsheet it is advisable to use freshly deionised water or, failing that, freshly drawn tap water. Water that has been standing is likely to be slightly acidic due to the absorption of CO_2 from the air.

Sodium ethanoate dissociates in solution:



CH_3COOH is a weak acid (proton donor); therefore its anion, CH_3COO^- , is a strong conjugate base (proton acceptor). This causes ethanoate ions to accept protons from water molecules:



Consequently, $[\text{OH}^-] > [\text{H}_3\text{O}^+]$, i.e. the solution is alkaline.

Ignore $\text{Na}^+(\text{aq})$. This cation is hydrated by ion-dipole attraction only and is neither an acid nor a base.

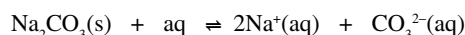
Remember - Opposites go together:

- A strong acid is related to a weak conjugate base, e.g. HCl & Cl^- .
- A weak acid is related to a strong conjugate base, e.g. CH_3COOH & CH_3COO^- .
- A strong base is related to a weak conjugate acid, e.g. OH^- & H_2O .
- A weak base is related to a strong conjugate acid, e.g. NH_3 & NH_4^+ .

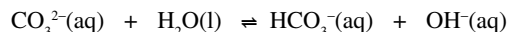
Practical 2 - Hydrolysis of sodium carbonate and sodium hydrogencarbonate

Dissolve small amounts of sodium carbonate and sodium hydrogencarbonate separately in water. Measure the pH value of each solution and try to account for the difference.

Sodium carbonate dissociates:



The carbonate ion is the conjugate base of an extremely weak acid (carbonic acid). It strongly attracts protons from H_2O molecules to give a solution with a pH of ~12:



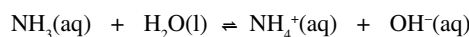
In contrast, the hydrogencarbonate ion, with its single negative charge, has a lower surface charge density than the carbonate ion and is a considerably weaker base. It exerts a feeble attraction for protons and the pH of the solution only reaches ~8.5.

Exam Hint - Beware of questions in which you are asked how, in the laboratory, you would distinguish between Na_2CO_3 and NaHCO_3 . If you are allowed to use any test, measuring the pH values of their solutions provides a good answer. If, however, you are asked for a chemical test, this will not do. For such a question you'd need to suggest a reagent such as magnesium sulphate solution. This would give a white precipitate of MgCO_3 with $\text{CO}_3^{2-}(\text{aq})$, but no precipitate with $\text{HCO}_3^-(\text{aq})$ because magnesium hydrogencarbonate is soluble in water.

Salts derived from a strong acid and a weak base

All such salts undergo partial hydrolysis to give an acidic solution. However, for study purposes, you must distinguish between two kinds of weak bases.

- Weak covalent bases, e.g. ammonia and amines. Despite being very soluble in water, such compounds give a low concentration of OH⁻ ions in solution because of a low degree of ionisation:



- Weak ionic bases, e.g. aluminium hydroxide and transition metal hydroxides. Like ammonia and the amines, these compounds give a low concentration of OH⁻ ions in solution but for a very different reason, namely their low solubility in water.

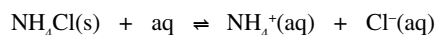
Salts derived from a strong acid and a weak covalent base

An example is ammonium chloride, which is derived from hydrochloric acid (a strong acid) and ammonia (a weak base).

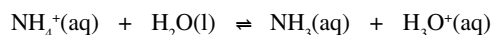
Practical 3 - Hydrolysis of ammonium chloride

Dissolve a few crystals of ammonium chloride in water and measure the pH of the solution.

Ammonium chloride dissociates in solution:



NH₃ is a weak base; therefore its related cation, NH₄⁺, is a strong conjugate acid which can donate a proton to a water molecule:



Consequently, [H₃O⁺] > [OH⁻], i.e. the solution is acidic.

Ignore Cl⁻(aq). This is the conjugate base of an extremely strong acid (HCl) and is therefore an extremely weak base.

Remember - For all practical purposes, HCl, HBr, HI, H₂SO₄ and HNO₃ are almost completely dissociated in aqueous solution.

Salts derived from a strong acid and a weak ionic base

An example is aluminium chloride, which is derived from hydrochloric acid and aluminium hydroxide.

Practical 4 Hydrolysis of aluminium chloride

Dissolve in water a few crystals of aluminium chloride-6-water and measure the pH of the solution.

The salt dissociates in solution:



As explained on p 2, the hydrated aluminium ion is an acid on the Brønsted-Lowry theory. One of its coordinated water molecules ionises into H⁺ and OH⁻. OH⁻ stays where it is, i.e. bonded to aluminium, but H⁺ (a proton) is donated to a molecule of solvent water:



Consequently, [H₃O⁺] > [OH⁻], i.e. the solution is acidic.

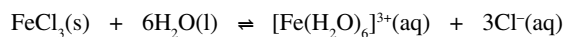
Again, Cl⁻(aq) should be disregarded for the reason given above.

Exam Hint - When writing the formulae of complex ions containing different sorts of ligands, ionic ligands (e.g. OH⁻) should be written before molecular ligands, (e.g. H₂O).

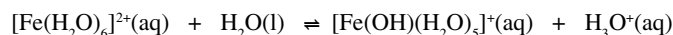
Practical 5 - Hydrolysis of iron(II) chloride and iron(III) chloride

Dissolve small amounts of iron(II) chloride and iron(III) chloride separately in water. Measure the pH of each solution and try to account for the difference.

Both salts dissociate in solution to give hexaaquacations:



Like [Al(H₂O)₆]³⁺, both hydrated cations are acidic, e.g.



Compared with Fe²⁺, however, Fe³⁺ has a greater charge and a smaller radius. It therefore has a higher surface charge density than Fe²⁺ and causes more polarisation of the O-H bonds of coordinated H₂O molecules. Proton transfer to solvent H₂O molecules can therefore occur more readily and the solution has a lower pH.

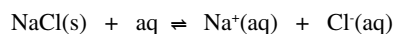
Salts derived from a strong acid and a strong base

Such salts do not undergo hydrolysis and their solutions are neutral. An example is sodium chloride, derived from hydrochloric acid and sodium hydroxide.

Practical 6 - Non-hydrolysis of sodium chloride

Dissolve a little sodium chloride in water and measure the pH of the solution.

Sodium chloride dissociates:



However, Na⁺(aq) is not an acid; neither is Cl⁻(aq) a base. There is therefore no proton transfer of any kind, i.e. no chemical reaction, and the pH of the solution is that of pure water (7.0).

Salts derived from a weak acid and a weak base

Again, for study purposes, you need to distinguish between weak covalent bases and weak ionic bases.

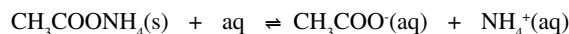
Salts derived from a weak acid and a weak covalent base

Such salts undergo extensive hydrolysis to give an approximately neutral solution. An example is ammonium ethanoate, derived from ethanoic acid and ammonia.

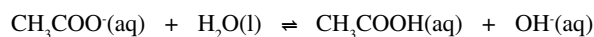
Practical 7 - Hydrolysis of ammonium ethanoate

Dissolve a little ammonium ethanoate in water and measure the pH of the solution.

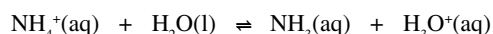
Ammonium ethanoate dissociates:



CH₃COO⁻(aq) is a base and accepts protons:



This change *by itself* would make the solution alkaline; but it is not the only reaction. NH₄⁺(aq) is an acid and donates protons:



This change tends to make the solution acidic. The two effects virtually cancel each other out, with the result that [H₃O⁺] ≈ [OH⁻], i.e. the solution is approximately neutral.

Salts derived from a weak acid and a weak ionic base

An example would be aluminium carbonate, derived from carbonic acid and aluminium hydroxide. Such salts are *completely* hydrolysed in the presence of water and, for this reason, are often said to be 'non-existent'.*

* This statement is debatable. Aluminium oxide is known to absorb carbon dioxide. Is aluminium carbonate formed? Possibly. But it is certain that such salts cannot exist in the presence of water.

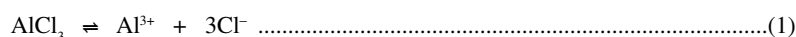
Remember

- Salt derived from a weak acid and a strong base
The base is dominant and the solution is alkaline (pH > 7.0)
- Salt derived from a strong acid and a weak base
The acid is dominant and the solution is acidic (pH < 7.0)
- Salt derived from a strong acid and a strong base
Neither acid nor base is dominant and the solution is neutral (pH = 7.0)
- Salt derived from a weak acid and a weak base
Neither acid nor base is dominant and the solution is more or less neutral (pH ≈ 7.0)

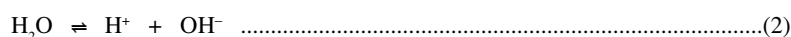
NOTE Although these rules of thumb are useful, they must never be used in an examination to explain salt hydrolysis.

Questions

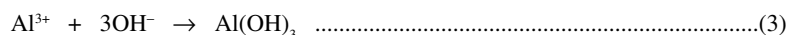
- 1 Explain why the hydrated beryllium ion, unlike other cations of the s-block elements, is a complex ion.
- 2 State whether you would expect each of the following salts to be acidic, alkaline or neutral in aqueous solution.
(a) CuSO₄ (b) NaNO₃ (c) KBr (d) ZnCl₂ (e) (NH₄)₂SO₄ (f) C₆H₅NH₃⁺Cl⁻ (g) Li₂CO₃
- 3 Unlike many other salts derived from a weak acid and a weak base, ammonium carbonate gives an alkaline solution. Explain this.
- 4 Unlike many other salts derived from a strong acid and a strong base, sodium hydrogensulphate gives a strongly acidic solution. Explain this.
- 5 "Aluminium chloride dissociates in solution to give aluminium ions and chloride ions:



Water ionises to a small extent into hydrogen ions and hydroxide ions:



Oppositely charged ions attract one another. H⁺ and Cl⁻ cannot join up to give molecules of HCl because HCl is a very strong acid and completely dissociated in solution, but Al³⁺ and OH⁻ ions can join together to give solid aluminium hydroxide:



This disturbs Equilibrium (2) to the right, so that more water ionises to replace the lost OH⁻ ions. In this way the solution contains many more hydrogen ions than hydroxide ions and is strongly acidic."

This extract from an old textbook contains one serious error of fact and one serious error of theory. What are they?

- 1 Be²⁺ is the smallest of the s-block cations. (Ionic radii decrease from left to right across the Periodic Table and also up the groups.) Be²⁺ therefore has the highest surface charge density and can attract lone pairs of electrons from the oxygen atoms of surrounding water molecules so that coordinate bonds are formed.
- 2 (a) Acidic (b) Neutral (c) Neutral (d) Acidic (e) Acidic (f) Acidic (g) Alkaline
- 3 Ammonium carbonate dissociates to give NH₄⁺(aq) and CO₃²⁻(aq) ions in solution. The former is an acid:
NH₄⁺(aq) + H₂O(l) ⇌ NH₃(aq) + H₃O⁺(aq) (Reaction 1)
and the latter is a base:
CO₃²⁻(aq) + H₂O(l) ⇌ HCO₃⁻(aq) + OH⁻(aq) (Reaction 2)
Although ammonia is a weak base, carbonic acid is an extremely weak acid. Hence the conjugate base CO₃²⁻ is stronger than the conjugate acid NH₄⁺, and Reaction 2 occurs to a greater extent than Reaction 1.
- 4 Sodium hydrogensulphate dissociates to give Na⁺(aq) and HSO₄⁻(aq) ions in solution. HSO₄⁻ is the conjugate base of H₂SO₄, a very strong acid, and is therefore an extremely weak base. However, because of its hydrogen atom, it can function as an acid:
HSO₄⁻(aq) + H₂O(l) ⇌ SO₄²⁻(aq) + H₃O⁺(aq)
The process is identical to the second stage in the ionisation of sulphuric acid.
- 5 **Error of fact** A solution of aluminium chloride is completely clear (i.e. transparent). It is not cloudy, as it would be if it contained particles of insoluble aluminium hydroxide. (Note A small amount of aluminium hydroxide is formed over a period of time if the solution is allowed to stand.)
Error of theory The aluminium ion in solution is not a simple ion, Al³⁺, but a hydrated complex ion, [Al(H₂O)₆]³⁺.

Answers