Aqueous Systems AS 91392

Demonstrate understanding of equilibrium principles in aqueous systems

Aqueous systems are limited to those involving sparingly soluble ionic solids

Equilibrium principles in aqueous systems are limited to qualitative descriptions and/or calculations involving:

- ❑ relative concentrations of dissolved species

- ❑ sparingly soluble ionic solids

  - – relating solubility to K_s

  - – solubility of solids in water and in solutions already containing one of the ions A or B (a common ion) or due to the formation of a complex ion, or the reaction of a basic anion with added acid

  - – predicting precipitation or dissolution

Sparingly soluble ionic solids are limited to AB, A_2B and AB_2 types where neither of the ions A nor B reacts further with water.

Aqueous systems are limited to those involving acidic and basic solutions (in which proton transfer occurs).

- ❑ acidic and basic solutions (includes buffers)

  - – acid/base strength, K_a (pK_a)

  - – concentration of species present in weak acidic and/or basic solutions (includes buffers)

  - – relating concentration of species to pH and conductivity

  - – Titration curves to represent an acid-base system including selection of indicators (titrations of weak acids with weak bases are excluded).

Acidic and basic solutions are monoprotic acids, bases, salts, and buffers (those in which the extent of reaction is small so that the equilibrium concentration of a dissolved weak acid or base can be approximated by the initial concentration).

Candidates are expected to recognise common strong acids (HCl, HBr, HNO_3, H_2SO_4); strong bases (KOH, NaOH); weak acids (HF, CH_3COOH, and NH_4^+); weak bases (NH_3, CH_3NH_2, and CH_3COO^-). Less familiar weak acids and bases may be included in the context of appropriate resource information. Values of K_b or pK_b will not be provided, but may be derived and used in calculations. Knowledge of specific complex ions covered in Chemistry Level 2 AS91162 will be assumed. Less familiar complex ions may be included in the context of appropriate resource information.

Equilibrium

Equilibrium is a state of dynamic balance where the rates of formation of product = equals the rate of formation of reactants
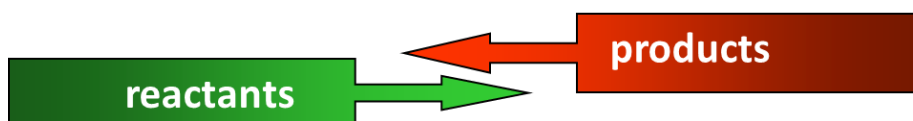
At equilibrium, the concentrations of reactants and products are constant. However, both the forward and reverse reactions are continuing

Some reactions go to completion
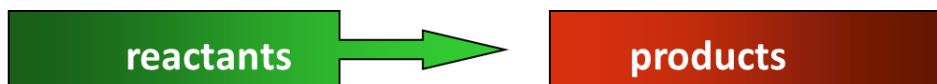
Reaction stops when one of the reactants is used up.

Other reactions are reversible:

Products are also forming reactants. Reaction continues

Solubility

The solubility of a substance is the amount of that substance that will dissolve in a given amount of solvent. Solubility is a quantitative term. Solubility varies depending on the solvent and the solute. The terms soluble and insoluble are relative. Some substances can be sparingly soluble where only a very small percentage dissolves. For a solute to dissolve the attraction to the solvent molecules must be stronger than the bonds holding the atoms/molecules of the solute together.
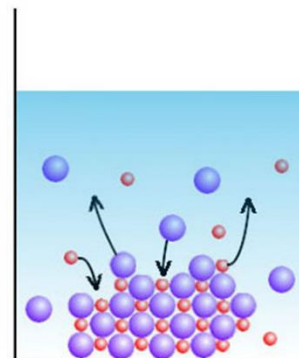
Equilibrium of solutions

A system reaches equilibrium when the rate the solid dissociates into ions matches the rate that the ions precipitate into solids. The equilibrium can be changed permanently by adjusting the system temperature (or temporarily - pressure or adding/removing reactants/product).
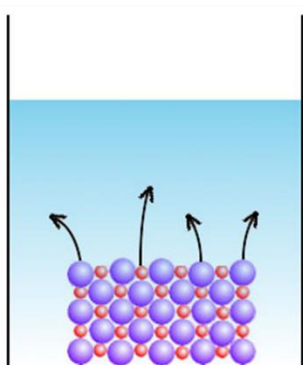
Salt is initially put into the water and begins dissolving.
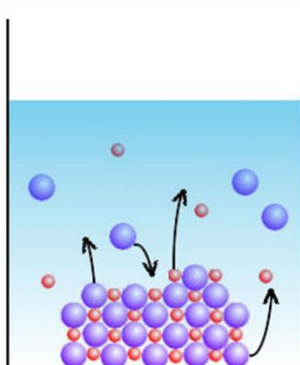
Salt continues to dissolve; however, dissolved ions will also precipitate. Because the salt dissolves faster than its ions precipitate, the net movement is towards dissolution.

Eventually, the rate of dissolution will equal the rate of precipitation. The solution will be in equilibrium, but the ions wil continue to dissolve and precipitate.

Sparingly Solubility

Many ionic salts are sparingly soluble in water. Even those that are commonly classified as insoluble still have a small amount of the solid dissolved in an aqueous solution so that when the solution is saturated an equilibrium exists between the dissolved ions and the insoluble solid.

The solubility of a salt is often measured in grams per litre, g L^{-1}, or moles per litre, mol L^{-1}. This is the number of grams or moles of the solid that will dissolve to make up 1 litre of a saturated solution at that temperature. If the solubility of a pure salt is given then it is possible to calculate the concentration of both the cation and anion in the solution.
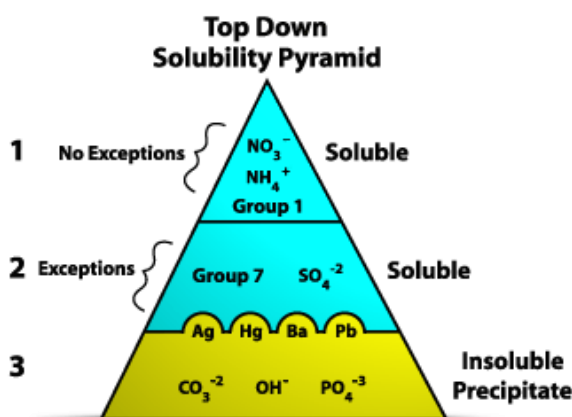

Sparingly Soluble Equilibrium Equations

When sparingly soluble ionic salts dissolve in water to form aqueous solutions, a small percentage of the salt dissociates into individual ions (anion and cation) in the same ratio that they exist as a solid salt.

Once the aqueous solution reaches equilibrium, the rate that the solid salt dissociates into the ions (breaking bonds holding solid together) is matched by the rate the ions reform ionic bonds and "reassemble" as an ionic solid in the solution.

NOTE: although we use an equation, dissolving is a physical change rather than a chemical reaction.

$$Ag_2CrO_{4(s)} \leftrightarrow 2Ag^+_{(aq)} + CrO_4^{2-}_{(aq)}$$
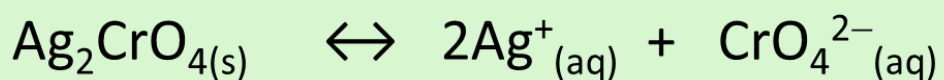
Water is not included in the equation because the very large concentration before and after means there is negligible change.

Solubility [s] and Concentration

[ ] indicates concentration
At room temperature the solubility of silver chromate, Ag_2CrO_4, is 6.5×10^{-5} mol L^{-1}.

What is the concentration of Ag^+ and CrO_4^{2-} ions [s] in 500 mL of a saturated solution?

Start with the equation for the dissolving process.

$$Ag_2CrO_{4(s)} \leftrightharpoons 2Ag^+_{(aq)} + CrO_4^{2-}_{(aq)}$$
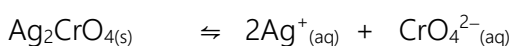
The equation shows that for every mole of dissolved solid there are 2 moles of Ag^+ ions and 1 mole of CrO_4^{2-} ions. Therefore

$[Ag^+] = 2 \times 6.5 \times 10^{-5} = 1.3 \times 10^{-9}$ mol L^{-1}

$[CrO_4^{2-}] = 6.5 \times 10^{-5}$ mol L^{-1}

Note: that because the calculation involves concentration it does not matter that the sample is a 500 mL sample rather than a litre sample since the concentration in any volume of saturated solution is always 6.5×10^{-5} mol L^{-1} (at room temperature).

Solubility from molL^{-1} to gL^{-1}

Example question: What is the solubility [s] of Ag$_2$CrO$_4$ in g L^{-1}?

To convert from moles per litre to grams per litre it is necessary to use the molar mass M(Ag$_2$CrO$_4$) = 332 g mol^{-1} and the relationship m = n x M.
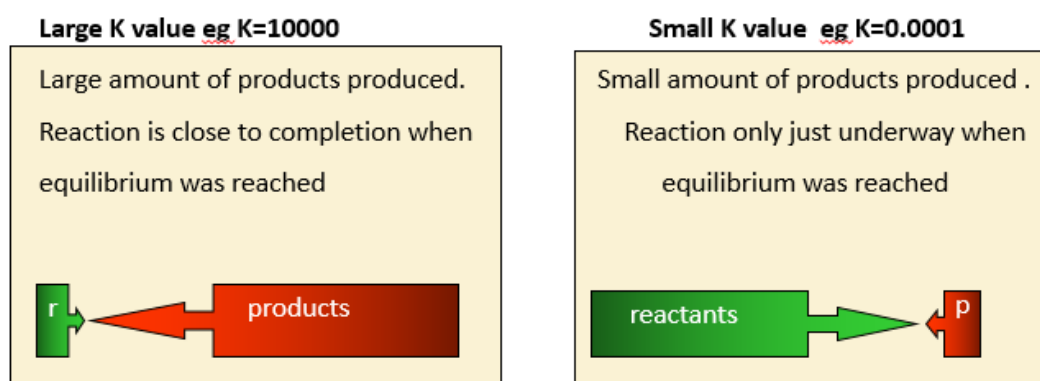
s= 6.5×10^{-5} mol L^{-1}.

Since there is 6.5×10^{-5} moles in 1 litre the number of grams in 1 litre would be

mass = $6.5 \times 10^{-5} \times 332$ = 0.0216 grams and the concentration is 0.0216 g L^{-1}.

Equilibrium Constant: K$_C$

The size of K calculated gives information as to how far a reaction has proceeded

Large K value eg K=10000

Large amount of products produced.

Reaction is close to completion when equilibrium was reached

r ← products

Small K value eg K=0.0001

Small amount of products produced .

Reaction only just underway when equilibrium was reached

reactants → p

Note: equilibrium does not mean there are equal amounts of reactants and products present

An equilibrium equation can be written as an expression (K$_c$) in which concentrations of products and reactants can be placed in to give us a value. The value will indication the proportion of reactants to products in any given reaction.

Given aA + bB ⇌ cC + dD

e.g. N$_2$(g) + 3H$_2$(g) ⇌ 2NH$_3$(g)
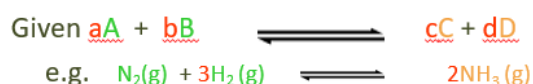
$$K_c = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

[ ] = concentration in molL^{-1} at equilibrium

e.g. $K_c = \dfrac{[NH_3]^2}{[N_2] \times [H_2]^3}$

Products are divided by reactants and the number of mols in the equation is written to the power of each reactant and product.

Note: only reactants and products in gas state or aqueous can be placed into an equilibrium expression. Do not place solids or liquids into the expression.

Solubility product K_s

The solubility product is the equilibrium constant for the equilibrium between an undissolved salt and its ions in a saturated solution. It is very similar to any other equilibrium constant and, for any particular salt, the value of K_s only changes if temperature changes.

Consider a saturated solution of $Ca(OH)_2$. For this equilibrium, we have the solubility product expression:

$$Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$$
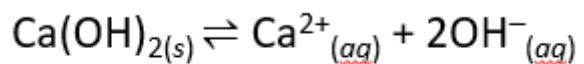
$$K_s(Ca(OH)_2) = [Ca^{2+}][OH^-]^2$$
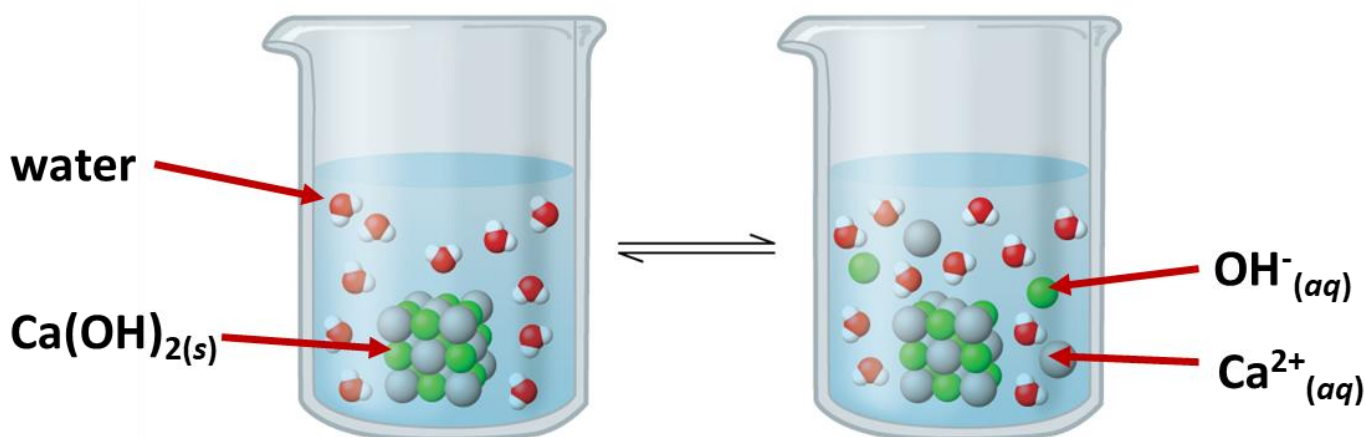
Remember: Water is not included in the equation or expression because the very large concentration before and after means there is negligible change.

Calculating K_s: ratio of cation to anion 1:1

Since the solubility can be used to calculate the concentration of ions in a saturated solution of a sparingly soluble salt, then these concentrations can be used to calculate the value of K_s.

1.   AB type of salt (ratio of cation to anion = 1:1)

The solubility of $BaSO_4$ is given as 1.05×10^{-5} mol L^{-1} at 25°C.   Calculate the value of K_s.

$$BaSO_4(s) \qquad \rightleftharpoons \qquad Ba^{2+}(aq) \quad + \quad SO_4^{2-}(aq)$$

From this equation $[Ba^{2+}] = [SO_4^{2-}] =$ solubility, s

$K_s(BaSO_4) = [Ba^{2+}] \times [SO_4^{2-}] = s^2 = (1.05 \times 10^{-5})^2 = 1.10 \times 10^{-10}$

NOTE: This equality is only true if there are no other sources of Ba^{2+} and SO_4^{2-} present in the solution ie if all the Ba^{2+} and SO_4^{2-} ions come from the dissolved solid

$$K_s = s^2$$

Determining K_s: ratio of cation to anion 2:1 or 1:2

AB$_2$ (or A$_2$B) type of salt (ratio cation to anion = 1:2 OR 2:1)

Calculate the solubility product for PbI$_2$ at 25 °C, given the solubility at 25 °C is 1.52×10^{-3} mol L^{-1}.

$$PbI_2(s) \quad \rightleftharpoons \quad Pb^{2+}(aq) \quad + \quad 2I^- (aq)$$
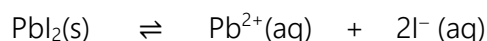
This tells us that $[Pb^{2+}]$ = solubility, s = 1.52×10^{-3} mol L^{-1}

And $[I^-]$ = 2 x solubility = 2s = $2 \times 1.52 \times 10^{-3} = 3.04 \times 10^{-3}$ mol L^{-1}

The expression for K_s is $\qquad K_s$ (PbI$_2$) $\quad = \quad [Pb^{2+}]$ x $[I^-]^2$

and substituting for solubility we get

K_s (PbI$_2$) = (1.52×10^{-3}) x $(3.04 \times 10^{-3})^2 \quad = 1.40 \times 10^{-8}$

NOTE: because $[2s]^2$ means everything inside the brackets is squared then expanding it out becomes $2^2 + s^2$ = $4s^2$. The other ion $[s]$ then is multiplied so the whole expression becomes $4s^3$ (cubed)
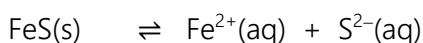
$$K_s = 4s^3$$

Determining S from K_s (1:1)

It is possible to use the value of K_s at any particular temperature to calculate the solubility of the salt $[s]$ at that temperature and to calculate the concentration of ions in the saturated solution.

Example

1. Calculate the solubility of iron(II) sulfide at 25°C given that

FeS(s) $\quad \rightleftharpoons \quad Fe^{2+}(aq) \quad + \quad S^{2-}(aq)$

K_s (FeS) $\quad = \quad [Fe^{2+}]$ x $[S^{2-}] = 6.3 \times 10^{-18}$

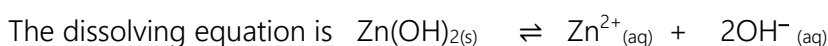From the equation it can be seen that, since the only source of ions is from the dissolving of FeS

Then $[Fe^{2+}] \quad = \quad [S^{2-}]$ = solubility, s

$\therefore \quad K_s$ (FeS) = s^2 and $\quad$ s = $\quad$ = $\quad = 2.51 \times 10^{-9}$ mol L^{-1}

$$s = \sqrt{K_s}$$

Determining S from K_s (2:1)

Calculate the solubility of zinc hydroxide at 25 °C given K_s (Zn(OH)$_2$) $\quad = 2.0 \times 10^{-17}$

The dissolving equation is $\quad Zn(OH)_{2(s)} \quad \rightleftharpoons \quad Zn^{2+}_{(aq)} \quad + \quad 2OH^-_{(aq)}$

This means that $[Zn^{2+}]$ = solubility = s and $\quad [OH^-]$ = 2 x solubility = 2s

The expression for K_s is $\quad K_s$ (Zn(OH)$_2$) = $[Zn^{2+}]$ x $[OH^-]^2$

OR $\quad K_s$ (Zn(OH)$_2$) = (s) x (2s)^2 = 4s^3

It is therefore possible to use this expression to solve for the solubility, s.

$$s = \sqrt[3]{\frac{K_s}{4}} \quad = \sqrt[3]{\frac{2.0 \times 10^{-17}}{4}} \quad = 1.71 \times 10^{-6}\ \text{mol L}^{-1}$$

Converting Mass to s(and Ks) and Ks to Mass

Some questions will provide the mass of a sparingly soluble salt and the volume of water that it is dissolved into. The molar mass of the salt will also be provided. You may need to <u>calculate the solubility or Ks</u>.
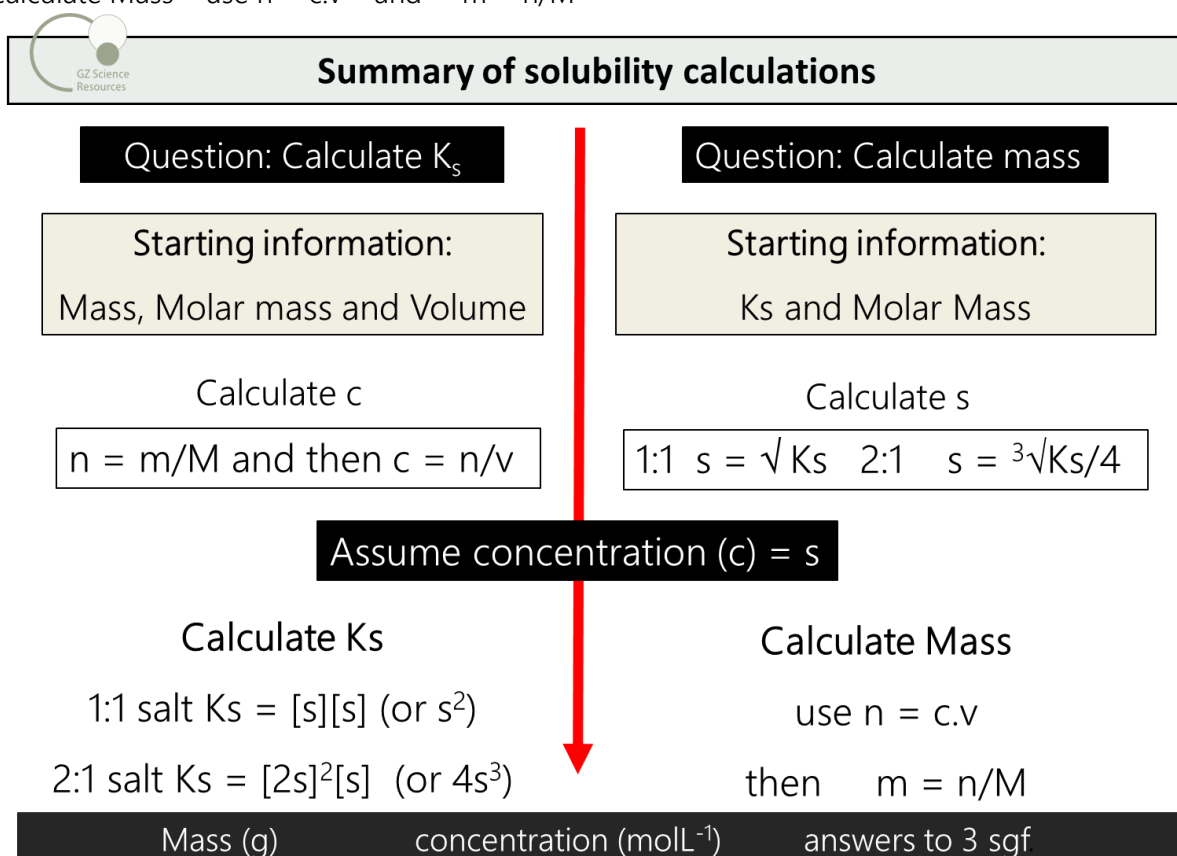
1. Write the ionic equation and expression
2. Calculate concentration (in molL^{-1}) Use n = m/M and then c = n/v
   (remember volume = L and Mass =g)　　　 Assume concentration (c) = s
3. Calculate Ks　　 1:1 salt Ks = [s][s] (or s^2)　 2:1 salt Ks = [2s]^2[s]　(or 4s^3)

Other questions may require you to <u>calculate mass (of salt)</u> given Ks or s. For example:

Silver carbonate, Ag$_2$CO$_3$, is a sparingly soluble salt.　　　　 K$_s$(Ag$_2$CO$_3$) = 8.10 × 10^{-12} at 25°C
M(Ag$_2$CO$_3$) = 276 g mol^{-1}

Calculate the mass of Ag$_2$CO$_3$ that will dissolve in 50 mL of water to make a saturated solution at 25°C.

1. Write the ionic equation and expression
2. Calculate s　 1:1 s = √ Ks　 2:1　 s = ^{3}√Ks/4　　 Assume s = concentration (c)
3. Calculate Mass　 use n = c.v　 and　　 m = n/M

Summary of solubility calculations

Question: Calculate K$_s$	Question: Calculate mass
Starting information:	**Starting information:**
Mass, Molar mass and Volume	Ks and Molar Mass
Calculate c	Calculate s
n = m/M and then c = n/v	1:1 s = √ Ks　 2:1　 s = ^{3}√Ks/4

Assume concentration (c) = s

Calculate Ks	Calculate Mass
1:1 salt Ks = [s][s] (or s^2)	use n = c.v
2:1 salt Ks = [2s]^2[s]　(or 4s^3)	then　　 m = n/M

| Mass (g) | concentration (molL^{-1}) | answers to 3 sgf |

Effects of Acid on Solubility

If the salt contains a carbonate i.e. Ag_2CO_3, which is sparingly soluble, it will dissociate into its ions – one ion being a cation and the other the anion carbonate.

$$Ag_2CO_3 \rightleftharpoons Ag^+ + CO_3^{2-}$$

If acid is added to this system then it will react with the carbonate ion effectively reducing the concentration of this in the solution. Acid neutralises carbonates

Accordingly, to the principals of equilibrium if a product is removed (carbonate) the reaction will increase in the forward direction to replace the depleted product – hence more salt will dissolve and the overall solubility of the system will increase.

Acids increase solubility if the salt contains a carbonate.

Effects of Base on Solubility

If a sparingly soluble salt contains an cation i.e. AgCl containing Ag^+ which reacts with NH_3 or OH- to produce a complex ion such as $[Ag(NH_3)_2]^+$

Then when a base is added to this system then it will react with the cation effectively reducing the concentration of this in the solution. Base "locks up" many cations into complex ions.

Accordingly, to the principals of equilibrium if a product is removed (silver ions) the reaction will increase in the forward direction to replace the depleted product – hence more salt will dissolve and the overall solubility of the system will increase.

Bases increase solubility if the salt contains a cation that forms a complex ion when pH is above10

Effects of adding hydroxide on Solubility

Decrease SOLUBILITY
If a sparingly soluble salt contains hydroxide i.e. $Zn(OH)_2$, a small amount of OH- added will decrease solubility as the reaction is shifted to the left to remove added product and produce more reactant (the solid salt)

This occurs when pH is above 4 but below 10
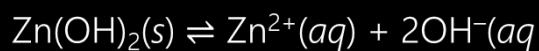
Increase SOLUBILITY

Then when excess hydroxide is added to this system then it will react with the cation to produce a complex ion, effectively reducing the concentration of this in the solution.
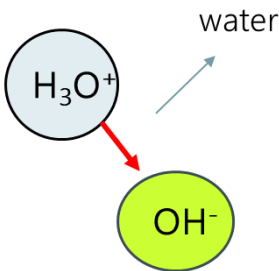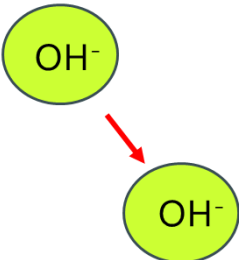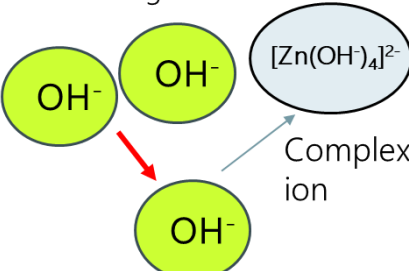
Accordingly, to the principals of equilibrium if a product is removed (silver ions) the reaction will increase in the forward direction to replace the depleted product – hence more salt will dissolve and the overall solubility of the system will increase.

Bases increase solubility if the salt contains a cation that forms a complex ion, when pH is above 10 only.

Summary of Equilibrium changes in Solubility

$$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq$$

pH is below 4	pH is above 4 but below 10	pH is above 10
water H_3O^+ OH^-	Adding few drops OH⁻ OH^- OH^-	Adding excess OH⁻ OH^- OH^- $[Zn(OH^-)_4]^{2-}$ OH^- Complex ion OH^-
Hydronium ions in acid solution **neutralise** OH-, and removing as product.	Total OH- concentration increases, therefore more product.	Complex ion forms, and removes product., by removing Zn^{2+} ions.
Forward reaction increases Solubility increases	Reverse reaction increases Solubility decreases	Forward reaction increases Solubility increases

Ionic product

In any solution, whether it is saturated or not, such as AgCl the product formed $[Ag^+][Cl^-]$ is called the ionic product and cannot exceed the K_s. If either Ag^+ ions or Cl^- ions are added from another source, such as by adding NaCl, and the new concentrations of ions exceed the K_s then a precipitate will form.

Example

What is the minimum concentration of Cl^- ions to give a precipitate of AgCl? $c(AgNO_3) = 0.01molL^{-1}$
$K_s = 2 \times 10^{-10}$ If IP > Ks then precipitate will form

1. $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

2. $K_s = [Ag^+][Cl^-]$ $K_s = [0.01][Cl^-]$

3. Rearrange $K_s = [Ag^+][Cl^-]$

   $[Cl^-] = \dfrac{K_s}{[0.01]}$ $= \dfrac{2 \times 10^{-10}}{0.01}$ $= 2 \times 10^{-8}$

 A precipitate will form if the concentration of Cl^- ions exceeds 2×10^{-8} molL⁻¹
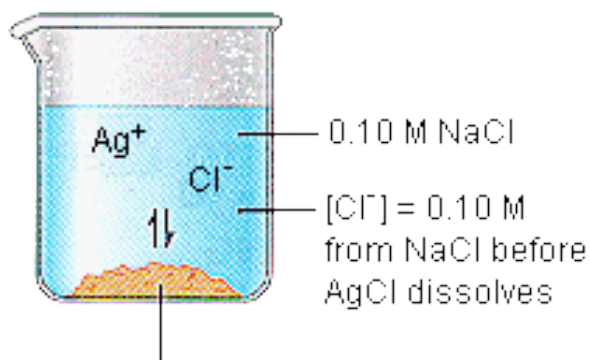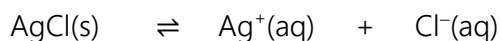
The ratio of the concentrations of products and reactants is called Q.

K_s is the maximum concentration of ions the solution can hold (at a given temperature)

Common ion effect

K_s is used to calculate the solubility of sparingly soluble salts in pure water. If a solution being added contains either one of the ions already present in the solution then this will reduce the solubility of the salt since the

presence of the common ion will move the equilibrium towards the side of precipitated salt. For example, the equation for the dissolving of AgCl is

$$AgCl(s) \quad \rightleftharpoons \quad Ag^+(aq) \quad + \quad Cl^-(aq)$$

Ag⁺
Cl⁻
⇅

0.10 M NaCl

[Cl⁻] = 0.10 M
from NaCl before
AgCl dissolves

AgCl (s) should be much
less soluble than in pure
H₂O

AgCl would be less soluble in sea water than in pure water because the presence of the Cl^- dissolved in the sea water means $[Cl^-]$ is higher which must reduce the concentration of $[Ag^+]$ at equilibrium (as the value of K_s cannot change). This reduces the amount of solid AgCl that can dissolve.

Common Ion effect an example of Le Chatelier's principle. It is possible to calculate the solubility of any salt in a solution containing a common ion, provided the concentration of the ion in the solution and the K_s is known.

Example

What is the solubility of AgCl in a 0.0025 mol L^{-1} solution of NaCl?

$$Ks \ (AgCl) \ = \ [Ag^+] \times [Cl^-] = 1.6 \times 10^{-10}$$

$[Ag^+]$ = solubility, s of the AgCl since the only source of silver ions is from dissolved AgCl.

$[Cl^-]$ = 0.0025 + s   since the final concentration of Cl^- ions is given by the concentration originally in the solution PLUS the extra dissolved to make a saturated solution.

Assume s is much less than 0.0025 and therefore $[Cl^-]$ = 0.0025

$$Ks \ (AgCl) \ = \ s \times 0.0025 \ = 1.6 \times 10^{-10}$$

$$and \quad s = \ \frac{1.6 \times 10^{-10}}{0.0025} \quad = \ 6.4 \times 10^{-8} \ mol \ L^{-1}.$$

NOTE :(a) This solubility of AgCl in a solution containing Cl^- ion is much less than (in this case by more than 1000x) the solubility in pure water of 1.26×10^{-5} mol L^{-1}. (b) The assumption made that $[Cl^-]$ = 0.0025 is valid since 6.4×10^{-8} is much less than 0.0025.

Ag Cl⁻   ⇌   Ag⁺ + Cl⁻

Cl⁻

extra Cl-
ions present
in sea water
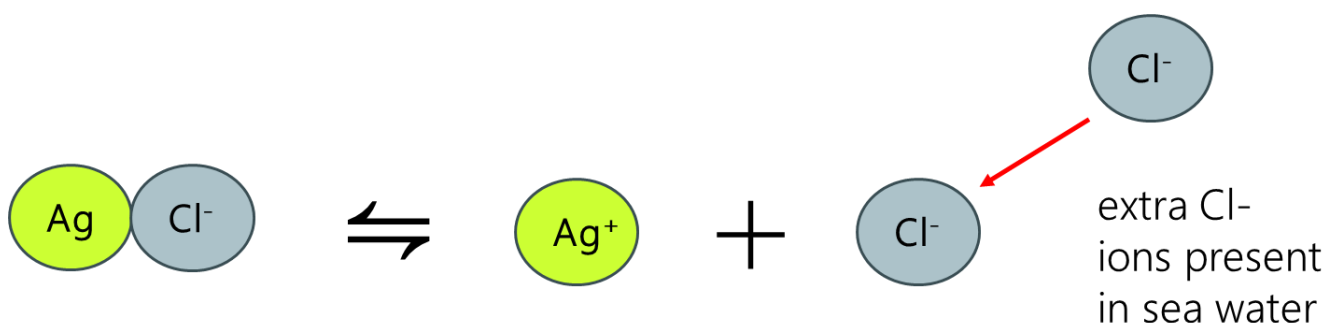
Favours reverse reaction therefore **solubility decreases**

Summary of Common ion calculations

Q = ratio of the concentrations of products and reactants.

Ks is the maximum concentration of ions the solution can hold (at a given temperature)

1:1 salt	2:1 salt
Q = (c) x (c)	$Q = (c) \times (c)^2$

Where can c come from?

S	n = m/M and	
(calculated from K_s)	then c = n/v	$c = \dfrac{\text{initial volume}}{\text{total volume}} \times \text{conc.}$

If I.P. < K_s NO precipitate   If I.P. > K_s precipitate forms
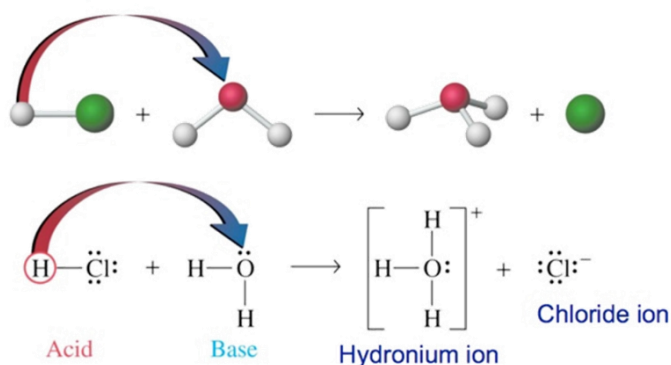
Acids – their characteristics

An Acid donates its Hydrogen ion (H^+), which is really just a proton - the electron remains behind.

Common acids (that you need to know) include:

Strong acids: HNO_3 - nitric acid, HCl - hydrochloric acid, H_2SO_4 – sulfuric acid, HBr - Hydrobromic acid

Weak acids: CH_3COOH – ethanoic acid, HF - Hydrofluoric acid, and NH_4^+ - ammonium

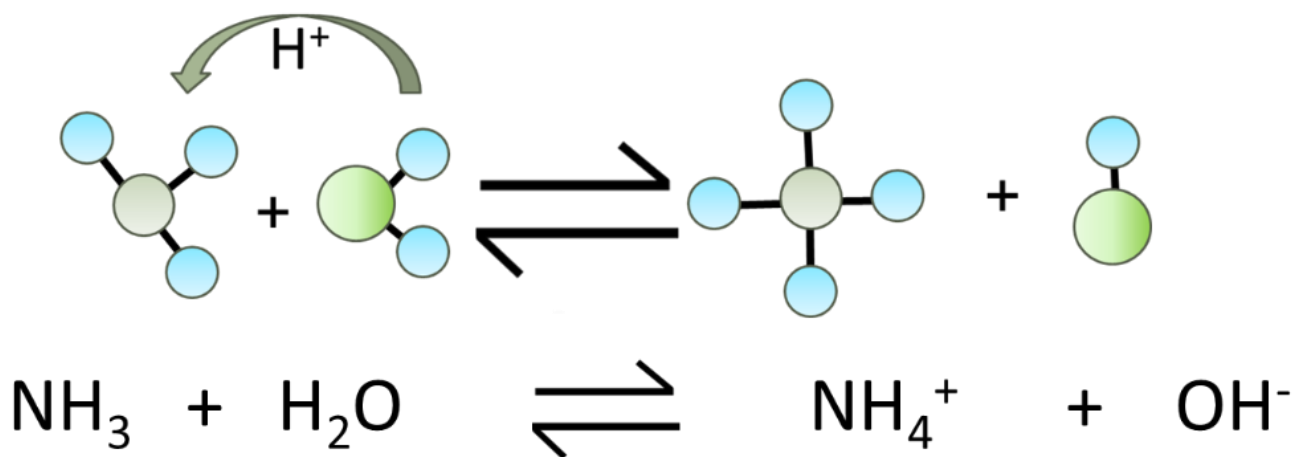Acid   Base   Hydronium ion   Chloride ion

Bases – their characteristics

A Base accepts a Hydrogen ion that have been donated from an Acid.

Common bases (that you need to know include:

Strong bases: NaOH – sodium hydroxide, KOH – potassium hydroxide
Weak bases: NH_3 – ammonia, CH_3NH_2 - methylamine and CH_3COO^- - ethanoate ion

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Some substances such as water are amphiprotic and can act as both an acid and a base depending on what other substance the water is with.

Brønsted–Lowry theory of Acid and Base reactions

Acid-Base reactions involve the transfer of Hydrogen ions, H^+. A hydrogen ion, H^+ is simply a lone proton (an H with the electron removed). In water (or aqueous solutions), H^+ ions exist as an H_3O^+ ion, called hydronium.

Acids are substances that donate protons (H^+) in solution	Bases are substances that accept protons (H^+) in solution
$HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$	$NH_{3(g)} + H_2O_{(l)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$
HCl gas dissolved in water	NH_3 gas dissolved in water
HCl has donated an H^+ so is acting as an acid	NH_3 has accepted an H^+ so it is acting as a base
H_2O has accepted an H^+ so it is acting as a base	H_2O has donated an H^+ so is acting as an acid
Solution becomes acidic since H_3O^+ ions form	Solution becomes basic since OH^- ions form.

Brønsted–Lowry acids and bases summary

Proton donation to a water molecule forms H_3O^+ (hydronium) ions.
$HA(aq)$ $+$ $H_2O(l)$ $\rightleftharpoons$ $H_3O^+(aq)$ $+$ $A^-(aq)$
acid base acid base
proton donor *proton acceptor*
Similarly, proton donation from water to a base produces OH^- ions.
$B(aq)$ $+$ $H_2O(l)$ $\rightleftharpoons$ $BH^+(aq)$ $+$ $OH^-(aq)$
base acid acid base
proton acceptor *proton donor*

NH₃ + H₂O ⇌ NH₄⁺ + OH⁻
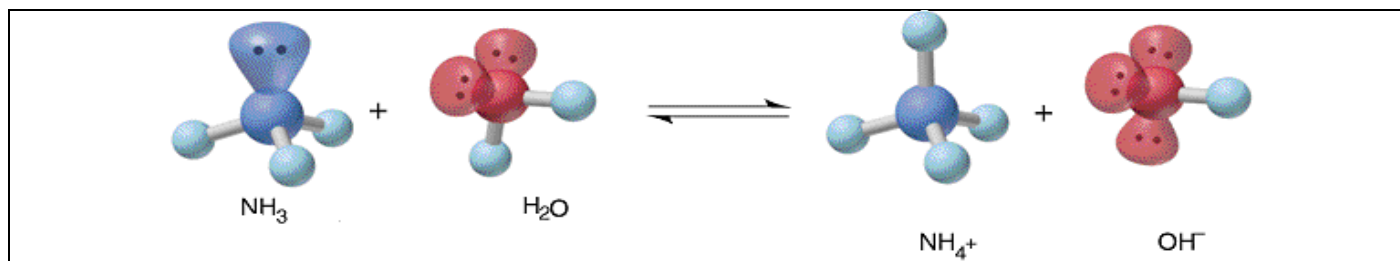
Amphiprotic substances

An amphiprotic substance is a substance that can donate or accept a proton, H^+

For a substance to be amphiprotic it must

1. Contain a hydrogen atom, which is able to be donated to another chemical species.

2. Be able to accept a hydrogen ion from another species.

Examples of amphiprotic species include, H_2O, HCO_3^- , HSO_4^- , HPO_4^{2-} and $H_2PO_4^-$

Name of amphiprotic species	Chemical formula	Able to donate a proton, H^+	Able to accept a proton, H^+
Water	H_2O	$H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$	$H_2O(l) + H^+(aq) \rightarrow H_3O^+(aq)$
Hydrogen carbonate ion	HCO_3^-	$HCO_3^-(aq) \rightarrow H^+(aq) + CO_3^{2-}(aq)$	$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$
Hydrogen sulfate ion	HSO_4^-	$HSO_4^-(aq) \rightarrow H^+(aq) + SO_4^{2-}(aq)$	$HSO_4^-(aq) + H^+(aq) \rightarrow H_2SO_4(aq)$
Dihydrogen phosphate ion	$H_2PO_4^-$	$H_2PO_4^-(aq) \rightarrow H^+(aq) + HPO_4^{2-}(aq)$	$H_2PO_4^-(aq) + H^+(aq) \rightarrow H_3PO_4(aq)$

Strong and Weak Acids

The strength of an acid is determined by how readily it will donate its H^+ ions. Strong acids will have a low pH (0-3) and include HNO_3 , HCl , H_2SO_4, and HBr Weak acids will have a higher pH (4-6). They are mostly organic acids and include CH_3COOH, HF and NH_4^+

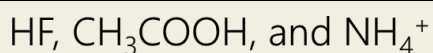| Strong acids	Weak acids
Donate protons (H^+) in aqueous solution to become completely dissociated. $HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$ HCl gas dissolved in water HCl has donated an H^+ so is acting as an acid H_2O has accepted an H^+ so it is acting as a base Solution contains virtually no intact HCl molecules after reaction.	Donate protons (H^+) in aqueous solution to become partially dissociated. $CH_3COOH_{(l)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$ CH_3COOH dissolved in water Only some of the acetic acid molecules dissociate into acetate ions (CH_3COO^-) Because the acetate ion is a strong base (conjugate pairs), it will readily accept H^+ (from H_3O^+) and become acetic acid. Solution contains mostly intact CH_3COOH molecules.
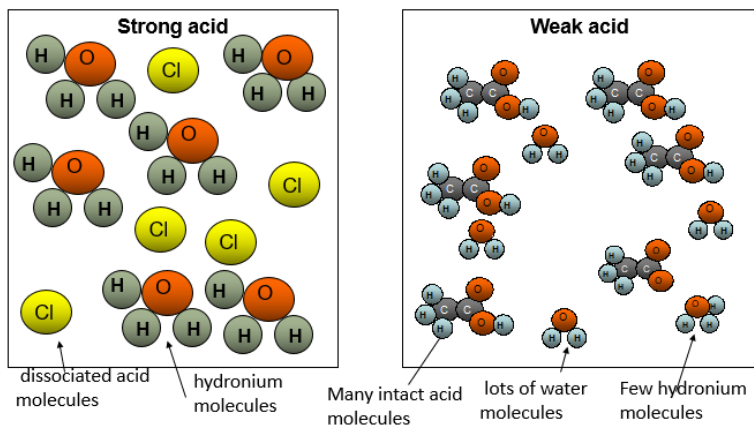
Strong and Weak Bases

The strength of a base is determined by how readily it will accept H^+ ions. Strong bases will have a high pH (12-14) and include NaOH and KOH. Weak acids will have a lower pH (8-11). They include NH_3, CH_3NH_2 and CH_3COO^-
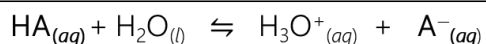
Strong Bases	Weak Bases
Completely accept protons (H^+) in aqueous solution $NaOH_{(s)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$ NaOH completely dissociates The OH- ions will readily accept H^+ ions. Solution contains very <u>few</u> intact NaOH molecules after reaction.	Partially accept protons (H^+) in aqueous solution $NH_{3(g)} + H_2O \leftrightharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$ Only some of the ammonia molecules dissociate into ammonium ions (NH_4^+) Because ammonium is a reasonably strong acid (conjugate pairs), it will readily donate H^+ and become ammonia. Solution contains <u>mostly</u> intact NH_3 molecules.

Summary of Dissociation equations and Equilibrium expressions

Weak Acids

HF, CH_3COOH, and NH_4^+

Write an equation using:

$HA_{(aq)} + H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + A^-_{(aq)}$

Weak Bases

NH_3, CH_3NH_2, and CH_3COO^-

Write an equation using:

$B_{(aq)} + H_2O_{(l)} \leftrightharpoons OH^-_{(aq)} + BH^+_{(aq)}$
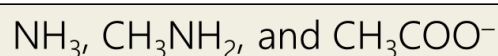
Assume H_2O has no change in concentration

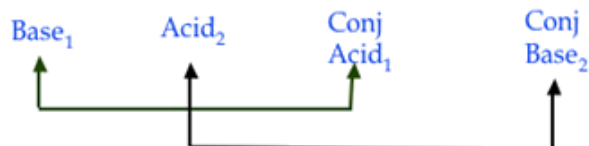Write an expression using:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$
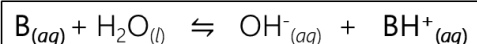
Write an expression using:

$$K_b = \frac{[OH^-][BH^+]}{[B]}$$

strong acids HCl, HBr, HNO_3, H_2SO_4 strong bases KOH, NaOH

Conjugate pairs

$$HNO_2 + H_2O \rightarrow NO_2^- + H_2O^+$$

Acid₁   Base₂   Conj Base₁   Conj Acid₂

$$HPO_4^{2-} + NH_4^+ \rightarrow H_2PO_4^- + NH_3$$

Base₁   Acid₂   Conj Acid₁   Conj Base₂

If two species differ by just one proton, they are classed as a conjugate acid-base pair. Examples of acid-base pairs are H_2SO_4/HSO_4^- and NH_4^+/NH_3.
The acid is always the species with the additional proton.
It can also be said that NH_3 is the conjugate base of NH_4^+.

When a base accepts a proton, it becomes an acid because it now has a proton that it can donate. In addition, when an acid donates a proton it becomes a base, because it now has room to accept a proton.
These are what we call conjugate pairs of acids and bases.
When an acid gives up its proton, what remains is called the conjugate base of that acid. When a base accepts a proton, the resulting chemical is called the conjugate acid of that original base.

Conjugate base

Hydrogen ion

Undissociated molecule
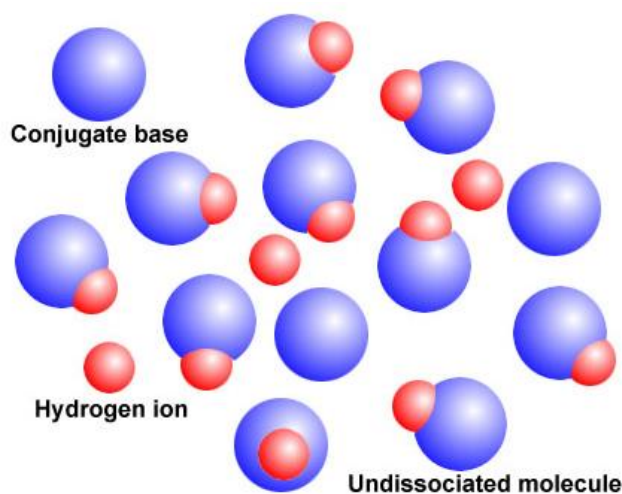
Conjugate Acid and Base pairs (Strong Acid)

HX is a symbol used for a strong acid. A conjugate acid can be seen as the chemical substance that releases a proton in the backward chemical reaction.

The base produced, X−, is called the conjugate base and it absorbs a proton in the backward chemical reaction.

paired   paired

Strong acid   base   conjugate base   conjugate acid
$$HX \quad + \quad H_2O \longrightarrow X^- \quad + \quad H_3O^+$$

transfer of H⁺
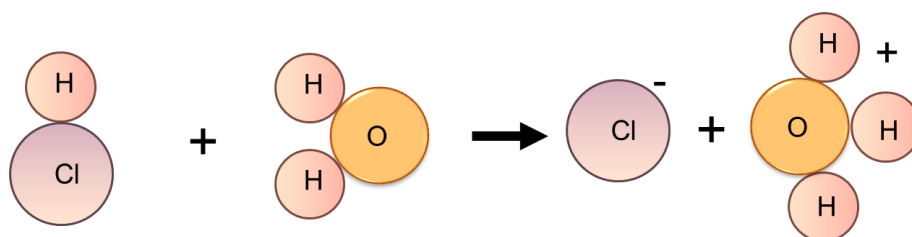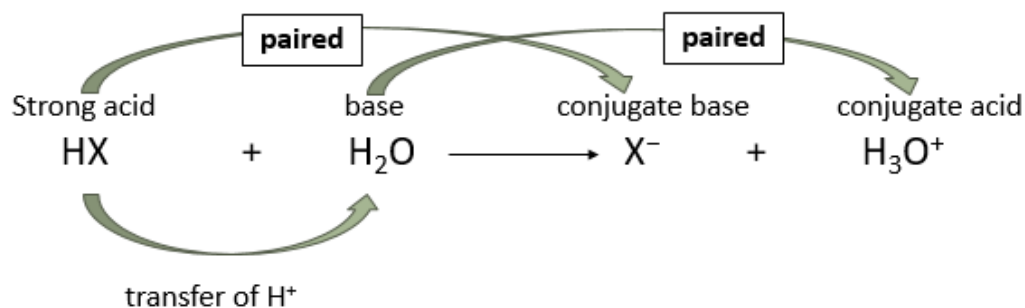
Where c(HX) = [H_3O^+]

Initial concentration of HX is equal to final concentration of H_3O^+

so pH= -log c(HX)

Conjugate Acid and Base pairs (weak acid)

HA is a symbol used for weak acid. Note the use of the double arrow. Because the weak acid only partially dissociates, in an equilibrium, a reaction occurs with a fixed amount of an acid and its conjugate remains in solution.
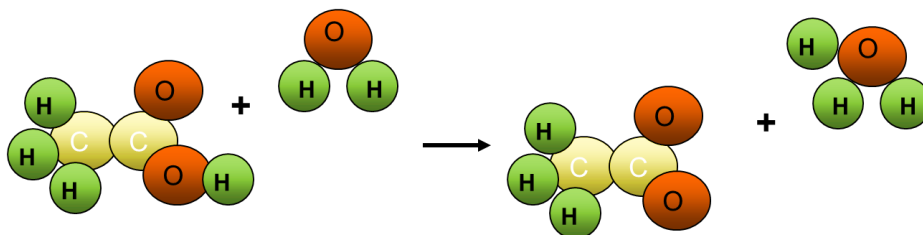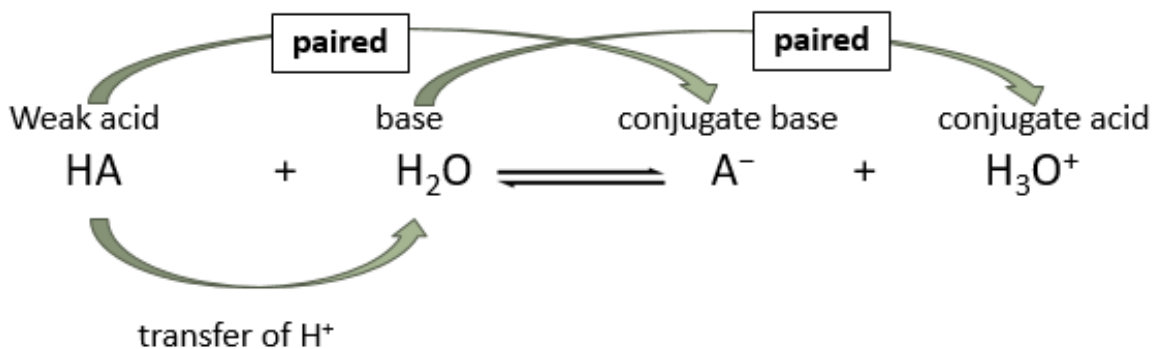
Conjugate Acid and Base pairs (Base)

B is a symbol used for a base. The base now accepts the hydrogen ion from the water. The hydroxide ion, OH⁻, is the paired conjugate of the water once the H⁺ has been removed. Strong bases use a single direction arrow and weak bases use a double arrow.
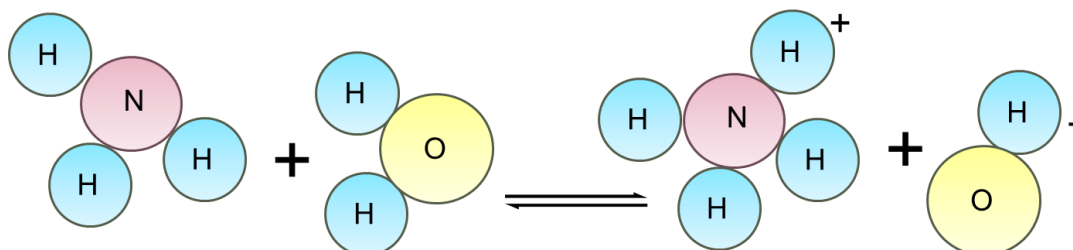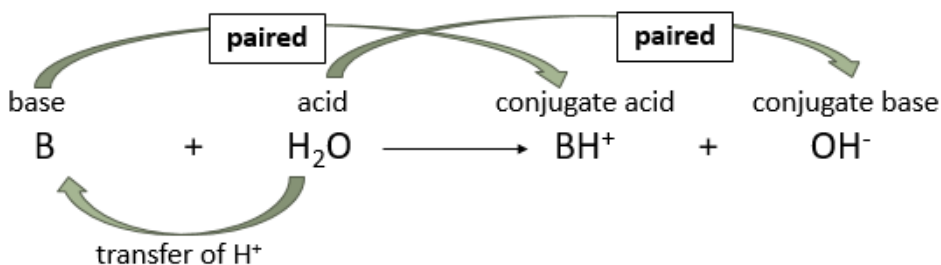
Conjugate Acid and Base pairs

Base		Conjugate Acid
H_2O	water	H_3O^+
SO_4^{2-}	sulfate ion	HSO_4^-
NH_3	ammonia	NH_4^+
OH^-	hydroxide ion	H_2O
HCO_3^-	hydrogen carbonate ion	H_2CO_3
CO_3^{2-}	carbonate ion	HCO_3^-

The stronger an acid, normally the weaker its conjugate base, and, conversely, the stronger a base, the weaker its conjugate acid.

A strong acid like HCl donates its proton so readily that there is essentially no tendency for the conjugate base Cl^- to reaccept a proton. Consequently, Cl^- is a very weak base. A strong base like the H^- ion accepts a proton and holds it so firmly that there is no tendency for the conjugate acid H_2 to donate a proton. Hence, H_2 is a very weak acid.

Species in solution

A solution is formed by mixing a solute (a dissolved substance) into a solvent (the solution that dissolves the solute.
In Aqueous Chemistry, the solvent is water, and the solute can be an acid, base or ionic salt.
A solute dissolves by bonds being broken between solute particles (endothermic) and new bonds being formed between solute and solvent (exothermic).
A small amount of H_3O^+ and OH^- will always be present in water due to $Kw = [OH^-][H_3O^+] = 1 \times 10^{-14}$
Water will always be present in large concentrations.
Concentration of species in solution

The relative concentration of the species in solution at equilibrium will depend upon the type of substances dissolved into water initially.

➢ In aqueous solutions, water will almost always be present in the highest concentration.
➢ Small quantities of H_3O^+ and OH^- will also be present, according to the $K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$
➢ Information on relative concentration can often be presented in a bar graph.

Weak and strong acids

In a strong acid there will be no original acid seen in the final solution. Equal quantities of conjugate base and hydronium are formed.

In a weak acid there will be mostly the original acid seen in the final solution. Equal quantities of conjugate base and hydronium are formed, but in small amounts.
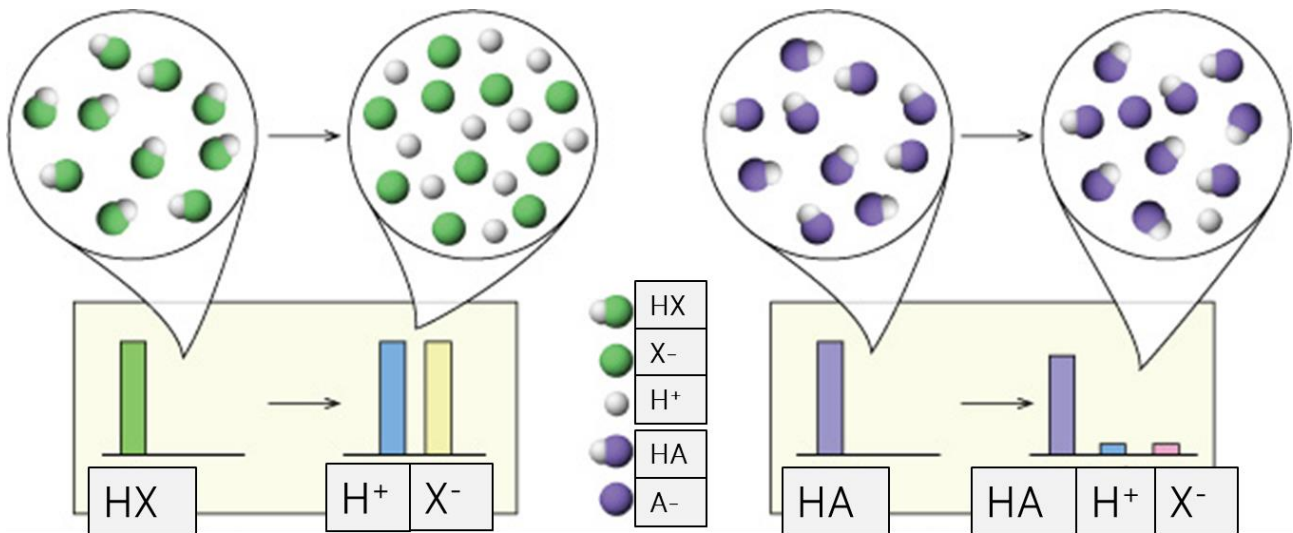
Concentration of ions in solution – Strong Acid	
Strong Acid i.e. HCl reacting with water $[Cl^-] = [H_3O^+] > [OH^-]$ Strong acids will provide good conductivity and pH 1-2 due to the high presence of H_3O^+ ions No strong acid will be left in the final mixture. H_3O^+ and Cl^- are produced in equal concentrations – in the same concentration as the original strong acid. A small amount of OH^- is present as water dissociates into H_3O^+ and OH^-	
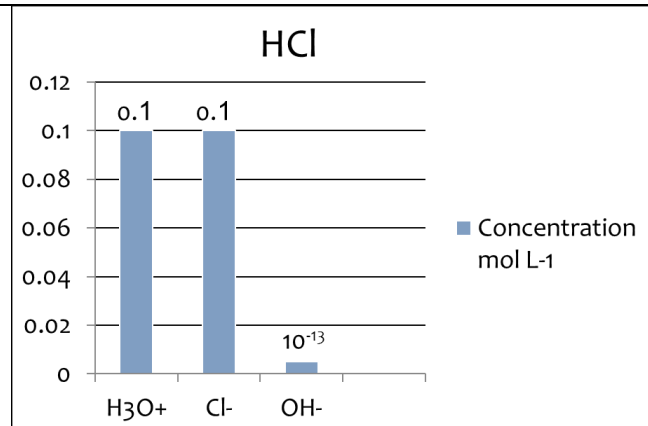
Concentration of ions in solution – Weak Acid	
Weak Acid i.e. CH_3COOH reacting with water $[CH_3COOH] > [CH_3COO^-] \approx [H_3O^+] > [OH^-]$ Weak acids will provide poor conductivity and pH 3-6 due to the low presence of H_3O^+ ions (but still higher than OH^- ions) Most weak acid will be left in the final mixture. H_3O^+ and CH_3COO^- are produced in equal concentrations – a small amount of the weak acid had dissociated. A small amount of OH^- is present as water dissociates into H_3O^+ and OH^-	
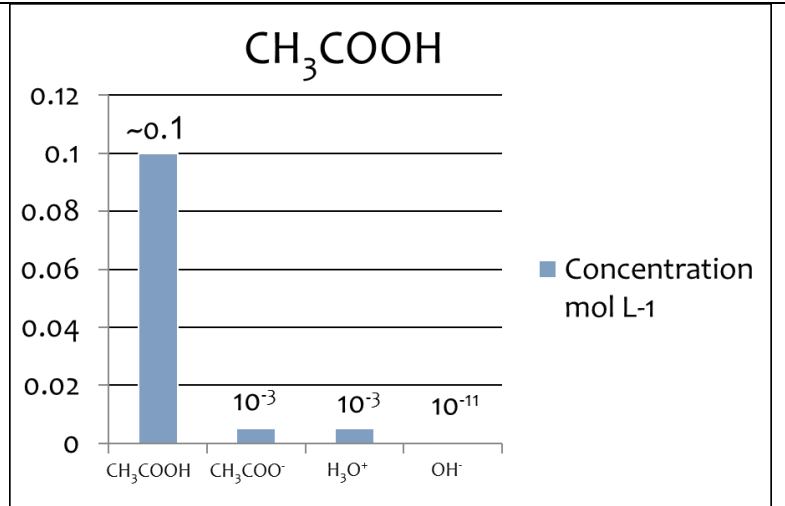
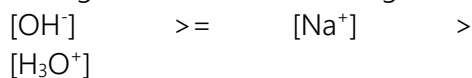|	
Concentration of ions in solution – Strong Base Strong Base i.e. NaOH reacting with water $[OH^-] \quad >= \quad [Na^+] \quad > \quad [H_3O^+]$ Strong bases will provide good conductivity and pH 12 – 14 due to the high presence of OH^- ions No strong base will be left in the final mixture. OH^- and Na^+ are produced in equal concentrations – in the same concentration as the original strong base. A small amount of H_3O^+ is present as water dissociates into H_3O^+ and OH^-	**NaOH** OH- : 0.1 Na+ : 0.1 H3O+ : 10^{-13} Concentration mol L-1
Concentration of ions in solution – Weak Base Weak Base i.e. NH_3 $[NH_3] \quad > \quad [OH-] \quad > \quad [NH_4^+] \quad > \quad [H_3O^+]$ Weak bases will provide poor conductivity and pH 8 – 11 due to the low presence of OH^- ions (but still higher than H_3O^+ ions) Most weak base will be left in the final mixture. OH^- and NH_4^+ are produced in equal concentrations – a small amount of the weak base had dissociated. A small amount of H_3O^+ is present as water dissociates into H_3O^+ and OH^-	**NH_3** NH3 : ~0.1 NH4+ : 10^{-3} OH- : 10^{-3} H3O+ : 10^{-11} Concentration mol L-1
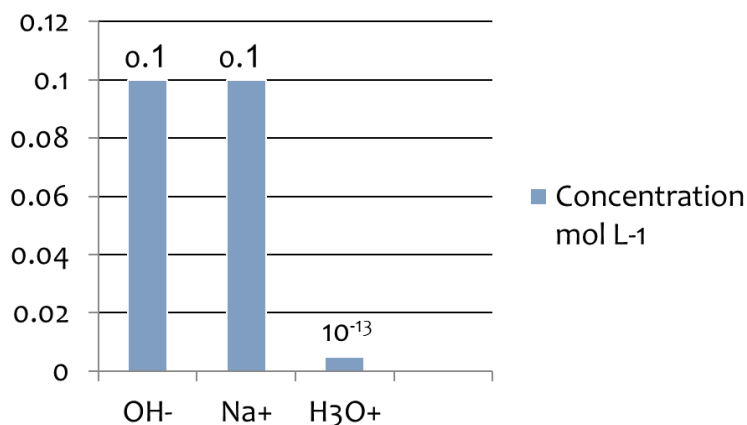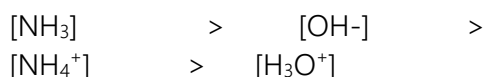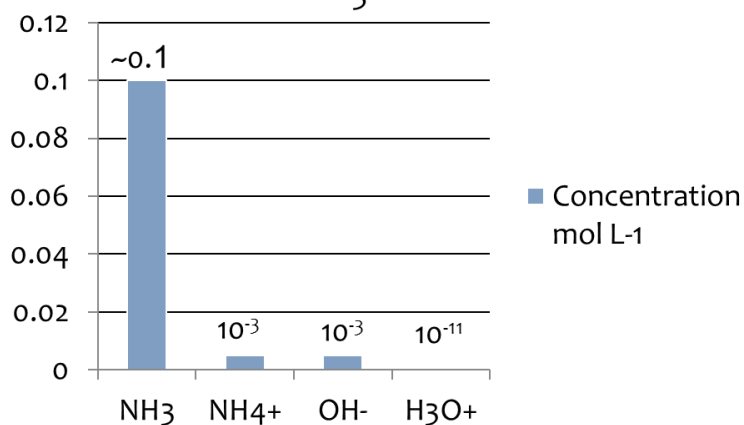
Concentration of ions in solution – acid salt Acid Salt i.e. NH_4Cl $[Cl^-] \quad > \quad [NH_4^+] \quad > \quad [H_3O^+] \quad = \quad [NH_3] \quad > \quad [OH^-]$ Acid salts will provide good conductivity and pH < 7 due to the high presence of ions from dissolving and to a lesser extent H_3O^+ ions The spectator ion will be left in the highest concentration followed by the weak acid. H_3O^+ and NH_3 are produced in equal concentrations – a small amount of the weak acid had dissociated. A small amount of OH^- is present as water dissociates into H_3O^+ and OH^-	**NH_4Cl** Cl⁻ : 0.1 NH_4^+ : ~0.1 H_3O^+ : 10^{-5} NH_3 : 10^{-5} OH⁻ : 10^{-9} Concentration mol L-1
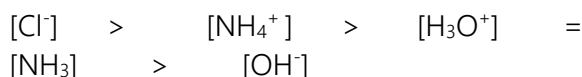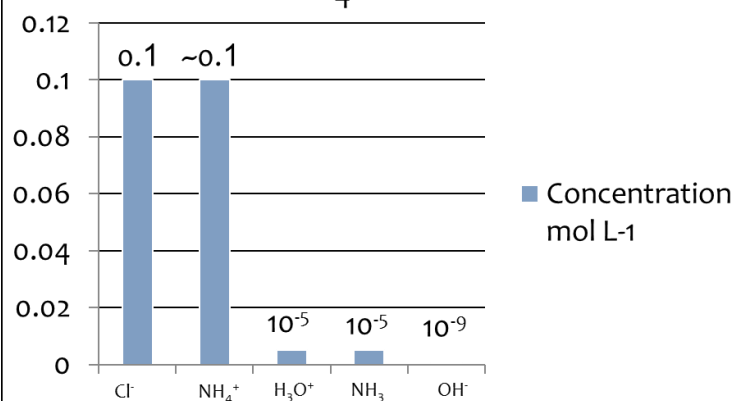
Concentration of ions in solution – base salt Base Salt i.e. CH_3COONa $[Na^+]$ ≈ $[CH_3COO^-]$ > $[CH_3COOH]$ = $[OH^-]$ > $[H_3O^+]$ Base salts will provide good conductivity and pH > 7 due to the high presence of ions from dissolving and to a lesser extent OH^- ions The spectator ion will be left in the highest concentration followed by the weak base. OH^- and CH_3COOH are produced in equal concentrations – a small amount of the weak base had dissociated. A small amount of H_3O^+ is present as water dissociates into H_3O^+ and OH^-	**CH_3COONa** Bar chart with y-axis "Concentration mol L-1" from 0 to 0.12. Na^+: 0.1 CH_3COO^-: ~0.1 CH_3COOH: 10^{-5} OH^-: 10^{-5} H_3O^+: 10^{-9}
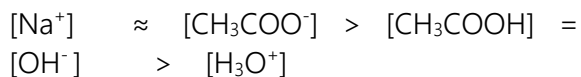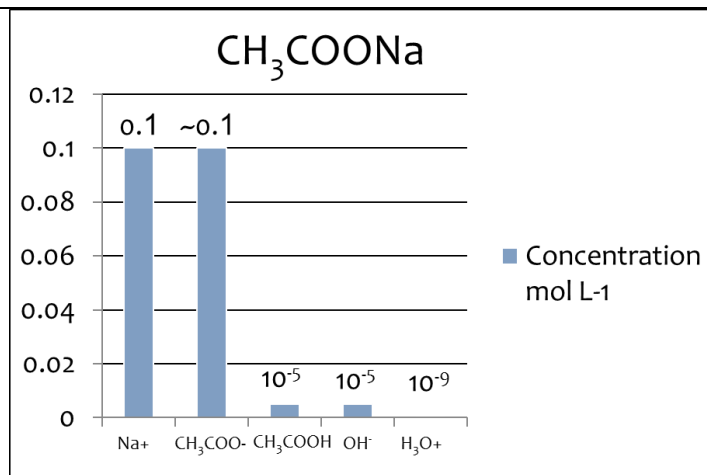
pH of salt solutions

All cations that are the conjugate acids of weak bases act as weak acids and lower the pH of the solution. This means that a salt solution containing this cation could be acidic. For example, a solution of ammonium chloride, NH_4Cl, contains the cation NH_4^+ and the anion Cl^-. The Cl^- ion acts as a neutral species and does not affect the pH (as it is the conjugate base of a strong acid and is so weakly basic that it effectively has no reaction with water). The NH_4^+ ion is the conjugate acid of the weak base NH_3 and so itself is a weak acid.

The ionic salt will first dissolve into its two ions. This equation needs to be shown.
There will then be a further equation as the ion acting as a weak acid or base undergoes an acid/base reaction with water.
The non-reacting ion is left off as the spectator.

$$NH_4Cl_{(s)} \leftrightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \leftrightarrow NH_{3(aq)} + H_3O^+{}_{(aq)}$$
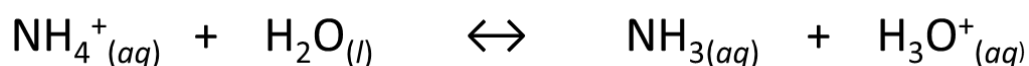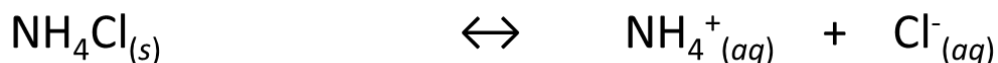
Conductivity of solutions

Conductivity is related to the availability of free moving charged particles.
The presence of ions in solution and the concentration of them determine conductivity.

High conductivity

A strong electrolyte (solution containing ions) is created when a strong acid /strong base is added to water and fully dissociates. An ionic salt added to water also produces a strong electrolyte when both anions and cations are formed.
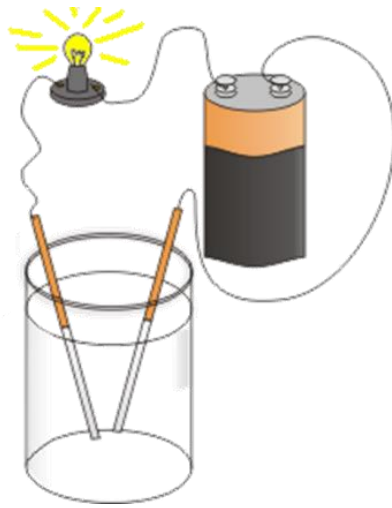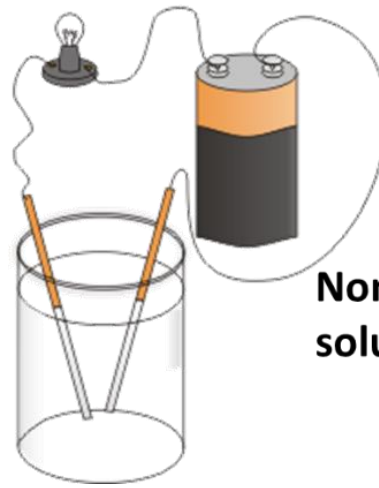
Low Conductivity

A weak electrolyte is formed from a weak acid or base that only partially dissociates. Only a small concentration of ions are created to carry charge. (Such as acetic acid)

No Conductivity

Polar molecular solids that dissolve in water have no free charge particles (such as glucose or alcohols) and therefore cannot conduct charge.

Summary of Species/conductivity in Solution - Acid

Strong Acids	Weak Acids	Acid salts

H_2O HCl

1×10^{-14} molL^{-1}

$H_3O^+ = OH^-$

$H_3O^+ = Cl^-$
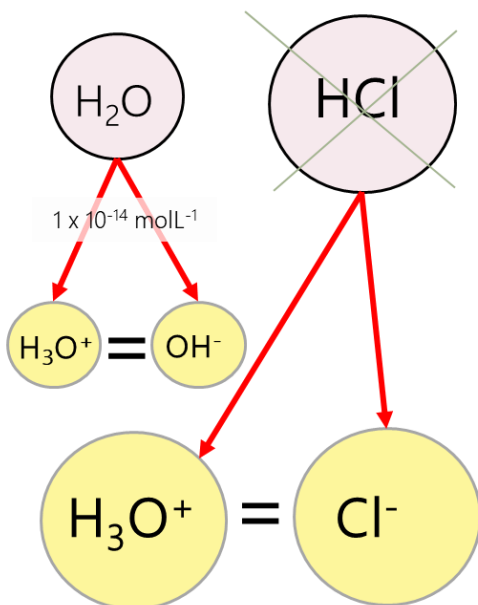
Complete dissociation
No strong acid remains

High conductivity

H_2O CH_3COOH

1×10^{-14} molL^{-1}

$H_3O^+ = OH^-$

$H_3O^+ = CH_3COO^-$
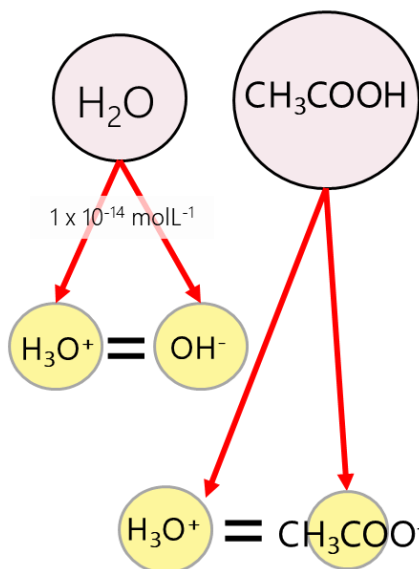
Partial dissociation
Most weak acid remains

Low conductivity

H_2O NH_4Cl

1×10^{-14} molL^{-1}

H_3O^+ OH^-

$NH_4^+ = Cl^-$

$H_3O^+ = NH_3$
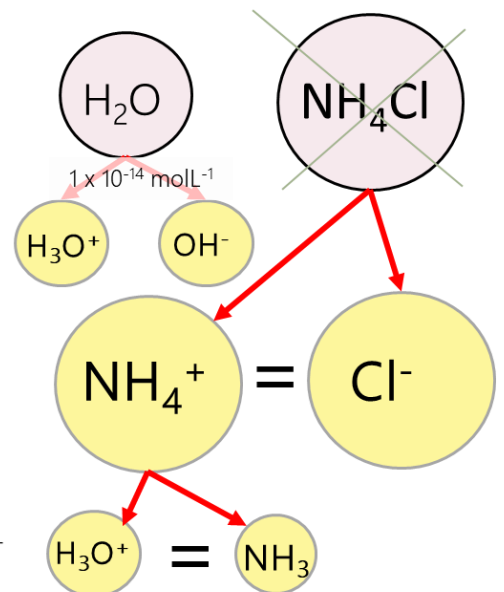
Weak acid reacts further
No salt remains

High conductivity

Water concentration is assumed to remain constant so is left out

Summary of Species / conductivity in Solution - Base

Strong Bases	Weak Bases	Base salts

Strong Bases

H_2O NaOH

1×10^{-14} molL^{-1}

$H_3O^+ = OH^-$

$OH^- = Na^+$
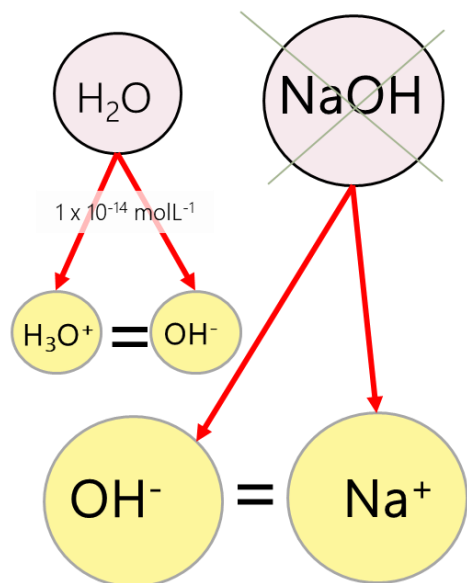
Complete dissociation
No strong base remains

High conductivity

Weak Bases

H_2O NH_3

1×10^{-14} molL^{-1}

$H_3O^+ = OH^-$

$OH^- = NH_4^+$
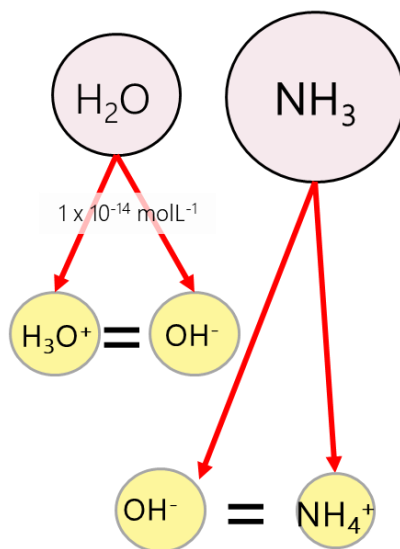
Partial dissociation
Most weak base remains

Low conductivity

Base salts

H_2O CH_3COONa

1×10^{-14} molL^{-1}

$H_3O^+ = OH^-$

$CH_3COO^- = Na^+$

$OH^- = CH_3COOH$
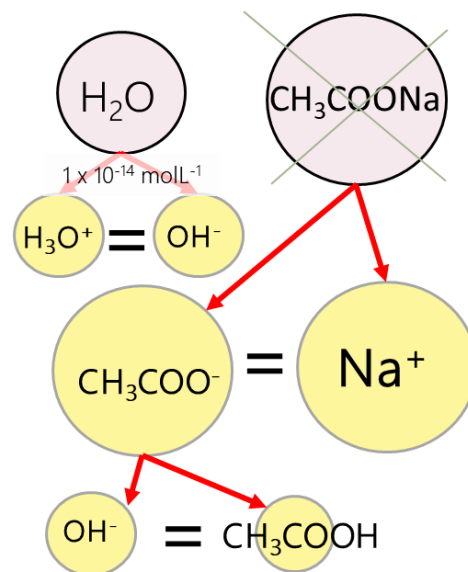
Weak base reacts further
No salt remains

High conductivity

water concentration is assumed to remain constant so is left out

Kw – the ionic product for water

K_w is ionic product for water and an equilibrium constant based on the reaction of water molecules transferring H^+ in an acid base reaction to create OH^- and H_3O^+ in equal quantities. The rate of reaction from reactants to products is the same as products to reactants once equilibrium is reached.

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \quad \text{from:} \quad 2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$(\Delta_r H = +ve)$$

Or $K_c \times [H_2O]^2 = [H_3O^+][OH^-]$

Because the concentration of water is so large it does not change → considered constant

So $K_c \times [H_2O]^2$ is also constant – called K_w

As $[H_3O^+] \times [OH^-]$ always equals 1×10^{-14} then so does K_w

Temperature increase causes an increase in Kw as the reaction is endothermic this favours the forward reaction (Le Chatelier's Principle)

Acidity constant

An acid dissociation constant, Ka, (also known as acidity constant) is a quantitative measure of the strength of an acid in solution.
It is the equilibrium constant for a chemical reaction known as dissociation in the context of acid-base reactions.
The equilibrium can be written symbolically as:
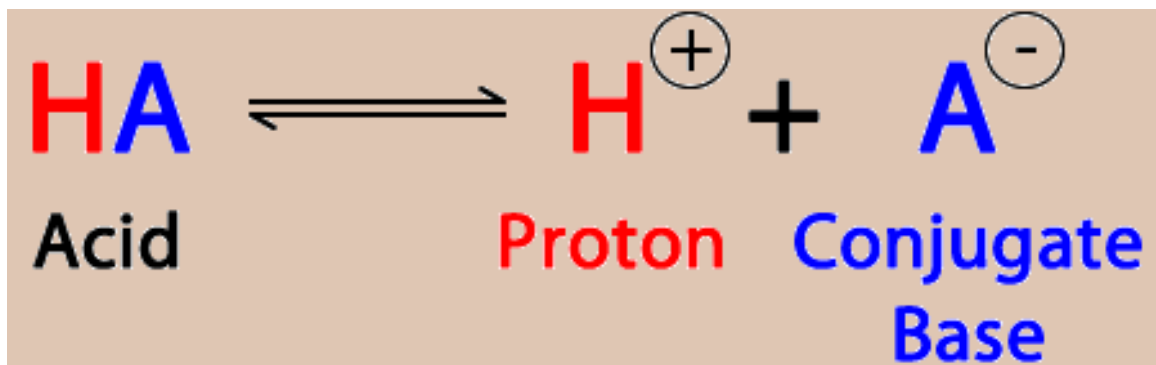
The chemical species HA, A− and H+ are said to be in equilibrium when their concentrations do not change with the passing of time.

Weak acids dissociate only slightly therefore in a solution mostly reactants will be found and the K value will be small

Strong acids completely (or nearly completely) dissociate therefore in a solution only a small amount of reactants will be found and the K value will be large

Magnitude of K increasing $\longrightarrow$

Small $(K < 10^{-3})$	Intermediate $(10^{-3} \leq K \leq 10^{3})$	Large $(K > 10^{3})$
Reactants / Products	Reactants / Products	Reactants / Products
Mostly reactants	Significant amounts of reactants and products	Mostly products
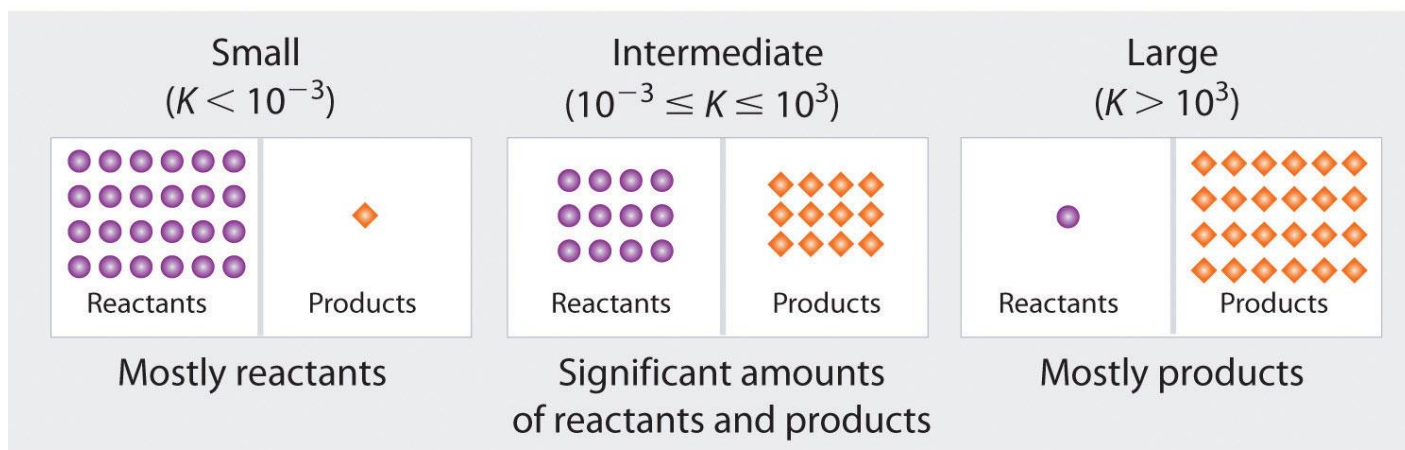
Composition of equilibrium mixture

From the equation:

HA + H_2O ↔ A^- + H_3O^+
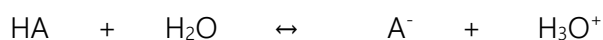
The equilibrium constant for a weak acid can be written as:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

We can also assume that the concentration of H_3O^+ and A^- are the same, as one mole of H_3O^+ forms every time one mole of A^- is created.

In a weak acid we can assume that the [HA] concentration at equilibrium is no different from the starting concentration c (HA) due to very limited dissociation.

We do not include H_2O because in an aqueous solution it is in such high concentrations that the difference before and after dissociation is negligible.

Acidity constant – assumptions	Pk$_a$
Acidity constant = K$_a$ [H$_3$0$^+$] = [A$^-$] hydronium concentration = conjugate base concentration K$_a$ = $\frac{[H_30^+]^2}{[HA]}$ → if K$_a$ small then [H$_3$0$^+$] much smaller than [HA] – <u>very little dissociation</u> [HA] can then be assumed to be equal to c(HA) $[H_3O^+] = \sqrt{K_a \times c(HA)}$	pK$_a$ = -log K$_a$ K$_a$ = 10^{-Pka} → negative for strong acids (HX) → gets larger (3 – 13) as acids get weaker – less dissociation →Weaker acid = stronger conjugate base → larger pKa more reactants

pH calculations – Weak acid

1. Convert pK$_a$ to K$_a$ (if required)

$$K_a = 10^{-Pka}$$

2. Calculate [H$_3$O$^+$]

$$[H_3O^+] = \sqrt{K_a \times c(HA)}$$

3. Calculate pH (start here if strong acid)

$$pH = -log[H_3O^+]$$

Use when

→ given Ka (acid dissociation constant)

→ given c(HA) – initial concentration of acid, as concentration at equilibrium [HA] and at the start c(HA)

 is the same

→ Weak acid, HA

$$HA \quad + \quad H_2O \quad \leftrightharpoons \quad A^- \quad + \quad H_3O^+$$
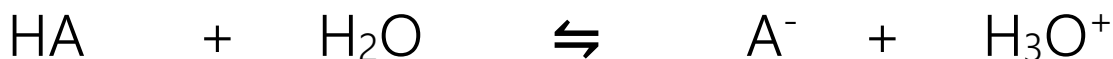
Use this equation to compare number of mols.

NOTE: As weak acids are diluted they become "stronger" as degree of dissociation (a = [H$^+$]/c$_{HA}$) increases.
(At infinite dilution, a weak acid is 100% dissociated)
This is because in the equilibrium HA + H$_2$O $\leftrightharpoons$ H$_3$O$^+$ + A$^-$, adding water dilutes all concentrations equally in the expression K$_a$ = [H$_3$O$^+$] x [A$^-$]/HA so to keep K constant, the equilibrium position needs to shift to the right.

Bases	Base dissociation constant (K_b)
$B_{(aq)} \quad + H_2O \quad \leftrightharpoons \quad BH^+ \quad + \quad OH^-$ Base water conjugate acid hydroxide <u>Strong base</u> – completely dissociates (accepts all H^+ ions) $pH = -\log[H_3O^+] \qquad [H_3O^+] = 1 \times 10^{-14}/[OH^-]$ Strong bases will have a conjugate weak acid <u>Weak base</u> – partly dissociates (accepts few H^+ ions) [B] assumed to be same as c(B) – initial concentration	$K_b = 1 \times 10^{-14} / K_a$ $[OH^-] = \sqrt{K_b \times c(B)}$ K_b is small if K_a is large – weak base and strong acid K_b is large if K_a is small – strong base and weak acid Use when → given Ka of conjugate acid (acid dissociation constant) → given concentration of reactant → Weak base, B (replace [A⁻]) $BH^+ \quad + \quad H_2O \qquad\qquad \leftrightharpoons$ $B \quad + \quad H_3O^+$ Use this equation to compare number of mols.

pH calculations – Weak base

1. Convert pK_a to K_a

    (if required)

Note the K_a is for the conjugate acid

$$K_a = 10^{-Pka}$$

2. Rearrange equation

$$[OH^-] = \sqrt{(K_b \times [B])}$$

$$[OH^-] = K_w / [H_3O^+] \qquad K_b = K_w/K_a$$

3. Calculate $[H_3O^+]$

$$[H_3O^+] = \sqrt{(K_a \times K_w \div [B])}$$

$$pH = -\log[H_3O^+]$$

4. Calculate pH

Buffer solutions

The transfer of protons between ions and water molecules controls the pH of aqueous solutions. The pH of blood, for example, is normally 7.4, and if it falls more than 0.4 from this value (because of disease or shock, both of which generate acidic conditions) then you could die. You could also die if your blood plasma pH rises to 7.8, as could happen during the early stages of recovery from severe burns. To survive, your blood system is buffered to maintain a constant pH.

 A buffer solution consists of a weak acid (to supply protons to any added strong base) and its conjugate weak base (to receive protons from any added strong acid). A buffer solution is a solution that resists changes in pH when small amounts of acid or base are added.

8 A⁻
24 HA
pH < pKa

16 A⁻
16 HA
pH = pKa

28 A⁻
4 HA
pH > pKa
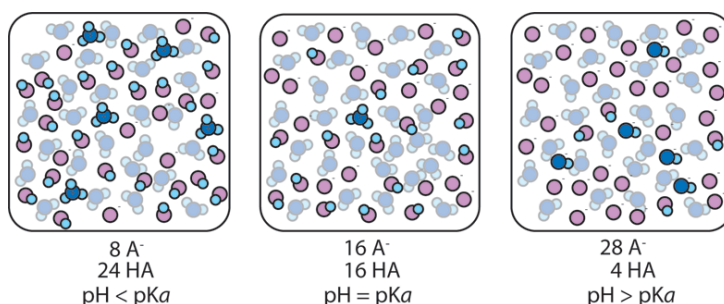
Buffer solutions

An example of a buffer solution would be one containing a mixture of ethanoic acid and sodium ethanoate. If base (OH⁻) ions are added, they will react with the ethanoic acid.

$CH_3COOH(aq) + OH^-(aq) \leftrightarrow CH_3COO^-(aq) + H_2O(l)$

If acid (H_3O^+) ions are added, they will react with the ethanoate ions.

$CH_3COO^-(aq) + H_3O^+(aq) \leftrightarrow CH_3COOH(aq) + H_2O(l)$
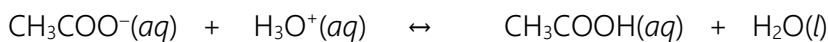
These reactions show that any added acid (H_3O^+) or base (OH^-) are largely consumed and the pH of the solution therefore hardly changes.

Buffers make use of equilibrium principles that "stabilize" the ratio of reactants to products and resist change of this

If there is a higher concentration of weak acid then the buffer will work better at neutralising acid and vice versa

Buffer calculations for monoprotic acids

Calculate pH of buffer given: k_a or Pk_a + conc of [HA] and [A⁻]

Rearrange formula

HA   +   H₂0   ↔ H_3O^+ + A⁻

$K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$ to $[H_3O^+] = K_a \times \dfrac{[HA]}{[A^-]}$

Convert to $pH = pK_a - \log \dfrac{[HA]}{[A^-]}$ or $pH = pK_a + \log \dfrac{[A^-]}{[HA]}$

Note: in a buffer solution $[H_3O^+]$ does not equal $[A^-]$ since the A^- has not been produced by the dissociation of the acid HA alone

Buffer calculations

$[H_3O^+]$ = Ka x $\dfrac{\text{[weak acid]}}{\text{[conjugate base]}}$ OR   pH = pKa + log $\dfrac{\text{[A-]}}{\text{[HA]}}$

[Weak acid or conjugate base] = $\dfrac{\text{original concentration x original volume}}{\text{final volume}}$

Note: because the buffer solution contains a higher concentration of acid than base the pH is lower (more acidic) than the pKa

Buffer capacity

The effectiveness of a buffer in maintaining pH depends on the relative concentrations of acid and base in the solution.

A buffer solution with a high concentration of acid and base can neutralise more added base and acid than one with low concentrations.

If [weak base] = [weak acid] in a buffer solution, then pH = pKa.

> **Example**
>
> If a buffer solution is made up of 0.050 mol L^{-1} benzoic acid and 0.050 mol L^{-1} sodium benzoate, show that the pH of the solution =4.19, given that pK_a(benzoic acid) =4.19.
>
> $$pH = pK_a + \log^{10}$$
>
> $$= 4.19 + \log^{10}$$
>
> $$= 4.19 + \log_{10} 1.0 = 4.19$$

Buffer Key Questions

definition ← Buffer solutions → What formula do we use to calculate pH of a buffer solution

What happens when an acid or base is added?

Draw a titration curve and show buffer zone

What pH would a buffer be if we added c(acid) with c(base) and ka given?

What is the significance of the half equivalence point?

What type of acid base titration has a buffer zone?

How could you make this a better buffer?

| $K_a = 10^{-pKa}$ | **Pathways for pH calculations** | $K_w = 1 \times 10^{-14}$ |

$B + H_2O \leftrightharpoons BH^+ + OH^-$ $HA + H_2O \leftrightharpoons A^- + H_3O^+$

| **pH of Base** | **pH of Acid** | **pH of buffer** |

$A^- = H_3O^+$ $[HA] = c(HA)$ $A^- = H_3O^+$

$K_b = \dfrac{[BH^+][OH^-]}{[B]}$

$K_a = \dfrac{[A^-][H_3O^+]}{[HA]}$

$[A-] = \dfrac{K_a \times [HA]}{10^{-pH}}$

$K_b = K_w / K_a$

$[OH^-] = \sqrt{K_b \times c(B)}$

$[H_3O^+] = \sqrt{K_a \times c(HA)}$

$n = c \times v$

$[H_3O^+] = K_w/[OH^-]$

mass ← $m = n \times M$

$pH = K_a + \log \dfrac{[A-]}{[HA]}$

$pH = -\log [H_3O^+]$

$[H_3O^+] = \sqrt{K_a \times K_w \div c(B)}$ **pH** → $[H_3O^+] = 10^{-pH}$ → $[H_3O^+]$

Acid – base titration curves

A plot of the pH of an acid solution against the volume of added base (or vice-versa) produces what is called a pH titration curve. The example below shows how the pH (measured using a pH meter) changes when a strong acid is added to a strong base. There are characteristic points on the curve that can be identified. One of these is the equivalence point, the midpoint of the section where the pH of the solution rises (or falls) sharply. The equivalence points for titrations between a strong acid and a strong base have a pH of 7. Both before and after this section the pH only changes slowly.
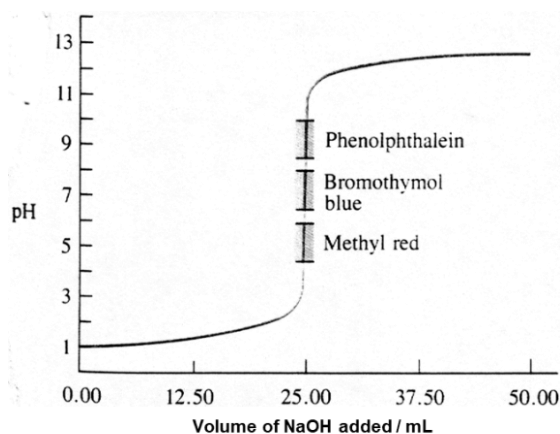
Because the pH rises so sharply at the equivalence point of a strong acid/strong base titration a range of indicators can be used to determine the end-point of the titration. If the indicator has a pKa value equal to a pH value within the steep rise in the curve then it will change colour at the equivalence point for this titration.

The pH curve below shows a typical shape for the titration of a weak acid with a strong base e.g. methanoic acid with sodium hydroxide.

Note that the equivalence point has a pH > 7 since at this point, it is a solution of sodium methanoate and the methanoate ion is a weak 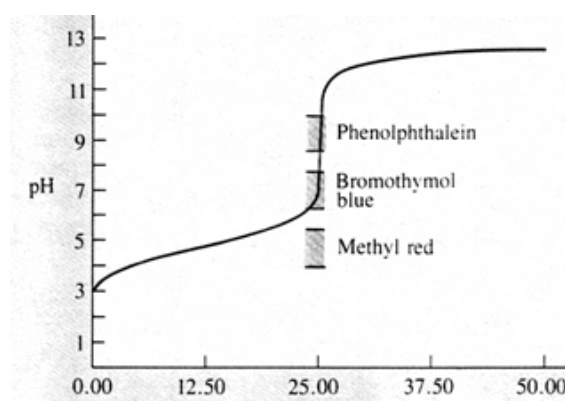base since it is the conjugate of the weak acid methanoic acid. At the equivalence point the $HCOO^-$ formed reacts with water:

$$HCOO^- + H_2O \quad \rightleftharpoons \quad HCOOH + OH^-$$

The equivalence point is at a pH greater than 7 so only indicators with a pK_a about 8-9 will change colour at the correct pH and be useful.

Neutralisation of acids
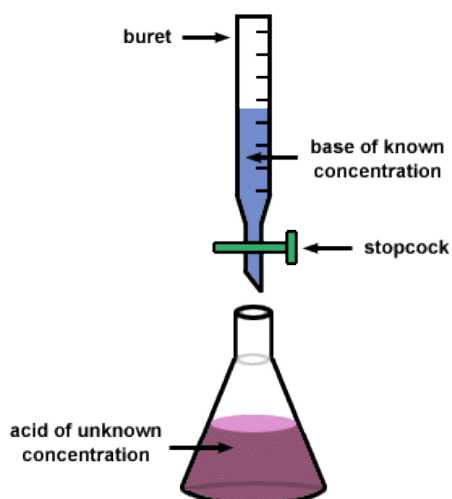
Acids are neutralised by bases. The amount of base needed to neutralise an acid depends only on the concentration and volume and is independent of the acid strength. The concentration of an acid solution is found by carrying out a titration with a base of accurately known concentration (called a standard solution). Such a titration is also called a volumetric analysis. Given the titration data, it is possible to calculate the acid concentration. To determine the amount of base needed to neutralise an acid we normally use an appropriate acid-base indicator and stop the titration at the point when the indicator changes colour. This is called the end-point of the titration. This is the point when the amount of added base is exactly equal to the initial amount of acid in the solution.

The pH of the equivalence point will determine the choice of indicator used.
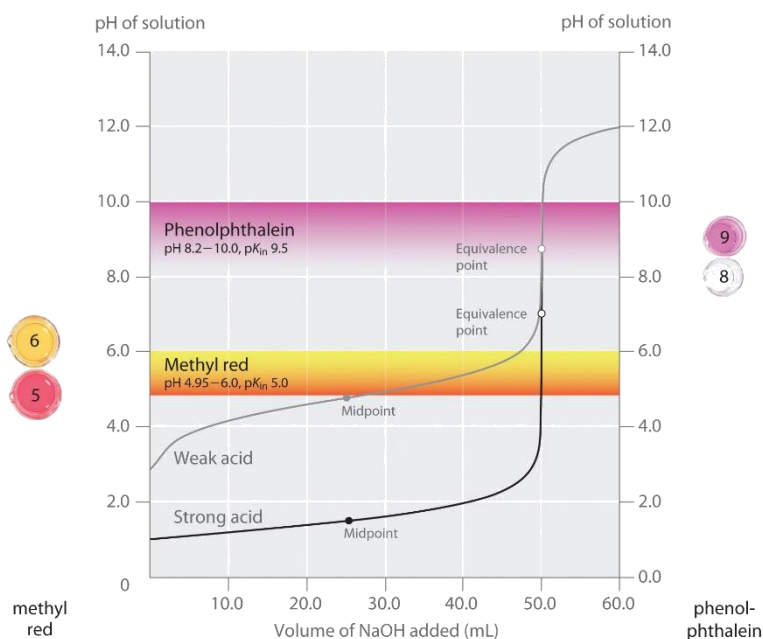
Features of a titration curve – strong base/weak acid
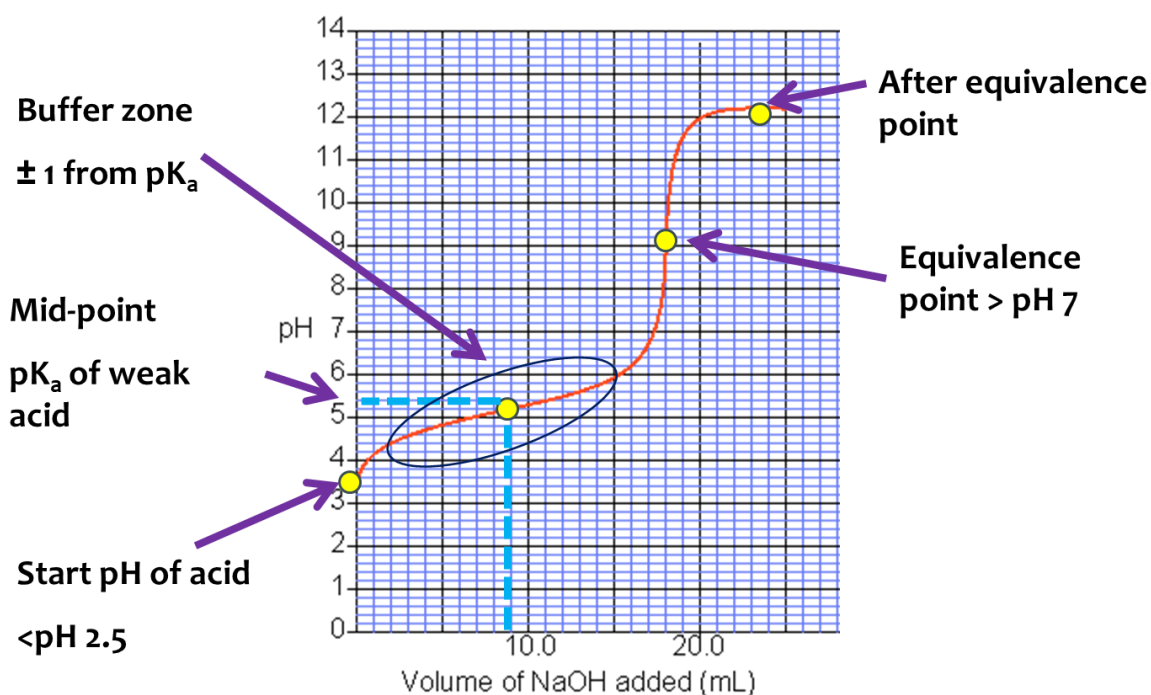
1. Start pH of acid - The initial pH of the solution is due to the starting acid or base in the flask. This is where your titration curve begins

2. Equivalence point - This is the point when all of the weak acid has reacted with the base being added. This will be the most vertical point on the graph.

3. Mid-point – This will be exactly half way in volume to the equivalence point. The pk_a will be the pH of the midpoint.

4. Buffer Zone – This will be an area 1 pH either side of the mid - point. It can be plotted on the graph as a circled area

5. After the equivalence point – The pH depends on the concentration of the solution being added from the burette.

Strong Base added to Strong Acid
Characteristics:
Start point below pH 3
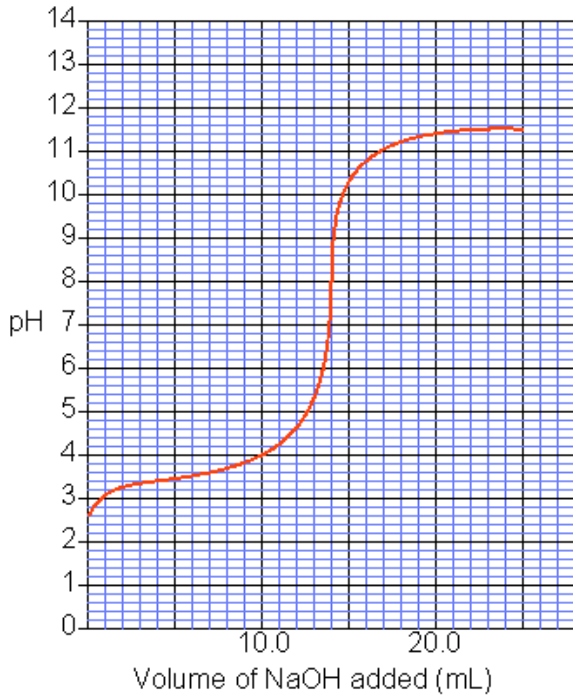Equivalence point at 7
End of titration below pH12
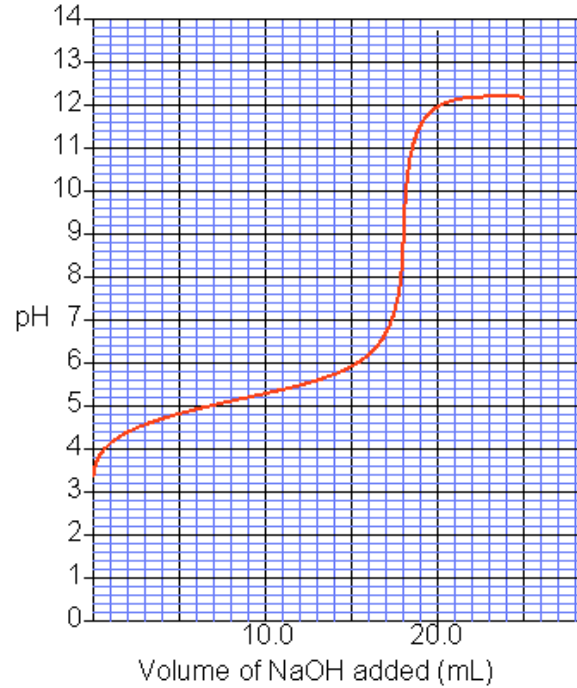Symmetrical shape

Strong Base added to Weak Acid
Characteristics:
Start point above pH 3
Equivalence point above 7
End of titration above pH12
Unsymmetrical shape
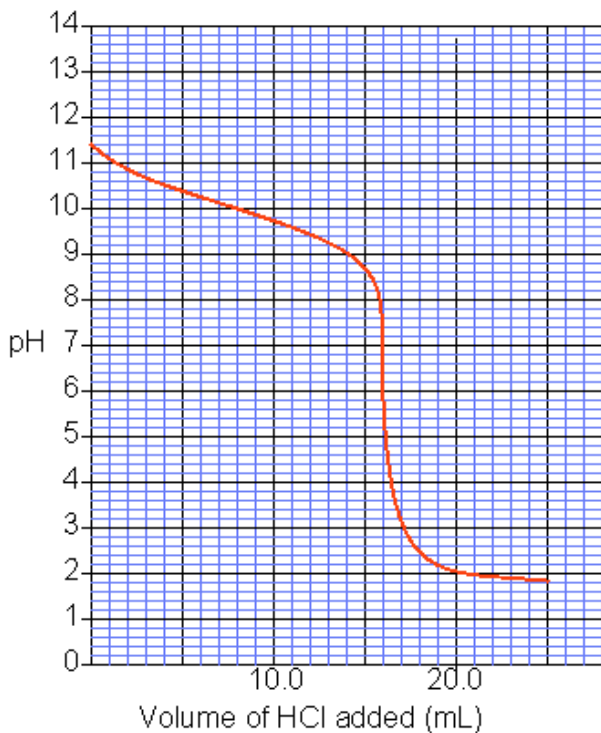

Strong Acid added to Weak Base
Characteristics:
Start point below pH 12
Equivalence point below 7
End of titration below pH3
Unsymmetrical shape

Drawing titration curves

Step One: Calculate the start pH (in flask) Weak acid $[H_3O^+] = \sqrt{K_a \times c(HA)}$ Weak base $[OH^-] = \sqrt{K_b \times c(B)}$ Assumptions: $[HA] = c(HA)$ H_2O concentration is the same before and after $[H_3O^+] = $ [conjugate base]	**Step One: Start pH** Information given Find the pH of: $0.0896\ molL^{-1}$ of $CH_3COOH_{(aq)}$ $pK_a = 4.76$ $CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$ $K_a = \dfrac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 10^{-pKa}$ Dissociation equation of weak acid $= 10^{-4.76}$ $= 1.74 \times 10^{-5}$ K_a expression Assume 1. $[CH_3COO^-] = [H_3O^+]$ Calculate K_a from pK_a given 2. $[CH_3COOH] = 0.0896\ molL^{-1}$ Assumptions for pH calculation
	Step One: Start pH Equilibrium expression of acid dissociation in water $K_a = \dfrac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$ $1.74 \times 10^{-5} = \dfrac{[H_3O^+]^2}{0.0896\ mol\ L^{-1}}$ Rearrange: $\sqrt{1.74 \times 10^{-5} \times 0.0896\ mol\ L^{-1}} = [H_3O^+]$ Calculate $[H_3O^+] = \sqrt{K_a \times c(HA)}$ Could also use 10^{-pKa} directly in formula $1.25 \times 10^{-3}\ molL^{-1} = [H_3O^+]$ $= -log(1.25 \times 10^{-3}\ molL^{-1})$ Double check your answer by making sure the pH fits within the range of your starting acid or base (weak or strong) $pH = 2.90$
Step Two: Calculate the volume at equivalence point a) Calculate the number of moles of known acid or base (the substance where the concentration has been given) $n = c \times v$ b) Multiply the number of moles by U/K c) Rearrange equation to calculate volume $v = n / c$ v = volume (L) c = concentration $(molL^{-1})$	**Step Two: Volume of equivalence** Calculate the volume of NaOH at the endpoint. Titration reaction is: $CH_3COOH_{(aq)} + NaOH_{(aq)} \rightarrow CH_3COONa_{(aq)} + H_2O_{(l)}$ $n(CH_3COOH) = cV$ Neutralisation equation at end point $= 0.0896\ mol\ L^{-1} \times 0.0200L$ $= 1.79 \times 10^{-3}\ mol$ From the equation 1:1. Every mole of $CH_3COOH = NaOH$ $n(NaOH) = n(CH_3COOH)$ Volume of acid in flask at start $= 1.79 \times 10^{-3}\ mol$ $V(NaOH) = n / c$ $V(NaOH) = \dfrac{1.79 \times 10^{-3}\ mol}{0.100\ molL^{-1}}$ Convert to mL for titration curve Rearrange n=c/v to calculate v of NaOH needed to neutralise CH_3COOH present $V(NaOH) = 17.9mL$

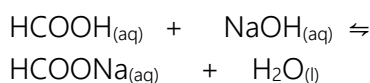| Step Three: Calculate the midpoint Volume of the buffer zone
 	
  a) Volume (x axis) = equivalence point volume / 2
 	
  b) pH (y axis) = pK_a of the Weak Acid (or conjugate acid of Weak base)
 	
The buffer zone is 1 pH either side of the mid-point
	Step Three:
	Mid-point of Buffer
	
	Calculate the volume of NaOH when pH = pKa
	
	The volume of NaOH at equivalence point is 17.9mL
	
	When exactly ½ way to end point then ½ acid has dissociated into conjugate (CH₃COOH) = (CH₃COO⁻)
	
	17.9mL /2 = 8.96mL (x)
	
	pKa = 4.76 (y)
	
	These points intercept on the graph
	
	The pH = pKa when **8.96 mL** of NaOH has been added
	
	The buffer zone will be 1 pH point above and below pH 4.76 Once the curve is drawn this can be sketched as a circle around the area from 3.76 – 5.76 on the line.
	
	The buffer zone is where pH will change slowly (flatter line) due to equilibrium principles

Step Four: Calculate pH of the equivalence point (end point) a) Use the number of moles (n) of base (as calculated in step two) required to completely react with n of acid present to reach equivalence. Each 1 mole of base required to react with acid produces 1 mole of conjugate base. Example $HCOOH_{(aq)}$ + $NaOH_{(aq)}$ ⇌ $HCOONa_{(aq)}$ + $H_2O_{(l)}$ b) Calculate c(conjugate base) using c = n/v V = initial volume in flask + volume added during titration to reach equivalence c) Use pH equations $$[H_3O^+] = \sqrt{\dfrac{k_a \times k_w}{c(\text{conjugate base})}}$$	**Step Four:** **pH of equivalence** Calculate the pH at equivalence point. At the Equivalence point we will have: 1.79×10^{-3} mol of CH₃COONa in (20mL + 17.9mL = 37.9mL) of solution C(CH₃COONa) = $\dfrac{1.79 \times 10^{-3} \text{ mol}}{0.0379L}$ = 0.0472 molL⁻¹ Total volume from starting flask + added from burette At neutralisation (from equation), for every mole of original acid there is now an equal amount of conjugate (CH₃COO-) formed c = n/v We need to calculate the pH of a solution of CH₃COONa with this concentration: 0.0472 molL⁻¹ As the pH of the equivalence point is determined by a conjugate that is base (paired with starting weak acid) then it will be above pH 7 The **amount of conjugate of the weak acid present will determine the pH** at end point. All acid at start has been now been neutralised --- **Step Four:** **pH of equivalence** $CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$ $[H_3O^+] = \sqrt{(K_a \times K_w \div [\text{Conj base}])}$ $[H_3O^+] = \sqrt{(10^{-4.76} \times 10^{-14} \div [0.0472 \text{ molL}^{-1}])}$ $[H_3O^+] = 1.92 \times 10^{-9}$ molL⁻¹ pH = -log (1.92×10^{-9} molL⁻¹) Intercept this this pH point with v calculated for the endpoint **pH = 8.72** Each mol of conjugate formed will produce 1 mol of OH- ions, which determines the pH Assume 1 [CH₃COO⁻] = [OH⁻] 2 [CH₃COO⁻] = 0.0472 molL⁻¹ Concentration calculated from previous step c=n/v

Step Five: Calculate pH after the equivalence point

$[OH^-]$ = start concentration x volume added after equivalence

total volume acid + base

Plot all of these points on the graph and join with a curved line.

If the acid or base is weak the curve will be gentle, if the acid or base is strong the curve will be sharp.

Step Five: Final pH

Calculate the pH after 30mL of NaOH has been added.

Since the equivalence point is at 17.9mL of NaOH, this results in an excess of 12.1mL of NaOH

Volume of after equivalence point

Calculate concentration of added base or acid. Although the conjugate does react we assume all $[OH^-]$ or $[H_3O^+]$ comes from excess added

Total volume of solution = 20mL + 30mL = 50mL

$C(NaOH) = \dfrac{12.1mL}{50\ mL} \times 0.100molL^{-1}$

Original concentration

Dilution calculation

= 0.0242 molL^{-1}

New concentration after dilution

(30mL - 17.9mL = 12.1mL)

Step Five: Final pH

NaOH is a strong base

Assume $[OH^-]$ = c(NaOH)

$[OH^-]$ = 0.0242 molL^{-1}

Strong bases or acids fully dissociate

$[H_3O^+] = K_w/[OH^-]$

$[H_3O^+]$ = K_w / 0.0242 molL^{-1}

$[H_3O^+]$ = 1×10^{-14} / 0.0242 molL$^-$

$[H_3O^+]$ = 4.13×10^{-13} molL^{-1}

pH = $-\log(4.13 \times 10^{-13}$ molL$^{-1})$

Plot this point on your graph

pH = 12.4

Drawing Curve

Now we have the key data points:

☐ The pH before any Base added = 2.90

☐ The volume of NaOH at equivalence point: 17.9 mL

☐ The volume of NaOH when pH = pKa: 8.96 mL

☐ The pH at equivalence point: 8.72

☐ The pH after 30mL of NaOH is added: 12.4

Drawing Curve

Plot these points on a graph

Titration of 20 mL of ≈0.1 mol/L acetic acid with 0.100 mol/L strong base

volume	pH
0.00 mL,	2.90
8.96 mL,	4.76
17.9 mL,	8.72
30.0 mL,	12.4

http://www.iq.usp.br/gutz/Curtipot_.html#Download

Why is pKa = pH at mid-point of the buffer?

At this point, half of the weak acid has reacted with the base to form equal quantities of conjugate.

Acid + water $\leftrightharpoons$ conjugate base + H_3O^+

So K_a = ~~[conjugate base]~~ $[H_3O^+]$
~~[acid]~~

If they are equal concentration they are cancelled and K_a = $[H_3O^+]$

Therefore pK_a = pH   as pK_a = -log K_a and   pH = -log $[H_3O^+]$

Calculating pH after an amount of base (or acid) is added

Sample question: 20.0 mL of 0.0896 mol L^{-1} ethanoic acid is titrated with 0.100 mol L^{-1} sodium hydroxide.

pKa (CH_3COOH) = 4.76

Calculate the pH of the titration mixture after 5.00 mL of NaOH has been added.

$NaOH(aq) + CH_3COOH_{(aq)} \rightarrow NaCH_3COO_{(aq)} + H_2O_{(l)}$

$n(CH_3COOH$ at start$) = 0.0896 \times (20 \times 10^{-3}) = 1.79 \times 10^{-3}$ mol

$n(NaOH$ added$)$ $= 0.1 \times (5 \times 10^{-3}) = 5 \times 10^{-4}$ mol

After 5 mL NaOH added: (total 25mL)

$n(CH_3COOH)$ $= 1.29 \times 10^{-3}$ mol

$n(CH_3COO^-)$ $= 5 \times 10^{-4}$ mol

$[CH_3COOH] = 0.0516$ mol L^{-1}

$[CH_3COO^-]$ $= 0.0200$ mol L^{-1}

pH   **= 4.35**

> Calculate the number of moles of **20ml** acid
> **n = c x v**

> Calculate the number of moles of **5ml** base

> Subtract moles of base from acid
> (n(CH_3COOH – n(NaOH) after 5mL)

> c=n/v
> Volume is **25ml** total

> pH = pK_a + log $\left(\dfrac{[CH_3COO-]}{[CH_3COOH]} \right)$

$K_a = 10^{-pKa}$ **Titration calculations** $K_w = 1 \times 10^{-14}$

1. Start pH

W BASE (add acid)
$B + H_2O \leftrightharpoons BH^+ + OH^-$

5. Final pH

W ACID (add base)
$HA + H_2O \leftrightharpoons A^- + H_3O^+$

$[H_3O^+] = \sqrt{K_a \times K_w \div c(B)}$

C(from burette) =
$\dfrac{V(\text{after eq.}) \; x \; C(\text{original})}{V(\text{total})}$

$[H_3O^+] = \sqrt{K_a \times c(HA)}$

pH = -log $[H_3O^+]$

Strong acid

2. Volume of endpoint

acid + base $\rightarrow$ salt + H_2O

pH

Strong base

$[H_3O^+] = Kw \div [OH^-]$

n(in flask) $= c \; x \; v$

n(acid) = n(base)

pH above 7

$[H_3O^+] = \sqrt{K_a \times c(HA)}$

$A^- + H_2O \leftrightharpoons HA + OH^-$

pH below 7

$[H_3O^+] = \sqrt{K_a \times K_w \div c(B)}$

$BH^+ + H_2O \leftrightharpoons B + H_3O^+$

V(from burette) $= n \; x \; c$

c(conj.)$= n \div$ total v

3. Midpoint buffer zone

x = Endpoint v ÷ 2

y = pKa

4. pH of equivalence point