

With 2017 NCEA  
Exam included

2018  
Version



**Chemistry AS 91392**  
C3.6 Aqueous Systems

# Achievement Criteria - Solubility

## 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<sub>2</sub>B and AB<sub>2</sub> types where neither of the ions A nor B reacts further with water.

Candidates are expected to recognise common strong acids (HCl, HBr, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>); strong bases (KOH, NaOH); weak acids (HF, CH<sub>3</sub>COOH, and NH<sub>4</sub><sup>+</sup>); weak bases (NH<sub>3</sub>, CH<sub>3</sub>NH<sub>2</sub>, and CH<sub>3</sub>COO<sup>-</sup>). 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.

AS 91392

C3.6

## Achievement Criteria – Acids and Bases

AS 91392

C3.6

### Demonstrate understanding of equilibrium principles in aqueous systems

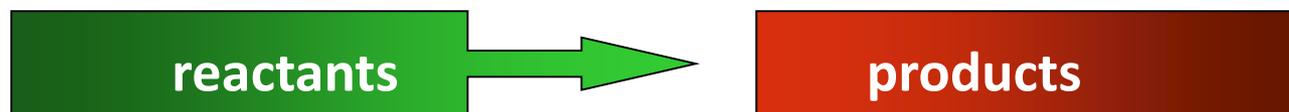
*Aqueous systems* are limited to those involving acidic and basic solutions (in which proton transfer occurs).

- ☐ 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).

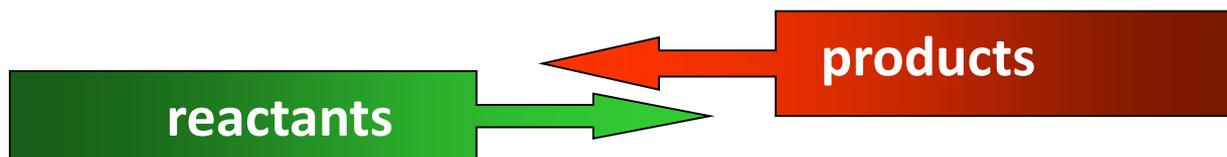
# Equilibrium

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

**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.

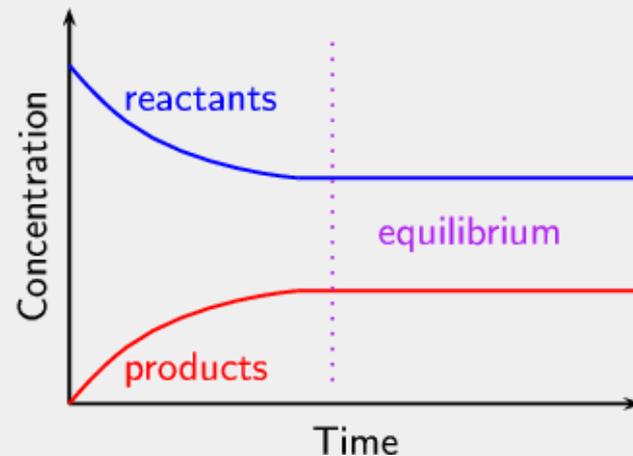
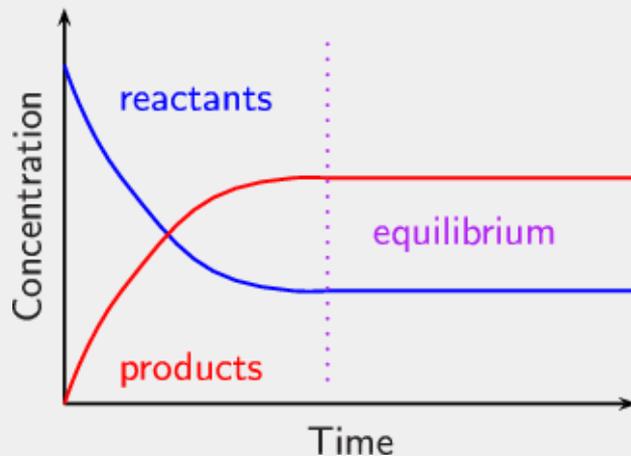
However, both the forward and reverse reactions are continuing

## Equilibrium

When a reaction has reached equilibrium then the proportion of reactants is fixed in relation to the proportion of products. Reactants particles are still colliding to form products but the same number of products are colliding (or breaking apart) to form reactants.

The proportion of reactants to products depends upon the reaction and the environmental conditions of a reaction such as temperature, pressure and concentration.

On the left hand side the proportion of products will be higher than the reactants and on the right hand side the proportion of reactants will be higher than products.



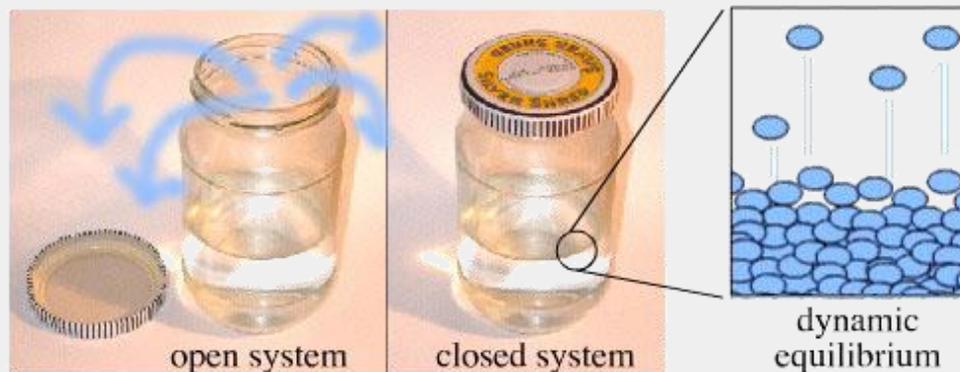
## Equilibrium – Evaporation case study

A dynamic equilibrium must occur in a closed system where all reactants and products are retained in an area where particles can collide with each other.

The example below shows a system where liquid water is evaporating into a gas.

In an open system the gas will escape and gradually the water level will decrease.

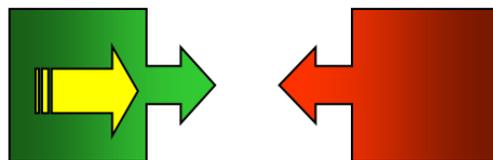
In a closed system, where the lid prevents the gas escaping, the proportion of liquid to gas will become fixed at a dynamic equilibrium. Liquid will evaporate into gas at the same rate that gas condenses into a liquid.



## Changes in Equilibrium

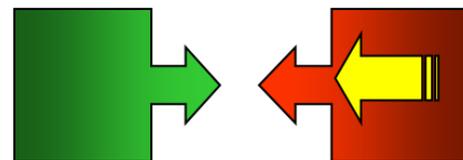
A system stays in equilibrium unless a change is made  
A change made to a system in equilibrium will **either**

Increase the rate of the  
**forward reaction**



OR

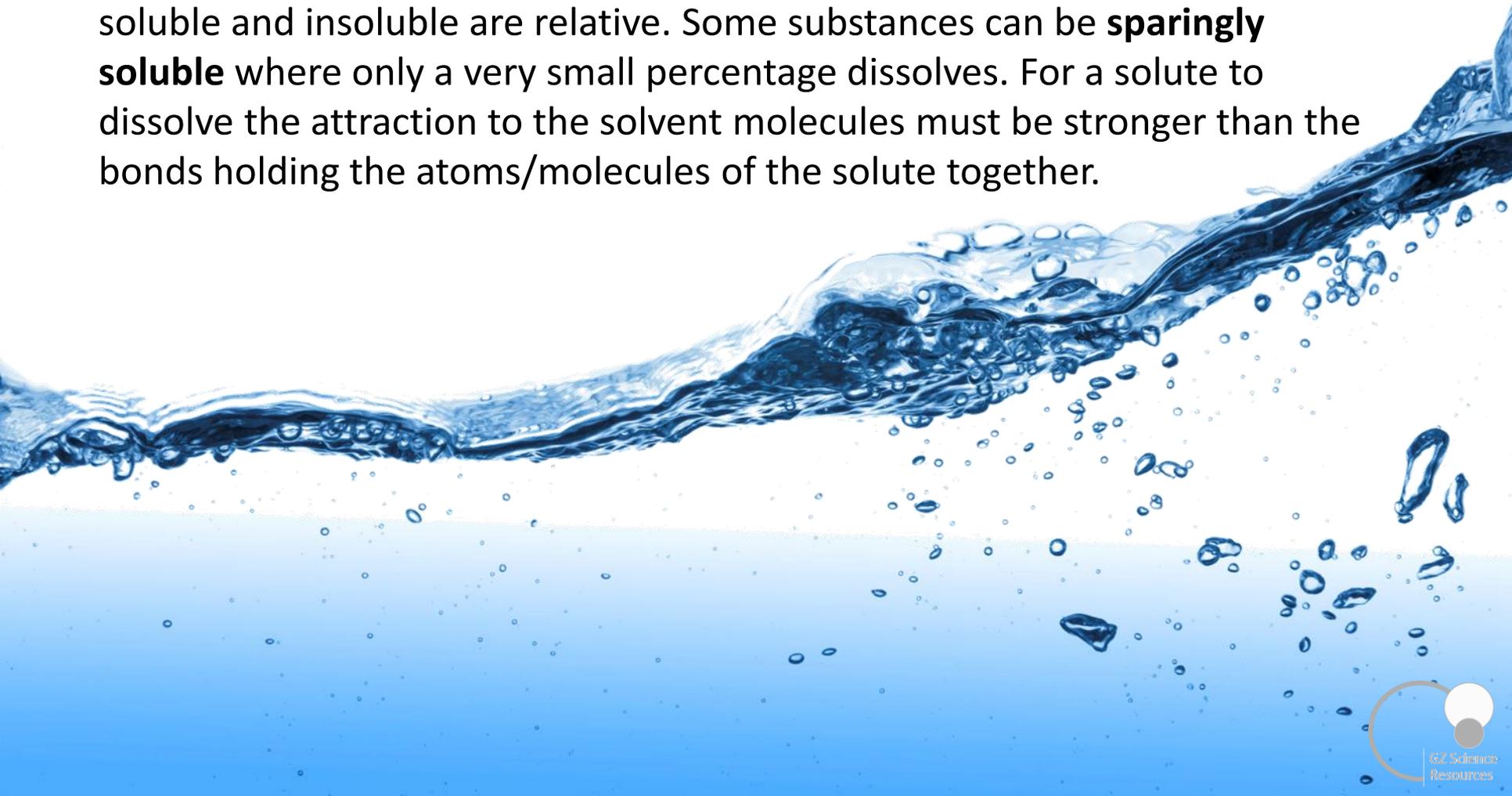
Increase the rate of the **reverse**  
reaction



**Eventually equilibrium is re-established** and the rate of forward reaction again **equals** rate of reverse reaction

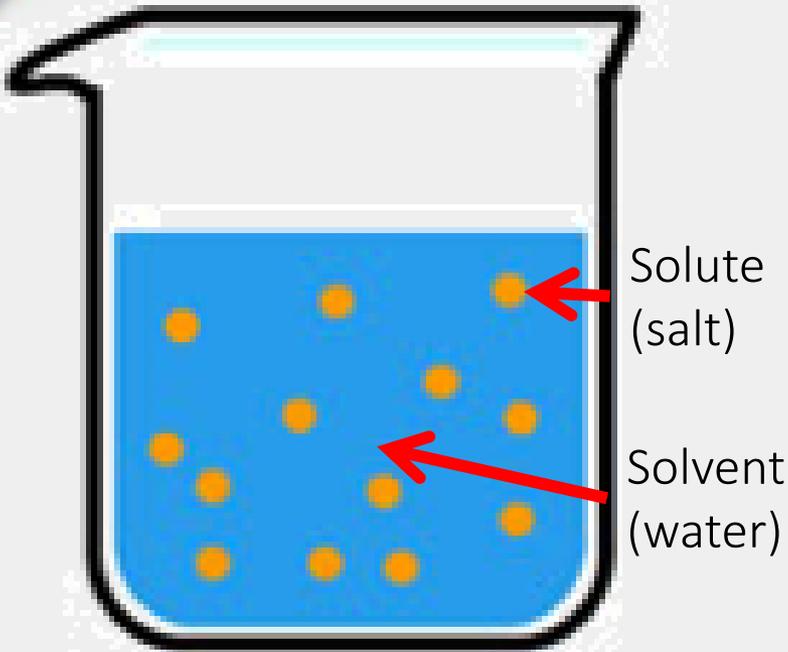
# Solubility

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.



## Aqueous Solutions

A **solution** is made up of a **solvent** and a **solute**. A solvent is a substance such as water that is able to dissolve a solute. A solution where the **solvent is water is called aqueous**. The solvent 'pulls apart' the bonds that hold the solute together and the solute particles **diffuse** (spread randomly by hitting into each other) throughout the solvent to create a solution. The solution is a **mixture** with evenly spread solvent and solute particles. These particles can be physically separated by **evaporation**.

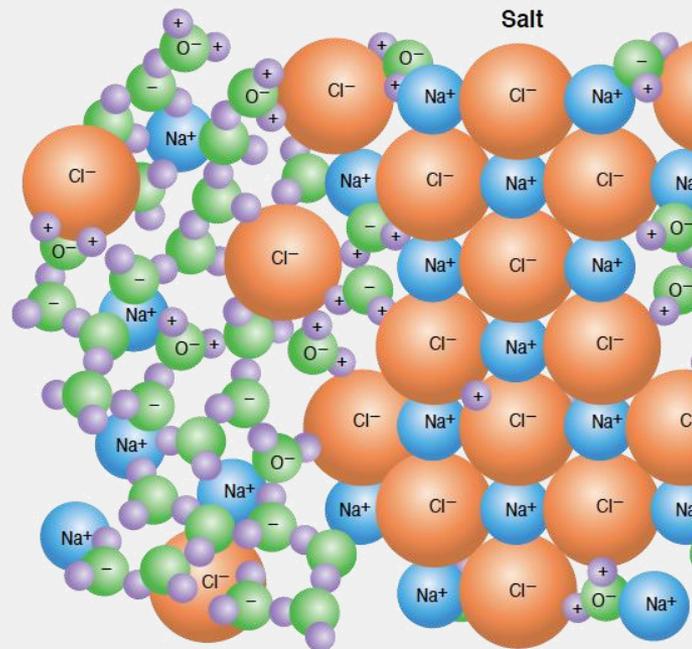


Solution  
(saltwater)



## Aqueous Solutions

When a solid mixes into a liquid and can no longer be seen it has dissolved. The liquid is called the solvent and it pulls apart the bonds between the solid particles, called the solute, and they diffuse. A solution is then created when the solvent particles (often water) are mixed up with the broken apart solute particles.



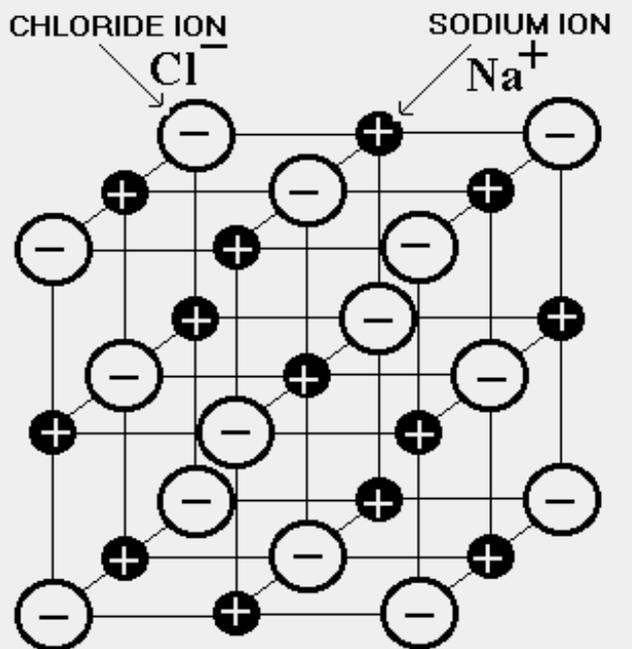
**For a solute to dissolve, the solvent particles must form bonds with the solute particles that are of similar strength, to the bonds between the solute particles.**

**Water, being polar attracts ions because they are charged and so dissolves many ionic substances.**

## The structure of Ionic Solids

### Metal + Non-Metal

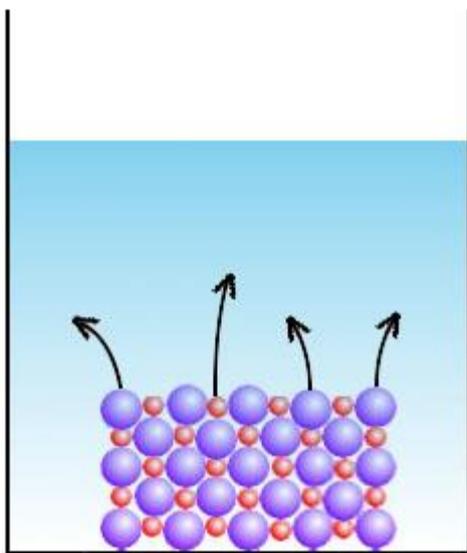
An ionic solid is made up of ions held together by strong directional electrostatic forces (ionic bonding) between +ve (cations) and -ve (anions) ions in a 3-dimensional lattice.



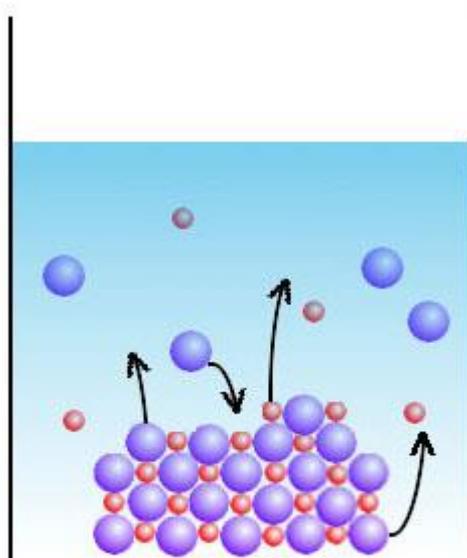
SODIUM CHLORIDE LATTICE STRUCTURE

# Equilibrium of solutions

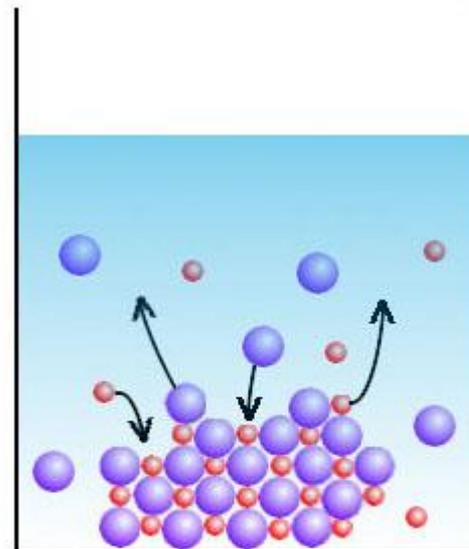
A system reaches **equilibrium** when the rate the solid dissociates into ions matches the rate that the ions precipitate into solids. The equilibrium can be changed permanently by adjusting the system temperature ( or temporarily - pressure or adding/removing reactants/product)



Salt is initially put into the water and begins dissolving.



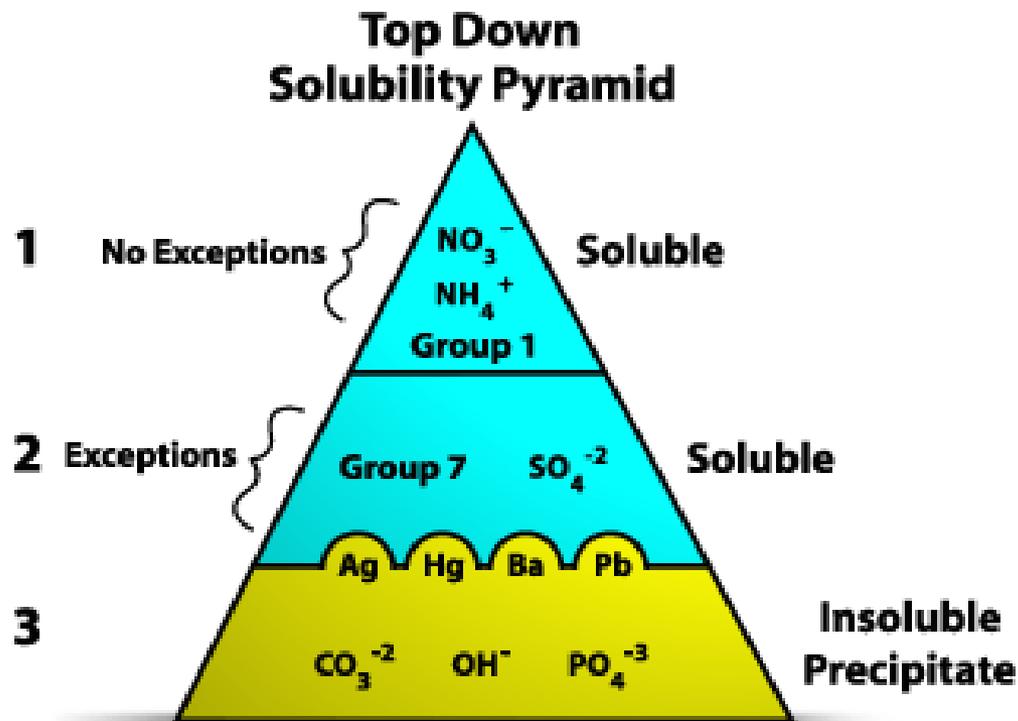
Salt continues to dissolve; however, dissolved ions will also precipitate. Because the salt dissolves faster than its ions precipitate, the net movement is towards dissolution.



Eventually, the rate of dissolution will equal the rate of precipitation. The solution will be in equilibrium, but the ions will 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.



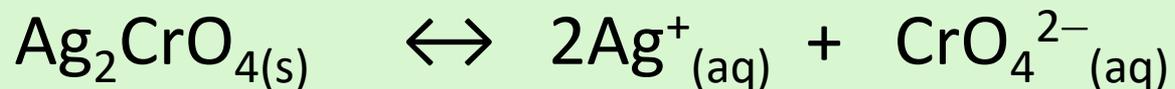
The solubility of a salt is often measured in grams per litre,  $\text{g L}^{-1}$ , or **moles per litre,  $\text{mol L}^{-1}$** . This is the number of grams or moles of the solid that will dissolve to make up 1 litre of a saturated solution at that temperature. If the solubility of a pure salt is given 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.



**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,  $\text{Ag}_2\text{CrO}_4$ , is  $6.5 \times 10^{-5} \text{ mol L}^{-1}$ .

What is the concentration of  $\text{Ag}^+$  and  $\text{CrO}_4^{2-}$  ions [s] in 500 mL of a saturated solution?

Start with the equation for the dissolving process.



The equation shows that for every mole of dissolved solid there are **2 moles of  $\text{Ag}^+$  ions** and **1 mole of  $\text{CrO}_4^{2-}$  ions**. Therefore

$$[\text{Ag}^+] = 2 \times 6.5 \times 10^{-5} = 1.3 \times 10^{-4} \text{ mol L}^{-1}$$

$$[\text{CrO}_4^{2-}] = 6.5 \times 10^{-5} \text{ mol L}^{-1}$$

**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  $6.5 \times 10^{-5} \text{ mol L}^{-1}$  (at room temperature).



## Solubility from molL<sup>-1</sup> to gL<sup>-1</sup>

**Example question: What is the solubility [s] of Ag<sub>2</sub>CrO<sub>4</sub> in g L<sup>-1</sup>?**

To convert from moles per litre to grams per litre it is necessary to use the molar mass  $M(\text{Ag}_2\text{CrO}_4) = 332 \text{ g mol}^{-1}$  and the relationship  **$m = n \times M$** .

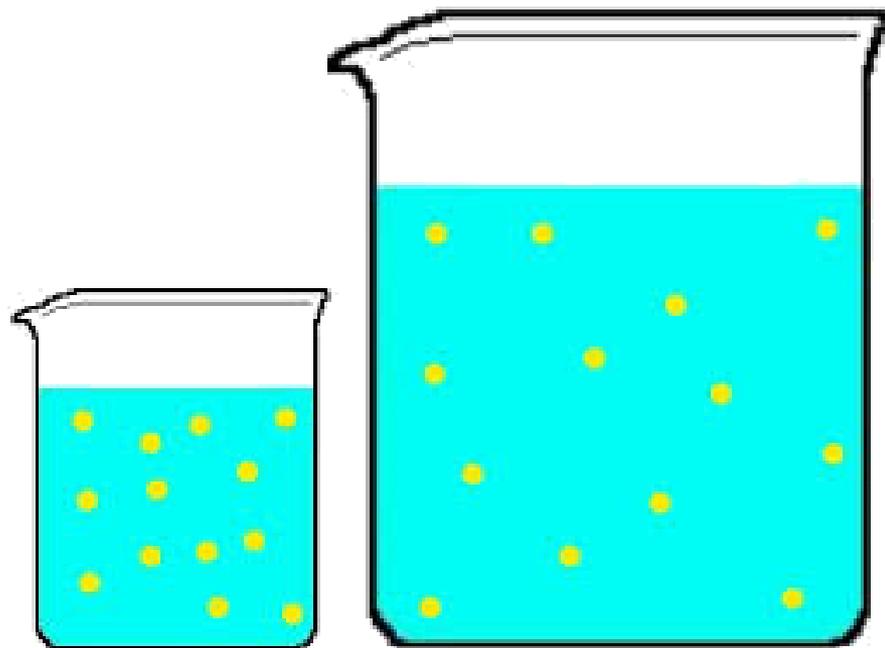
$$s = 6.5 \times 10^{-5} \text{ mol L}^{-1}.$$

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

$$\text{mass} = 6.5 \times 10^{-5} \times 332$$

$$= 0.0216 \text{ grams}$$

and the concentration is  $0.0216 \text{ g L}^{-1}$ .



# Equilibrium Constant: $K_c$

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

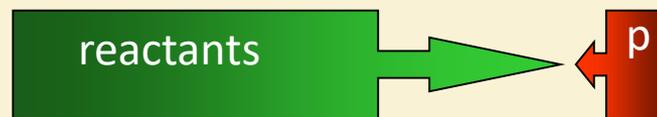
## Large $K$ value eg $K=10000$

Large amount of products produced.  
Reaction is close to completion when equilibrium was reached



## Small $K$ value eg $K=0.0001$

Small amount of products produced .  
Reaction only just underway when equilibrium was reached

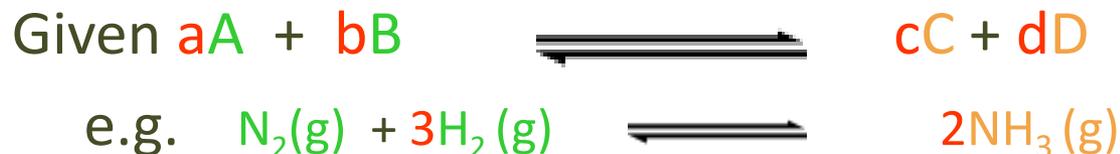


**Note:** equilibrium does not mean there are equal amounts of reactants and products present

## Equilibrium Constant: $K_c$

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 indicate the proportion of reactants to products in any given reaction.

**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.



$$K_c = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

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

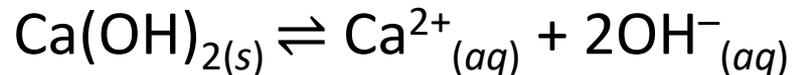
e.g.  $K_c = \frac{[NH_3]^2}{[N_2] \times [H_2]^3}$

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

## Solubility product $K_s$

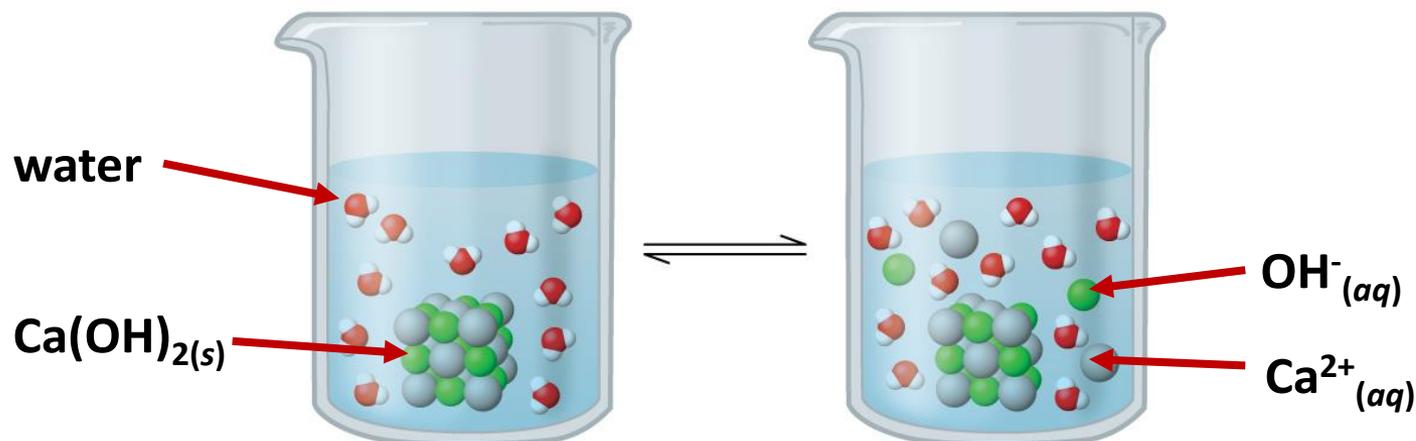
The solubility product is the equilibrium constant for the equilibrium between an **undissolved salt and its ions in a saturated solution**. It is very similar to any other equilibrium constant and, for any particular salt, the value of  $K_s$  only changes if temperature changes.

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



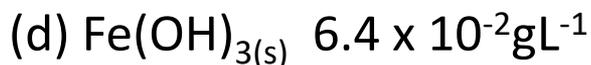
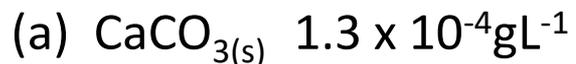
$$K_s (\text{Ca}(\text{OH})_2) = [\text{Ca}^{2+}] [\text{OH}^{-}]^2$$

**Remember: Water is not included in the equation or expression because the very large concentration before and after means there is negligible change**



## Solubility product $K_s$

**Exercise:** For each of the following sparingly soluble salts write the equation for the solid dissolving, calculate the **concentration of each ion [s]** and then the **expression for the solubility product [K<sub>s</sub>]**.



$$K_s = [C]^c \times [D]^d$$

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

**Remember: The solid salt is not included in the expression only the ions in aqueous state.**

NOTE: If there is a 2:1 or 1:2 ratio of ions in the salt, the appropriate ion concentration must be multiplied **AND** also squared in the  $K_s$  expression.

## 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  $\text{BaSO}_4$  is given as  $1.05 \times 10^{-5} \text{ mol L}^{-1}$  at  $25^\circ\text{C}$ . Calculate the value of  $K_s$ .



From this equation  $[\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = \text{solubility, } s$

$$K_s = s^2$$

$$\begin{aligned} K_s(\text{BaSO}_4) &= [\text{Ba}^{2+}] \times [\text{SO}_4^{2-}] = s^2 = (1.05 \times 10^{-5})^2 \\ &= 1.10 \times 10^{-10} \end{aligned}$$

**NOTE:** This equality is only true if there are no other sources of  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$  present in the solution ie if all the  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$  ions come from the dissolved solid

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



$AB_2$  (or  $A_2B$ ) 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  $1.52 \times 10^{-3} \text{ mol L}^{-1}$ .



This tells us that  $[Pb^{2+}] = \text{solubility, } s = 1.52 \times 10^{-3} \text{ mol L}^{-1}$

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

The expression for  $K_s$  is  $K_s (PbI_2) = [Pb^{2+}] \times [I^{-}]^2$

and substituting for solubility we get

$$K_s (PbI_2) = (1.52 \times 10^{-3}) \times (3.04 \times 10^{-3})^2 = 1.40 \times 10^{-8}$$

$$K_s = 4s^3$$

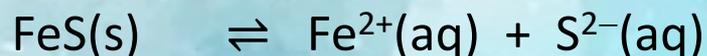
**NOTE:** because  $[2s]^2$  means everything inside the brackets is squared then expanding it out becomes  $2^2 \times s^2 = 4s^2$ . The other ion  $[s]$  then is multiplied so the whole expression becomes  $4s^3$  (cubed)

## 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 also to calculate the concentration of ions in the saturated solution.

### Example

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



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

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

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

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

$$s = \sqrt{K_s}$$

## Determining S from $K_s$ (2:1)

$$s = \sqrt[3]{\frac{K_s}{4}}$$

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

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

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

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

$$\text{OR } K_s (\text{Zn}(\text{OH})_2) = (s) \times (2s)^2 = 4s^3$$

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

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

**From the solubility it is possible to then calculate the concentration of the ions.**

$$[\text{Zn}^{2+}] = \text{solubility} = 1.71 \times 10^{-6} \text{ mol L}^{-1}$$

$$[\text{OH}^-] = 2s = 2 \times 1.71 \times 10^{-6} = 3.42 \times 10^{-6} \text{ mol L}^{-1}$$

## Effects of Acid on Solubility

If the salt contains a carbonate i.e.  $\text{Ag}_2\text{CO}_3$  which is sparingly soluble, it will dissociate into its ions – one ion being a cation and the other the anion carbonate.



**Acid neutralises carbonates**

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

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  $\text{Ag}^+$  which reacts with  $\text{NH}_3$  or  $\text{OH}^-$  to produce a complex ion such as  $[\text{Ag}(\text{NH}_3)_2]^+$

**Base “locks up” many cations into complex ions**

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.

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**

## Effects of adding hydroxide on Solubility

### Decrease SOLUBILITY

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

**Bases decrease solubility if the salt contains a hydroxide ion**

**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.

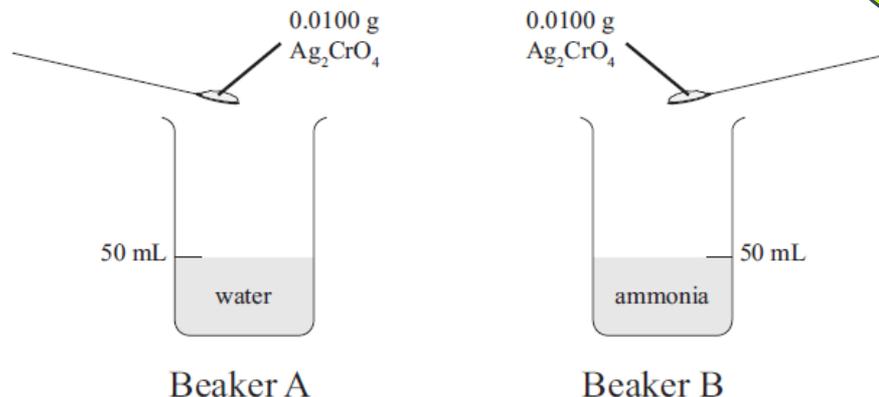
**Bases increase solubility if the salt contains a cation that forms a complex ion**

**When pH is above 10 only**

## NCEA 2013 solubility and base

Excellence  
Question

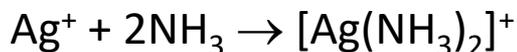
**Question: 2c:** In another experiment, 0.0100 g of  $\text{Ag}_2\text{CrO}_4$  in beaker A was made up to a volume of 50.0 mL with water. In beaker B, 0.0100 g of  $\text{Ag}_2\text{CrO}_4$  was made up to a volume of 50.0 mL with 0.100 mol  $\text{L}^{-1}$  ammonia solution.



Dissolving 0.0100g of silver chromate in 50 mL water will result in solid being present, as the required amount to make a saturated solution is  $1.44 \times 10^{-3}$  g in 50 mL, so any more than this will form a solid.

If the same mass is added to 50 mL of ammonia, more will dissolve and less solid will be present due to the formation of a complex ion.

The  $\text{Ag}_2\text{CrO}_4$  will dissociate completely and form an equilibrium.



The silver ion will then react further with  $\text{NH}_3$ , removing it from the above equilibrium. Thus, more  $\text{Ag}_2\text{CrO}_4$  will dissolve to re-establish equilibrium.

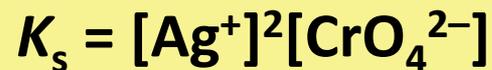
## NCEA 2013 solubility

Achieved  
Question

**Question: 2a:** In an experiment, a saturated solution was made by dissolving  $1.44 \times 10^{-3}$  g of  $\text{Ag}_2\text{CrO}_4$  in water, and making it up to a volume of 50.0 mL.

$M(\text{Ag}_2\text{CrO}_4) = 332 \text{ g mol}^{-1}$

(a) Write the  $K_s$  expression for  $\text{Ag}_2\text{CrO}_{4(s)}$ .



**Question: 2b:** In an experiment, a saturated solution was made by dissolving  $1.44 \times 10^{-3}$  g of  $\text{Ag}_2\text{CrO}_4$  in water, and making it up to a volume of 50.0 mL.  $M(\text{Ag}_2\text{CrO}_4) = 332 \text{ g mol}^{-1}$

(i) Calculate the solubility of  $\text{Ag}_2\text{CrO}_{4(s)}$ , and hence give the  $[\text{Ag}^+]$  and  $[\text{CrO}_4^{2-}]$  in the solution.

$$K_s = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$$

(ii) Determine the  $K_s(\text{Ag}_2\text{CrO}_4)$ .

$$\begin{aligned} n(\text{Ag}_2\text{CrO}_4) &= \frac{1.44 \times 10^{-3}}{332} \\ &= 4.33 \times 10^{-6} \text{ mol in 50 mL} \end{aligned}$$

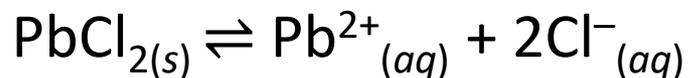
$$\begin{aligned} [\text{Ag}_2\text{CrO}_4] &= \frac{4.33 \times 10^{-6}}{50 \times 10^{-3}} \\ &= 8.67 \times 10^{-5} \text{ mol L}^{-1} \end{aligned}$$

$$[\text{Ag}^+] = 8.67 \times 10^{-5} \times 2 = 1.73 \times 10^{-4} \text{ mol L}^{-1}$$

$$[\text{CrO}_4^{2-}] = 8.67 \times 10^{-5} \text{ mol L}^{-1}$$

$$\begin{aligned} K_s &= (1.73 \times 10^{-4})^2 (8.67 \times 10^{-5}) \\ &= 2.61 \times 10^{-12} \end{aligned}$$

**Question: 2a:** A flask contains a saturated solution of  $\text{PbCl}_2$  in the presence of undissolved  $\text{PbCl}_2$ . (i) Write the equation for the dissolving equilibrium in a saturated solution of  $\text{PbCl}_2$ .



**Question: 2a: (ii)**

Write the expression for  $K_s(\text{PbCl}_2)$ .

$$K_s = [\text{Pb}^{2+}][\text{Cl}^{-}]^2$$



## NCEA 2014 solubility

Merit  
Question

**Question: 2a: (iii)** Calculate the solubility (in mol L<sup>-1</sup>) of lead(II) chloride in water at 25°C, and give the [Pb<sup>2+</sup>] and [Cl<sup>-</sup>] in the solution.

$$K_s(\text{PbCl}_2) = 1.70 \times 10^{-5} \text{ at } 25^\circ\text{C}$$

$$[\text{Pb}^{2+}] = x \quad [\text{Cl}^-] = 2x$$

$$K_s = 4x^3$$

$$x = \sqrt[3]{\frac{K_s}{4}}$$

$$= \sqrt[3]{\frac{1.70 \times 10^{-5}}{4}}$$

$$= 1.62 \times 10^{-2} \text{ mol L}^{-1}$$

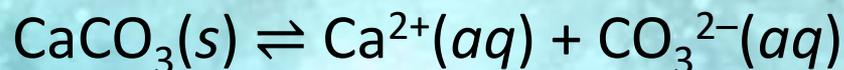
$$[\text{Pb}^{2+}] = 1.62 \times 10^{-2} \text{ mol L}^{-1}$$

$$[\text{Cl}^-] = 3.24 \times 10^{-2} \text{ mol L}^{-1}$$

$$s = \sqrt[3]{\frac{K_s}{4}}$$

**Question: 2a: (i)** Sufficient calcium carbonate,  $\text{CaCO}_{3(s)}$ , is dissolved in water to make a saturated solution.

- Write the equation for the equilibrium occurring in a saturated solution of  $\text{CaCO}_3$ .



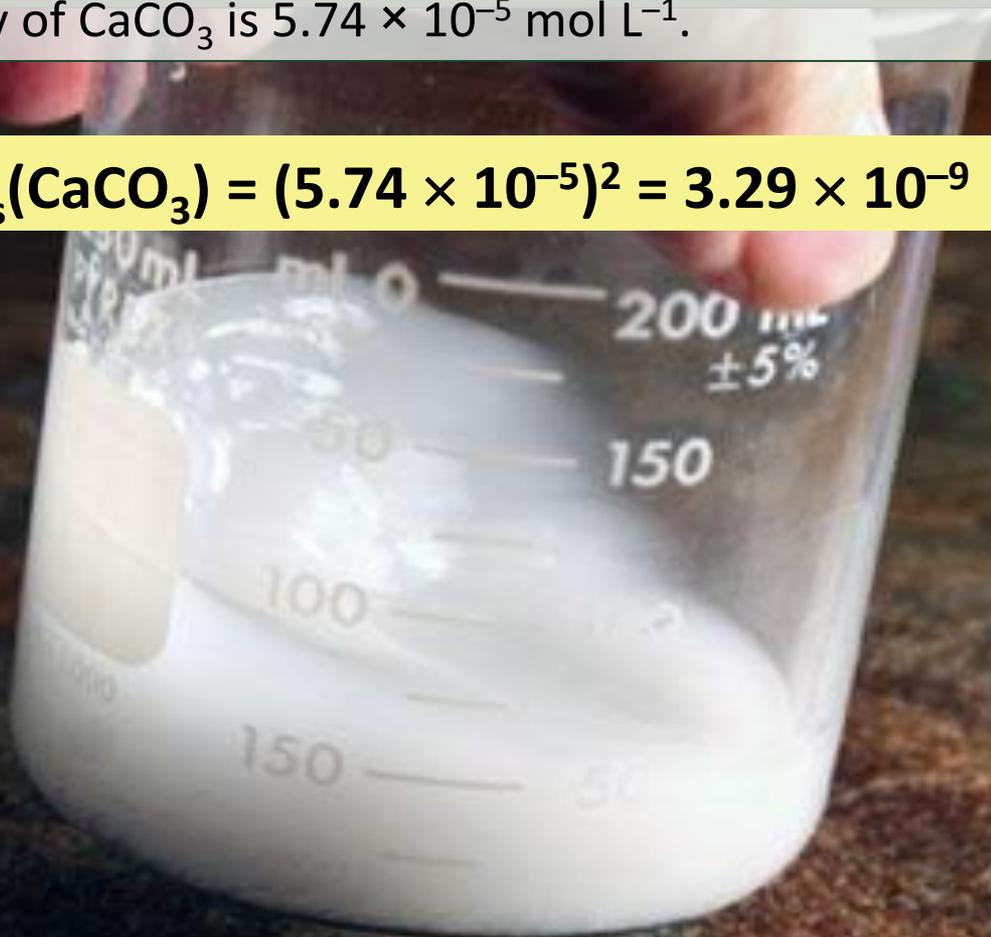
**Question: 2a: (ii)** Write the expression for  $K_s(\text{CaCO}_3)$ .

$$K_s = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

**Question: 2a: (iii)** Calculate the solubility product of  $\text{CaCO}_3$ ,  $K_s(\text{CaCO}_3)$ .

The solubility of  $\text{CaCO}_3$  is  $5.74 \times 10^{-5} \text{ mol L}^{-1}$ .

$$K_s(\text{CaCO}_3) = (5.74 \times 10^{-5})^2 = 3.29 \times 10^{-9}$$



**Question: 1a:** Silver carbonate,  $\text{Ag}_2\text{CO}_3$ , is a sparingly soluble salt.

$$K_s(\text{Ag}_2\text{CO}_3) = 8.10 \times 10^{-12} \text{ at } 25^\circ\text{C}$$

$$M(\text{Ag}_2\text{CO}_3) = 276 \text{ g mol}^{-1}$$

(a) Write the solubility product expression,  $K_s$ , for silver carbonate ( $\text{Ag}_2\text{CO}_3$ ).

$$K_s = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$$



**Question: 1b:** Silver carbonate,  $\text{Ag}_2\text{CO}_3$ , is a sparingly soluble salt.

$$K_s(\text{Ag}_2\text{CO}_3) = 8.10 \times 10^{-12} \text{ at } 25^\circ\text{C}$$

$$M(\text{Ag}_2\text{CO}_3) = 276 \text{ g mol}^{-1}$$

Calculate the mass of  $\text{Ag}_2\text{CO}_3$  that will dissolve in 50 mL of water to make a saturated solution at  $25^\circ\text{C}$ .

Let  $s$  = solubility

$$[\text{Ag}^+] = 2s$$

$$[\text{CO}_3^{2-}] = s$$

$$K_s = 4s^3$$

$$s = 1.27 \times 10^{-4} \text{ mol L}^{-1}$$

$$n = c \times v = 6.33 \times 10^{-6} \text{ mol}$$

$$m = n \times M = 1.75 \times 10^{-3} \text{ g}$$

**OR**

$$\text{g L}^{-1} = c \times M = 0.0349 \text{ g L}^{-1}$$

$$\text{so mass in 50 mL} = \frac{0.0349 \times 50}{1000}$$

$$= 1.75 \times 10^{-3} \text{ g}$$

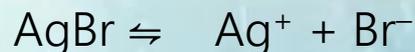
## Question 1b:

(i) Write the equation for the equilibrium occurring in a saturated solution of copper(II) hydroxide,  $\text{Cu}(\text{OH})_2$ .

(ii) Write the expression for  $K_s(\text{Cu}(\text{OH})_2)$ .

(iii) Calculate the solubility of  $\text{Cu}(\text{OH})_2$  in water at  $25^\circ\text{C}$ .

$$K_s(\text{Cu}(\text{OH})_2) = 4.80 \times 10^{-20}$$



$\text{Br}^-$  is a common ion / added to solution

An increase in  $[\text{Br}^-]$  will result in the reverse reaction being favoured, to restore

equilibrium / minimise the change.

This results in a decrease in  $[\text{Ag}^+]$  (since  $\text{Ag}^+$  reacts with some of the added  $\text{Br}^-$  to help

use it up) /  $\text{AgBr}$  becomes less soluble, (until  $[\text{Ag}^+][\text{Br}^-]$  is again equal to  $K_s$ .)

**Question: 2c:** The solubility of zinc hydroxide,  $\text{Zn}(\text{OH})_2$ , can be altered by changes in pH. Some changes in pH may lead to the formation of complex ions, such as the zincate ion,  $[\text{Zn}(\text{OH})_4]^{2-}$

Use equilibrium principles to explain why the solubility of zinc hydroxide increases when the pH is less than 4 or greater than 10.

$\text{Zn}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$  When pH is less than 4 / low,  $[\text{OH}^{-}]$  is decreased due to the reaction with  $\text{H}_3\text{O}^{+}$  to form water,

$\text{H}_3\text{O}^{+} + \text{OH}^{-} \rightarrow \text{H}_2\text{O}$  so equilibrium shifts to the right to produce more  $[\text{OH}^{-}]$ , therefore more  $\text{Zn}(\text{OH})_2$  will dissolve.

When pH is greater than 10 / high, then more  $\text{OH}^{-}$  is available and the complex ion (zincate ion) will form.

$\text{Zn}(\text{OH})_2(\text{s}) + 2\text{OH}^{-} \rightarrow [\text{Zn}(\text{OH})_4]^{2-}$  OR  $\text{Zn}^{2+} + 4\text{OH}^{-} \rightarrow [\text{Zn}(\text{OH})_4]^{2-}$

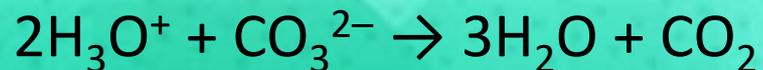
This decrease in  $[\text{Zn}^{2+}]$  causes the position of equilibrium to shift further to the right, therefore more  $\text{Zn}(\text{OH})_2$  dissolves.

**Question: 2b:** Some marine animals use calcium carbonate to form their shells. Increased acidification of the oceans poses a problem for the survival of these marine animals.

Explain why the solubility of  $\text{CaCO}_3$  is higher in an acidic solution.

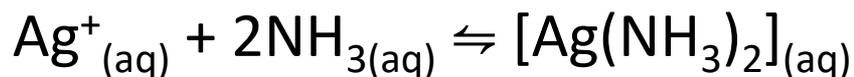
Use an equation to support your explanation.

The  $\text{H}_3\text{O}^+$  from the acidic solution reacts with the  $\text{CO}_3^{2-}$ . This reduces  $[\text{CO}_3^{2-}]$ , causing the equilibrium to shift towards the products / RHS to replace some of the lost  $\text{CO}_3^{2-}$ . Therefore more solid  $\text{CaCO}_3$  will dissolve.



**Question: 1c:** Explain how the solubility of  $\text{Ag}_2\text{CO}_3$  will change if added to 50 mL of a  $1.00 \text{ mol L}^{-1}$  ammonia,  $\text{NH}_3$ , solution.

Support your answer with balanced equations.



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.

The equilibrium responds by favouring the forward reaction and thus more dissolves.

**Base “locks up” many cations into complex ions**

**Question 2c:** Explain why the solubility of  $\text{Cu}(\text{OH})_2$  increases when dilute hydrochloric acid is added.

When copper(II) hydroxide is dissolved in an acidic solution, the  $\text{H}_3\text{O}^+$  ions neutralise

the  $\text{OH}^-$  ions /  $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$

A decrease in  $[\text{OH}^-]$  will result in the forward reaction being favoured, to restore equilibrium / minimise the change.

This causes more solid  $\text{Cu}(\text{OH})_2$  to dissolve, i.e. the solubility of  $\text{Cu}(\text{OH})_2$  increases /

so that  $[\text{Cu}^{2+}][\text{OH}^-]$  will again equal  $K_s$ .

## Ionic product

The ratio of the concentrations of products and reactants is called Q.

In any solution, whether it is saturated or not, such as AgCl the product formed  $[Ag^+][Cl^-]$  is called the **ionic product** and can not 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?  $c(AgNO_3) = 0.01 mol L^{-1}$        $K_s = 2 \times 10^{-10}$

If  $IP > K_s$  then precipitate will form



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

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

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

A precipitate will form if the concentration of  $Cl^-$  ions exceeds  $2 \times 10^{-8} mol L^{-1}$

**$K_s$  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 would be less soluble in sea water than in pure water because the presence of the  $\text{Cl}^-$  dissolved in the sea water means  $[\text{Cl}^-]$  is higher which must reduce the concentration of  $[\text{Ag}^+]$  at equilibrium (as the value of  $K_s$  cannot change).

This reduces the amount of solid AgCl that can dissolve.

# Common ion effect

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  $0.0025 \text{ mol L}^{-1}$  solution of NaCl?

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

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

$[\text{Cl}^-] = 0.0025 + s$  since the final concentration of  $\text{Cl}^-$  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  $[\text{Cl}^-] = 0.0025$

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

$$\text{and } s = \frac{1.6 \times 10^{-10}}{0.0025}$$

$$= 6.4 \times 10^{-8} \text{ mol L}^{-1}.$$

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

**Question: 2b:** A sample of seawater has a chloride ion concentration of  $0.440 \text{ mol L}^{-1}$ .

Determine whether a precipitate of lead(II) chloride will form when a  $2.00 \text{ g}$  sample of lead(II) nitrate is added to  $500 \text{ mL}$  of the seawater.

$$K_s(\text{PbCl}_2) = 1.70 \times 10^{-5} \quad M(\text{Pb}(\text{NO}_3)_2) = 331 \text{ g mol}^{-1}$$

$$\begin{aligned} n(\text{Pb}(\text{NO}_3)_2) &= \frac{2.00 \text{ g}}{331 \text{ g mol}^{-1}} \\ &= 6.04 \times 10^{-3} \text{ mol} \\ \therefore [\text{Pb}^{2+}] &= 6.04 \times 10^{-3} \text{ mol} / 0.500 \text{ L} \\ &= 1.21 \times 10^{-2} \text{ mol L}^{-1} \end{aligned}$$

$$\begin{aligned} Q &= (1.21 \times 10^{-2}) \times (0.440)^2 \\ &= 2.34 \times 10^{-3} \end{aligned}$$

As  $Q > K_s$ , a precipitate will form.

**Question: 2c:** Show, by calculation, that a precipitate of lead(II) hydroxide,  $\text{Pb}(\text{OH})_2$ , will form when 25.0 mL of a sodium hydroxide solution, NaOH, at pH 12.6 is added to 25.0 mL of a  $0.00421 \text{ mol L}^{-1}$  lead(II) nitrate,  $\text{Pb}(\text{NO}_3)_2$ , solution.

$$K_s(\text{Pb}(\text{OH})_2) = 8.00 \times 10^{-17} \text{ at } 25^\circ\text{C}$$

**The ratio of the concentrations of products and reactants is called Q.**



$$Q = [\text{Pb}^{2+}][\text{OH}^-]^2$$

$$[\text{Pb}^{2+}] = 0.5 \times 0.00421 = 2.105 \times 10^{-3}$$

$$[\text{OH}^-] = 0.5 \times 0.0398 = 1.99 \times 10^{-2}$$

$$Q = (2.105 \times 10^{-3}) \times (1.99 \times 10^{-2})^2$$

$$Q = 8.34 \times 10^{-7}$$

Since  $Q > K_s$ , a precipitate of  $\text{Pb}(\text{OH})_2$  will form.

$$\text{pH} = 12.6$$

$$\text{pOH} = 1.4$$

$$[\text{OH}^-] = 0.0398$$

**Question: 1d:** Show by calculation whether a precipitate of  $\text{Ag}_2\text{CO}_3$  will form when 20.0 mL of  $0.105 \text{ mol L}^{-1}$  silver nitrate,  $\text{AgNO}_3$ , solution is added to 35.0 mL of a  $0.221 \text{ mol L}^{-1}$  sodium carbonate,  $\text{Na}_2\text{CO}_3$ , solution.

$$K_s(\text{Ag}_2\text{CO}_3) = 8.10 \times 10^{-12} \text{ at } 25^\circ\text{C}$$

$$\text{AgNO}_3 \text{ dilution: } \frac{20}{55} \times 0.105 = 0.0382$$

$$\text{Na}_2\text{CO}_3 \text{ dilution: } \frac{35}{55} \times 0.221 = 0.141$$

$$Q / I.P. = [0.03818]^2[0.1406] = 2.06 \times 10^{-4}$$

As  $Q / I.P. > K_s$ , a precipitate will form.

**The ratio of the concentrations of products and reactants is called Q.**

$$K_s = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$$

Question 1b (iii) : 40.0 mL of 0.150 mol L<sup>-1</sup> HBr solution was added to 25.0 mL of a saturated silver bromide, AgBr, solution. Show by calculation whether a precipitate of Ag<sub>2</sub>CO<sub>3</sub> will form when 20.0 mL of 0.105 mol L<sup>-1</sup> silver nitrate, AgNO<sub>3</sub>, solution is added to 35.0 mL of a 0.221 mol L<sup>-1</sup> sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>, solution.

$$K_s(\text{Ag}_2\text{CO}_3) = 8.10 \times 10^{-12} \text{ at } 25^\circ\text{C}$$

**The ratio of the concentrations of products and reactants is called Q.**



$$K_s(\text{AgBr}) = [\text{Ag}^+] [\text{Br}^-]$$

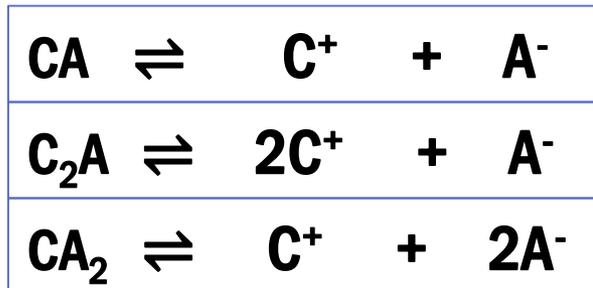
$$5 \times 10^{-13} = [\text{Ag}^+] \times \frac{0.150 \times 40}{65}$$

65

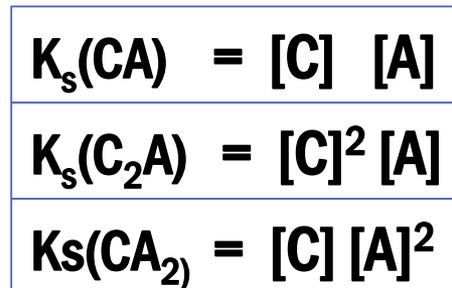
$$[\text{Ag}^+] = 5.42 \times 10^{-12} \text{ mol L}^{-1}$$

# Solubility Key concepts

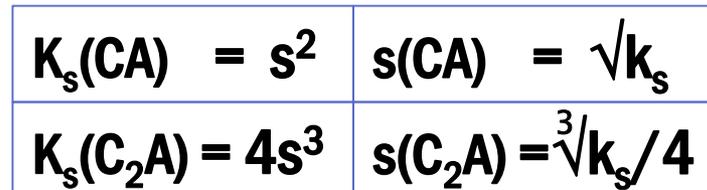
## equations



## Solubility expressions



## Ks/s calculations



C = cation A = anion

## Equilibrium effects

Acids increase solubility if the salt contains a carbonate

Bases increase solubility if the salt contains a cation that forms a complex ion  
 When pH is above 10

Bases decrease solubility if the salt contains a hydroxide ion  
 This occurs when pH is above 4 but below 10

## Common ion effect

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

If  $IP > K_s$  then precipitate

If  $IP < K_s$  then no precipitate

IP = ionic product

Ks = solubility product

## Acids – their characteristics

Acids are a family of substances which all show **acidic characteristics** or properties. These properties relate to how the acids react with other chemicals.



They have a **sour taste** and react with metals. Acids can be found in nature and called **organic acids** or manufactured in the laboratory and called **mineral acids**.



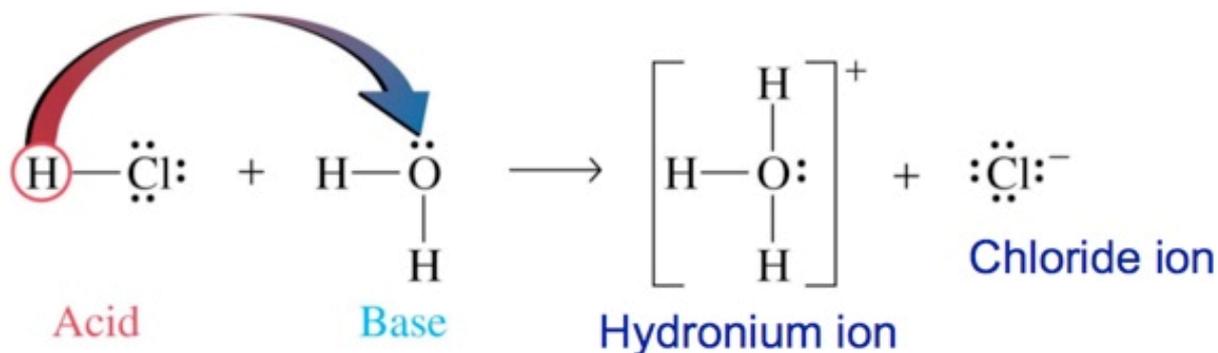
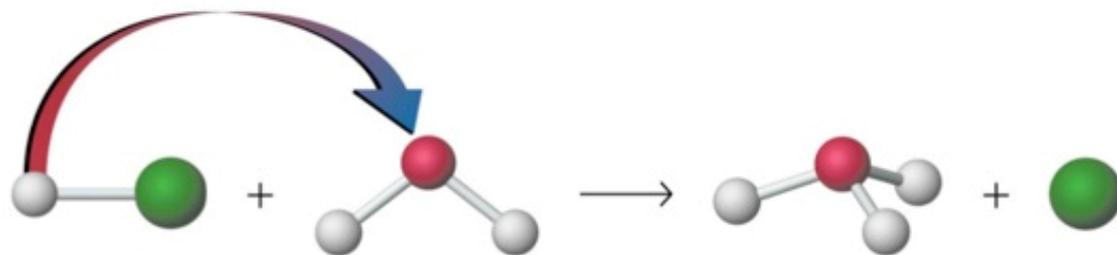
## Acids – their characteristics

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

Common acids (that you need to know) include:

**Strong acids:**  $\text{HNO}_3$  - nitric acid,  $\text{HCl}$  - hydrochloric acid,  $\text{H}_2\text{SO}_4$  – sulfuric acid,  $\text{HBr}$  - Hydrobromic acid

**Weak acids:**  $\text{CH}_3\text{COOH}$  – ethanoic acid,  $\text{HF}$  - Hydrofluoric acid, and  $\text{NH}_4^+$  - ammonium



## Bases – their characteristics

**Bases** are a family of Chemicals that can remove acid particles ( $H^+$ ) from a solution. They have opposite properties from acids.

Bases have a slippery feel to them and common house hold bases include floor clearers and antacid tables to fix indigestion. **Bases that dissolve into water are called an alkali, and produce  $OH^-$  ions.**



## Bases – their characteristics

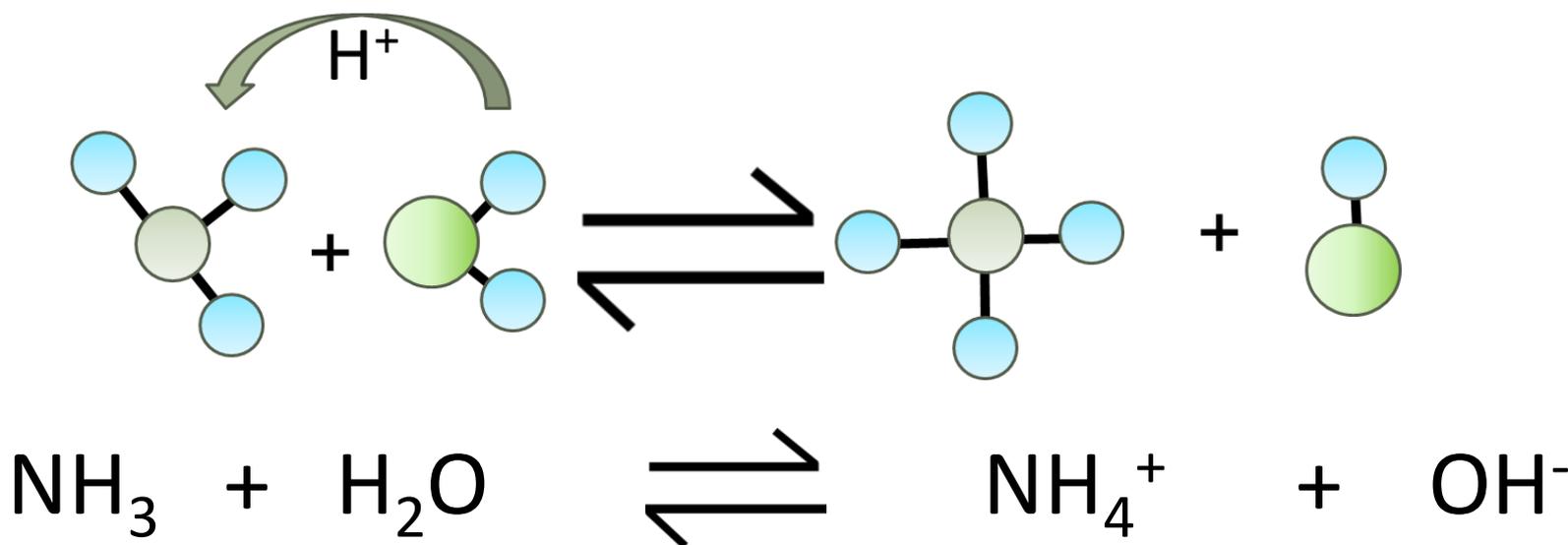
A **Base** accepts a **Hydrogen ion** that have been donated from an Acid.

Common bases (that you need to know) include:

**Strong bases:** NaOH – sodium hydroxide, KOH – potassium hydroxide

**Weak bases:** NH<sub>3</sub> – ammonia, CH<sub>3</sub>NH<sub>2</sub> - methylamine and CH<sub>3</sub>COO<sup>-</sup> - ethanoate ion

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<sup>+</sup>**

A hydrogen ion, H<sup>+</sup> is simply a lone proton (an H with the electron removed)

In water (or aqueous solutions ) H<sup>+</sup> ions exist as an H<sub>3</sub>O<sup>+</sup> ion, called **hydronium**.

Acids are substances that donate protons (H<sup>+</sup>) in solution



HCl gas dissolved in water

HCl has donated a H<sup>+</sup> so is acting as an acid

H<sub>2</sub>O has accepted a H<sup>+</sup> so it is acting as a base

Solution becomes acidic since H<sub>3</sub>O<sup>+</sup> ions form

Bases are substances that accept protons (H<sup>+</sup>) in solution



NH<sub>3</sub> gas dissolved in water

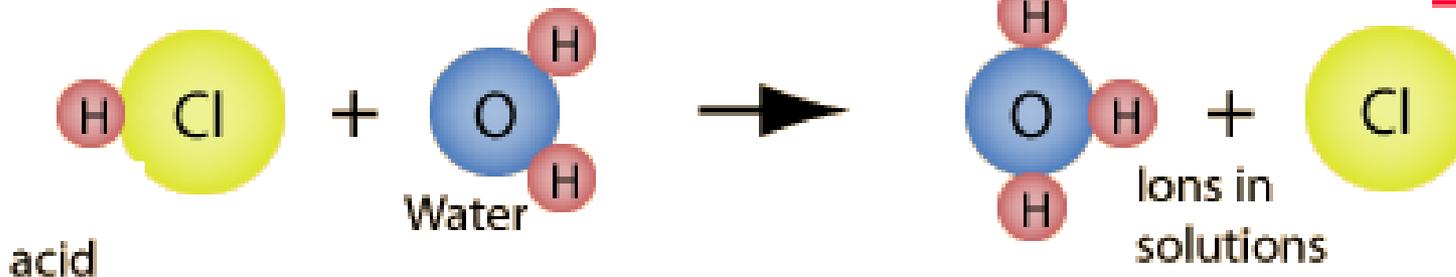
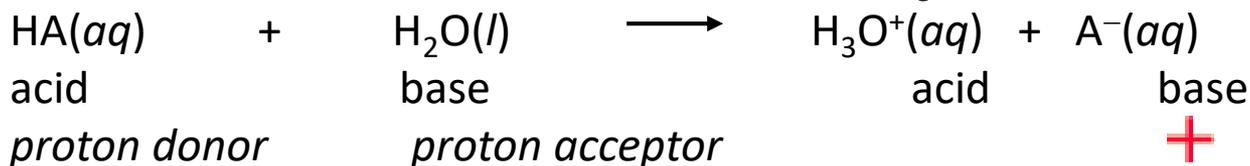
NH<sub>3</sub> has accepted a H<sup>+</sup> so it is acting as a base

H<sub>2</sub>O has donated a H<sup>+</sup> so is acting as an acid

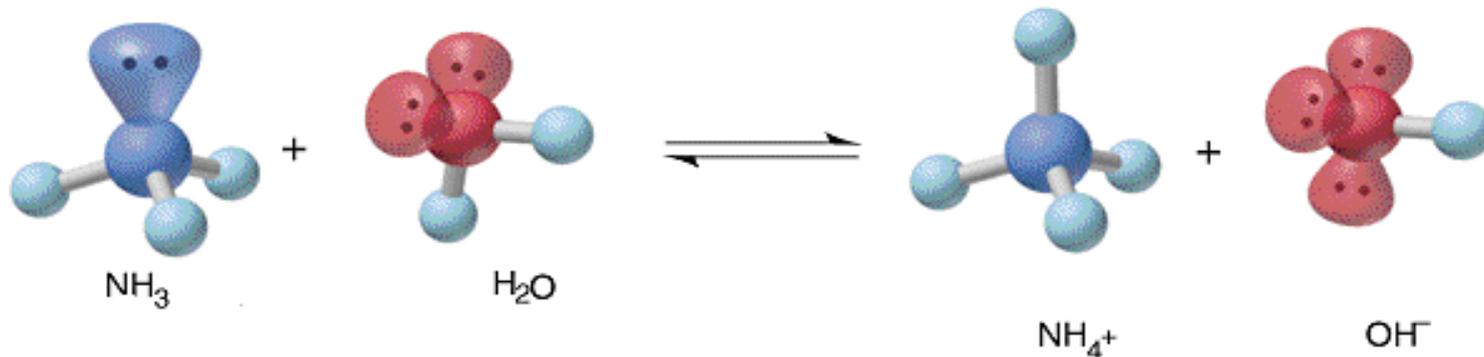
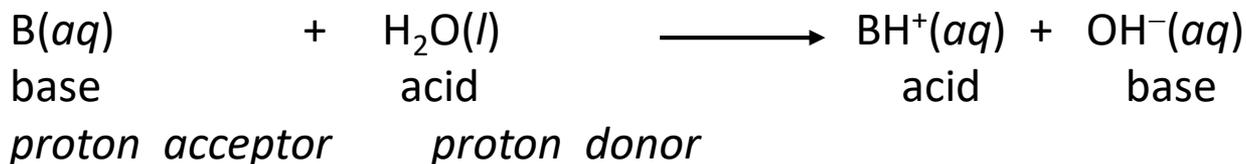
Solution becomes basic since OH<sup>-</sup> ions form.

## Brønsted–Lowry acids and bases summary

Proton donation to a water molecule forms  $\text{H}_3\text{O}^+$  (hydronium) ions.



Similarly, proton donation from water to a base produces  $\text{OH}^-$  ions.



## Amphiprotic substances

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

For a substance to be amphiprotic it must

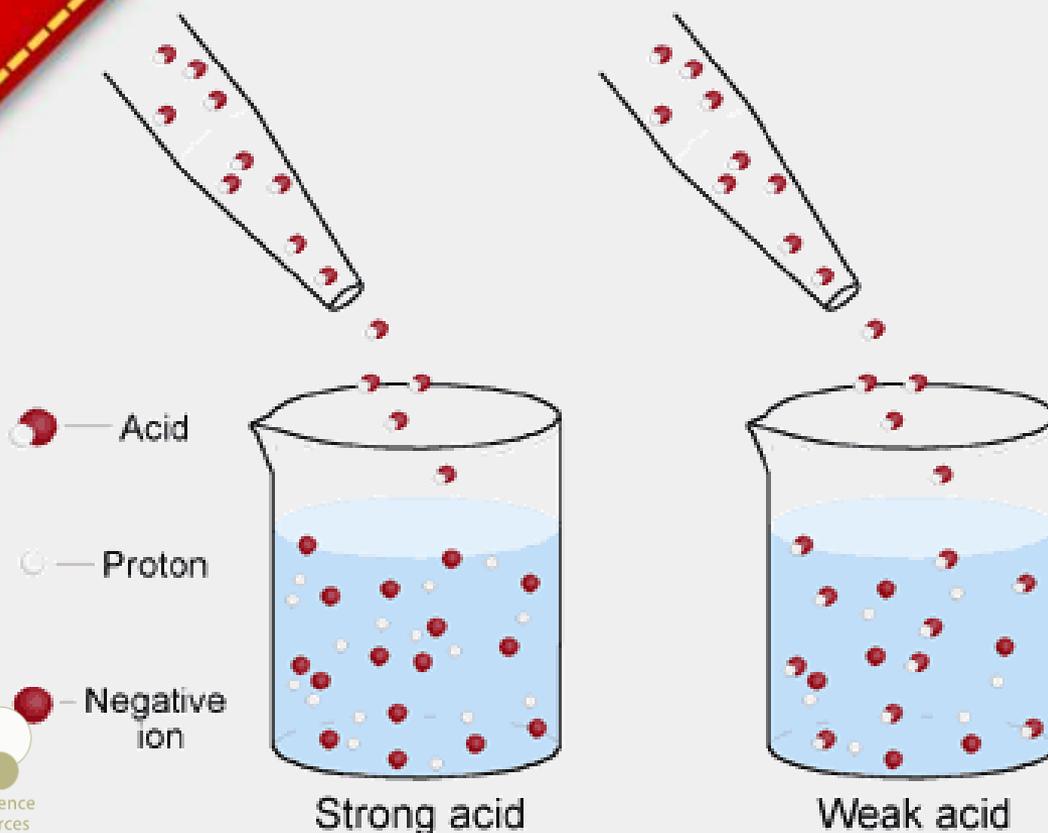
1. contain a hydrogen atom which is able to be donated to another chemical species.

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	$H_2PO_4^-$	$H_2PO_4^-(aq) \rightarrow H^+(aq) + HPO_4^{2-}(aq)$	$H_2PO_4^-(aq) + H^+(aq) \rightarrow H_3PO_4(aq)$

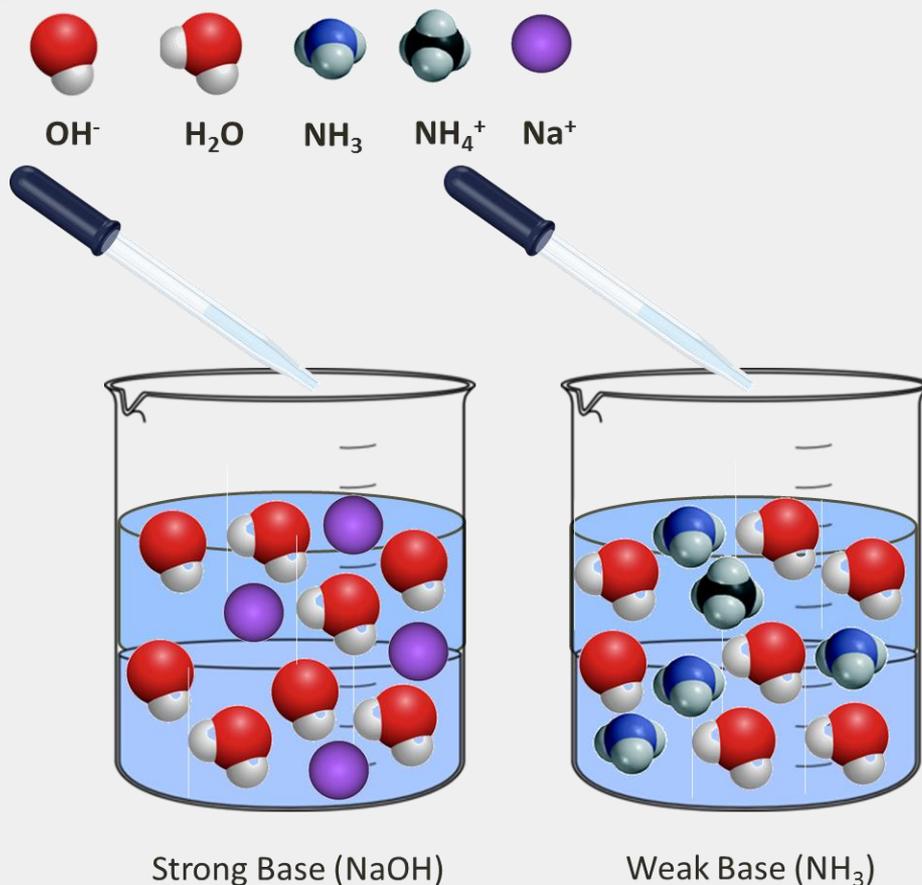
## Strong and weak acids



You can define acids and bases as being "strong" or "weak". **Strong acids** are compounds that **completely dissociate** (break up) in water. All of the  $\text{H}^+$  ions (protons) break away from the original acid molecule in water. A **weak acid** only **partially dissociates** and loses just some of its  $\text{H}^+$  ions (protons) in water.

For strong bases, all of the  $\text{OH}^-$  ions break away from the molecule in water.

## Strong and weak bases



You can define bases as being "strong" or "weak". **Strong bases** are compounds where each molecule will accept an H<sup>+</sup> ion. A **weak base** is a compound where only some of the molecules will accept a H<sup>+</sup> ion. Most weak base molecules remain unreacted.

**Note:** For strong alkalis, all of the OH<sup>-</sup> ions break away from the molecule in water.

## Strong and Weak Acids

The strength of an acid is determined by how readily it will donate its H<sup>+</sup> ions. Strong acids will have a low pH (0-3) and include HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>, and HBr

Weak acids will have a higher pH (4-6). They are mostly organic acids and include CH<sub>3</sub>COOH, HF and NH<sub>4</sub><sup>+</sup>

### Strong acids

Donate protons (H<sup>+</sup>) in aqueous solution to become **completely dissociated**.



HCl gas dissolved in water

HCl has donated an H<sup>+</sup> so is acting as an acid

H<sub>2</sub>O has accepted an H<sup>+</sup> so it is acting as a base

Solution contains **virtually no** intact HCl molecules after reaction.

### Weak acids

Donate protons (H<sup>+</sup>) in aqueous solution to become **partially dissociated**.



CH<sub>3</sub>COOH dissolved in water

Only some of the acetic acid molecules dissociate into acetate ions (CH<sub>3</sub>COO<sup>-</sup>)

Because the acetate ion is a strong base (conjugate pairs) it will readily accept H<sup>+</sup> (from H<sub>3</sub>O<sup>+</sup>) and become acetic acid.

Solution contains **mostly** intact CH<sub>3</sub>COOH molecules.

## Strong and Weak Bases

The strength of a base is determined by how readily it will accept  $\text{H}^+$  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  $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{COO}^-$

### Strong Bases

Completely accept protons ( $\text{H}^+$ ) in aqueous solution



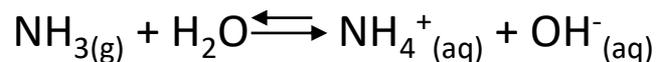
NaOH completely dissociates

The  $\text{OH}^-$  ions will readily accept  $\text{H}^+$  ions.

Solution contains very **few** intact NaOH molecules after reaction.

### Weak Bases

Partially accept protons ( $\text{H}^+$ ) in aqueous solution



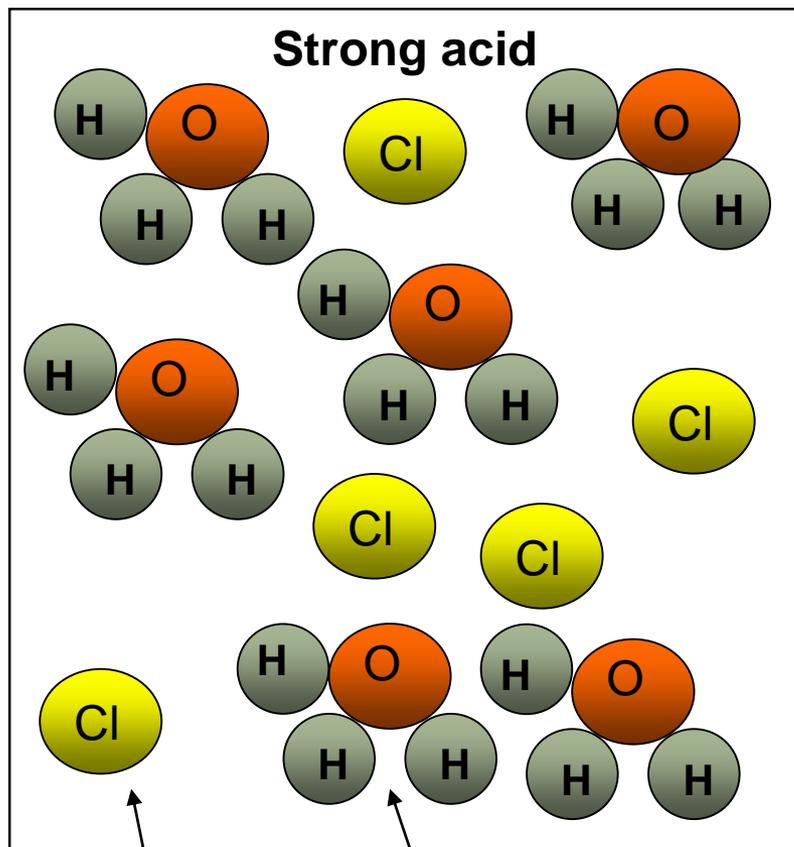
Only some of the ammonia molecules dissociate into ammonium ions ( $\text{NH}_4^+$ )

Because ammonium is a reasonably strong acid (conjugate pairs) it will readily donate  $\text{H}^+$  and become ammonia.

Solution contains **mostly** intact  $\text{NH}_3$  molecules.

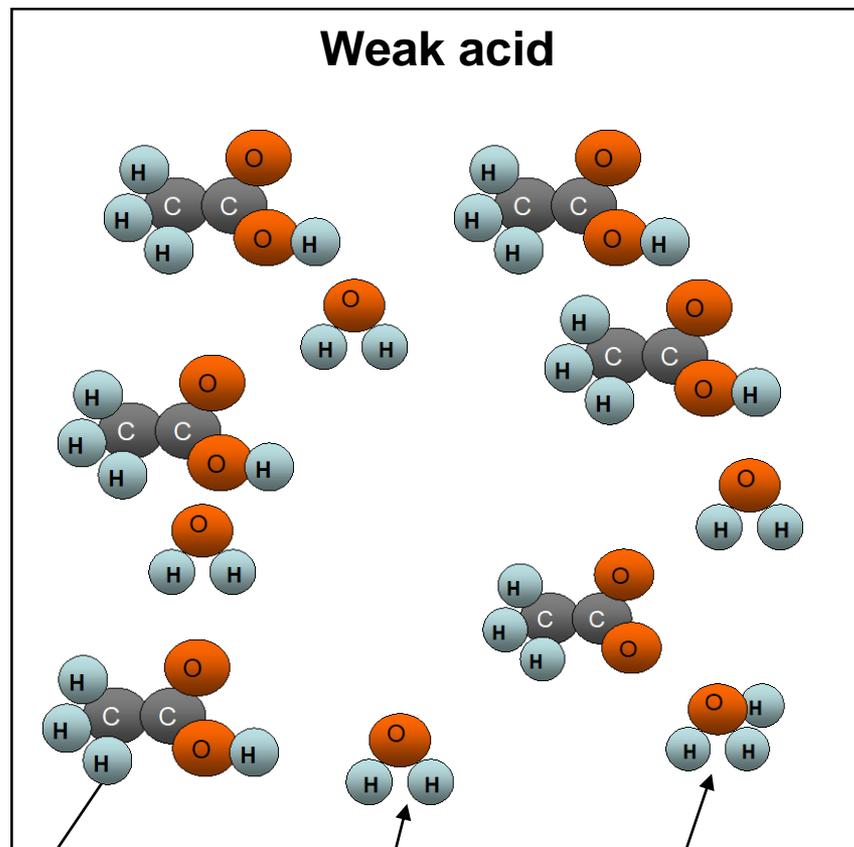
## Strong and Weak Acids

In reality the strong acid molecules would be almost completely dissociated in an aqueous solution. The  $\text{Cl}^-$  would remain in solution and free  $\text{H}^+$  ions would join with available water to form hydronium ions



dissociated acid molecules

hydronium molecules



Many intact acid molecules

lots of water molecules

Few hydronium molecules

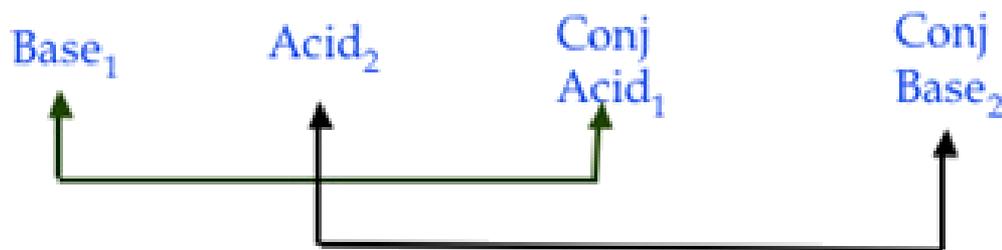
## Conjugate pairs

If 2 species differ by just 1 proton they are classed as a conjugate acid-base pair.

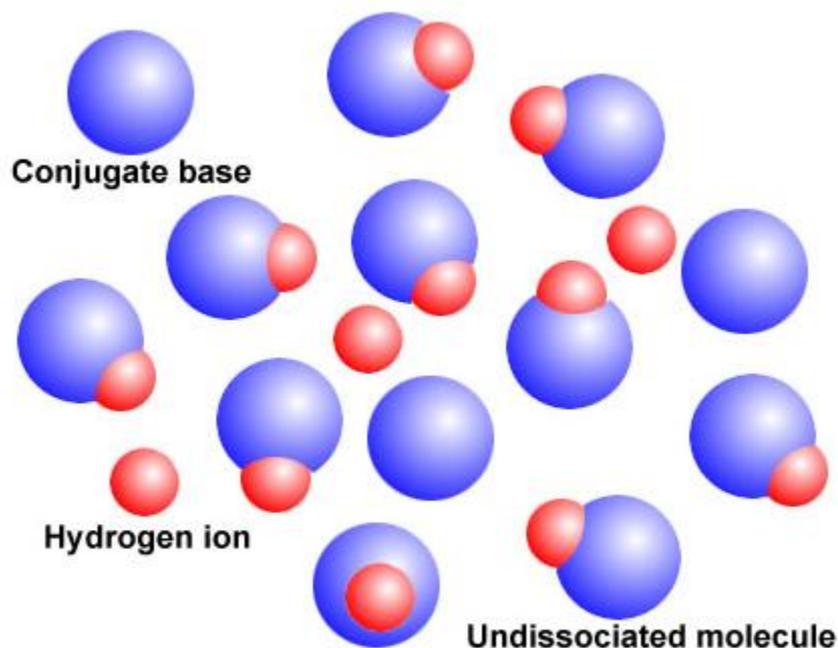
Examples of acid-base pairs are  $\text{H}_2\text{SO}_4/\text{HSO}_4^-$  and  $\text{NH}_4^+/\text{NH}_3$ .

The acid is always the species with the additional proton.

It can also be said that  $\text{NH}_3$  is the conjugate base of  $\text{NH}_4^+$ .



## Transfer of hydrogen ions in conjugate pairs



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.

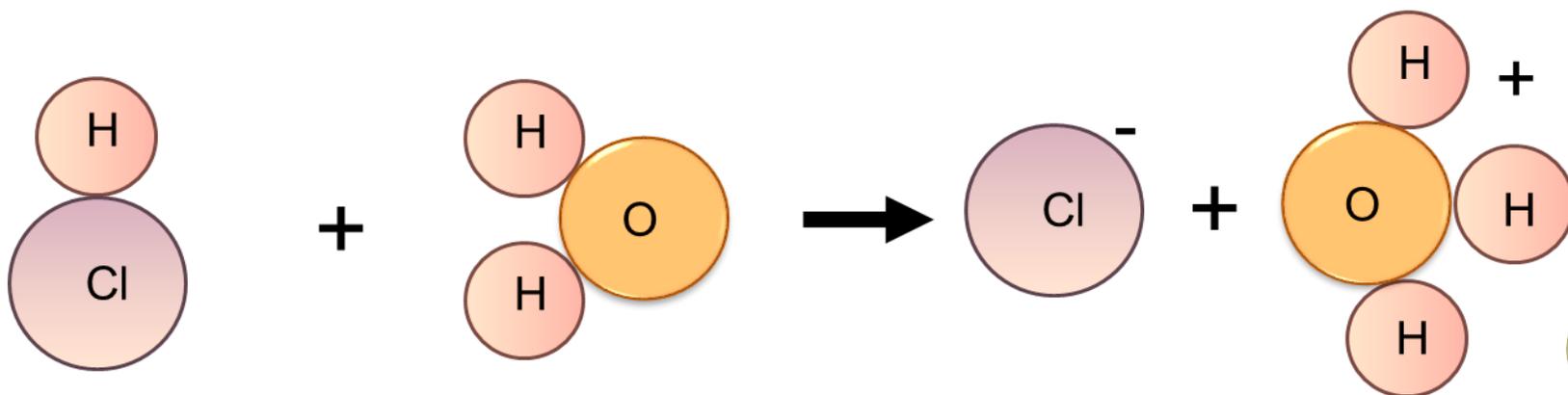
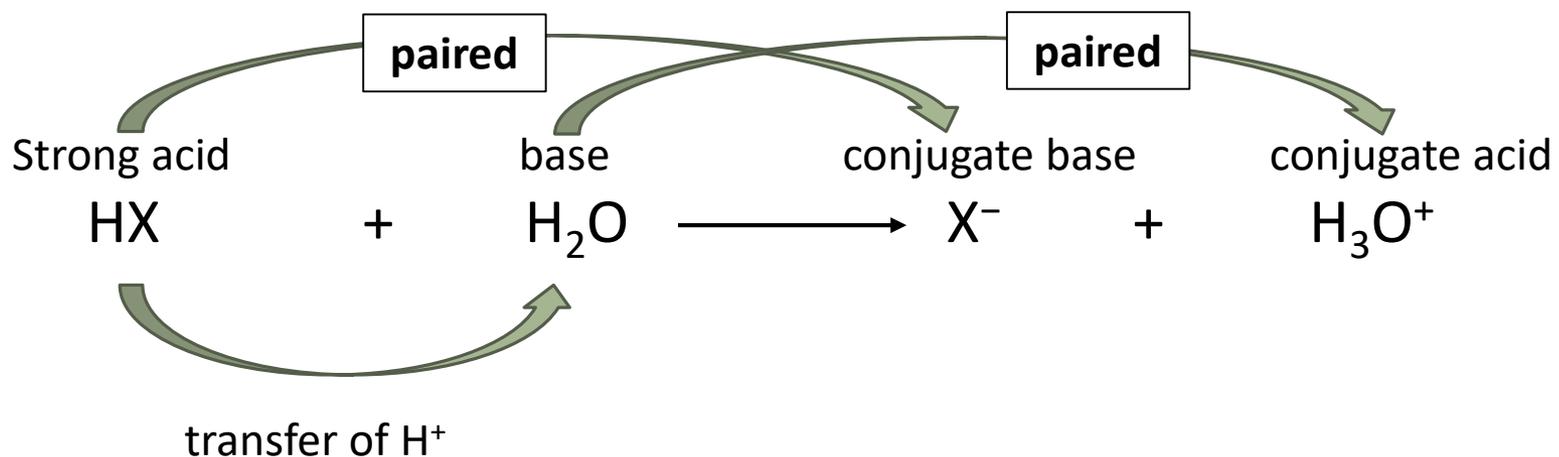
These are what we call **conjugate pairs** of acids and bases.

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 Acid and Base pairs (Strong Acid)

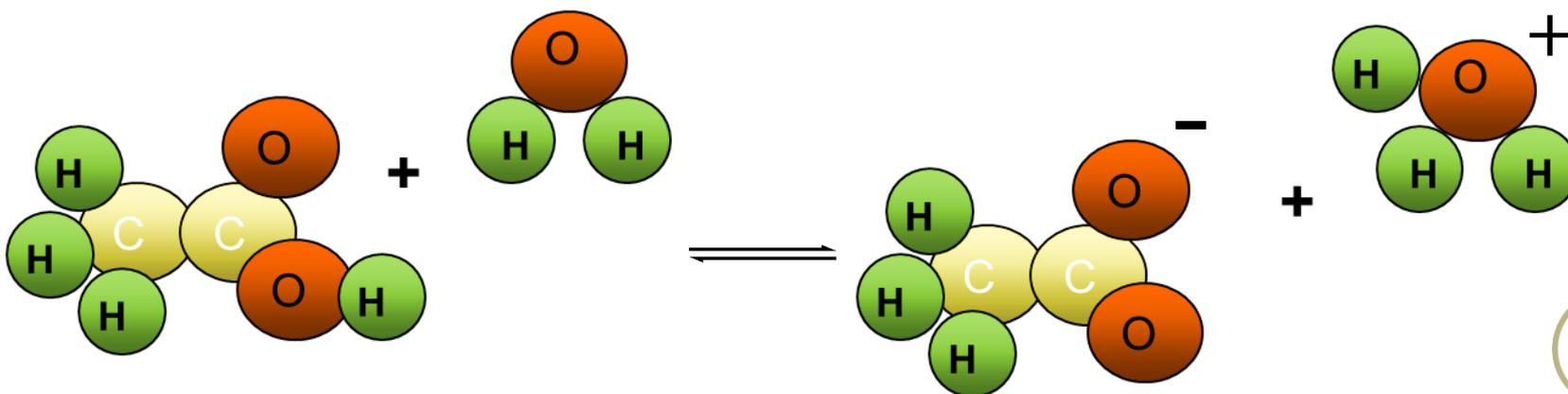
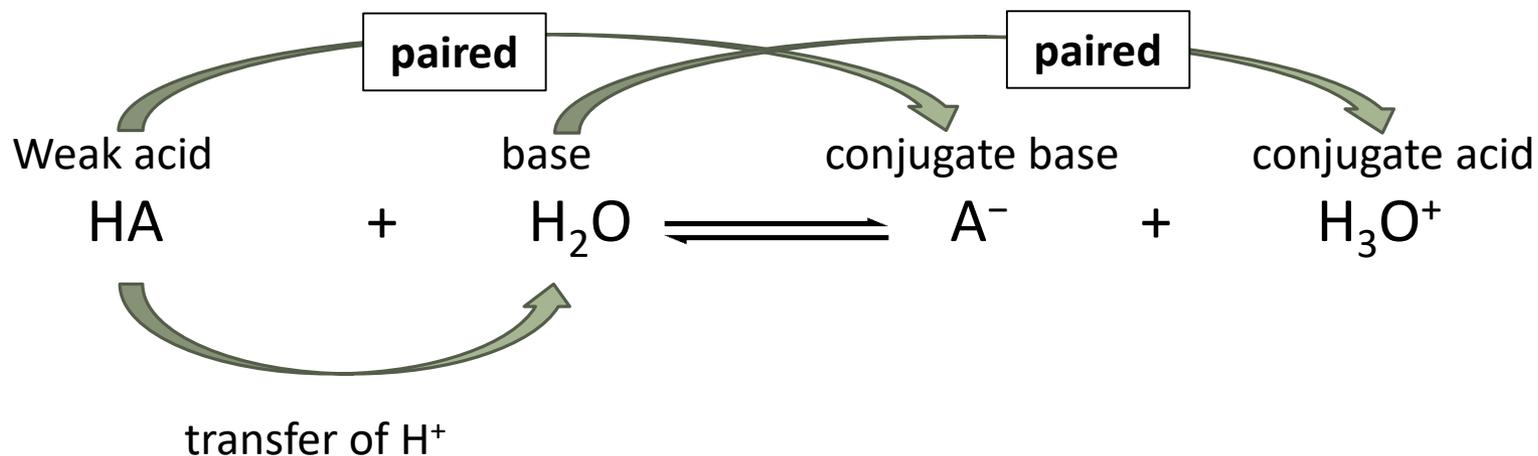
**HX** is a symbol used for a strong acid. A conjugate acid can be seen as the chemical substance that releases a proton in the **backward** chemical reaction.

The base produced,  $X^-$ , is called the **conjugate base** and it absorbs a proton in the **backward** chemical reaction.



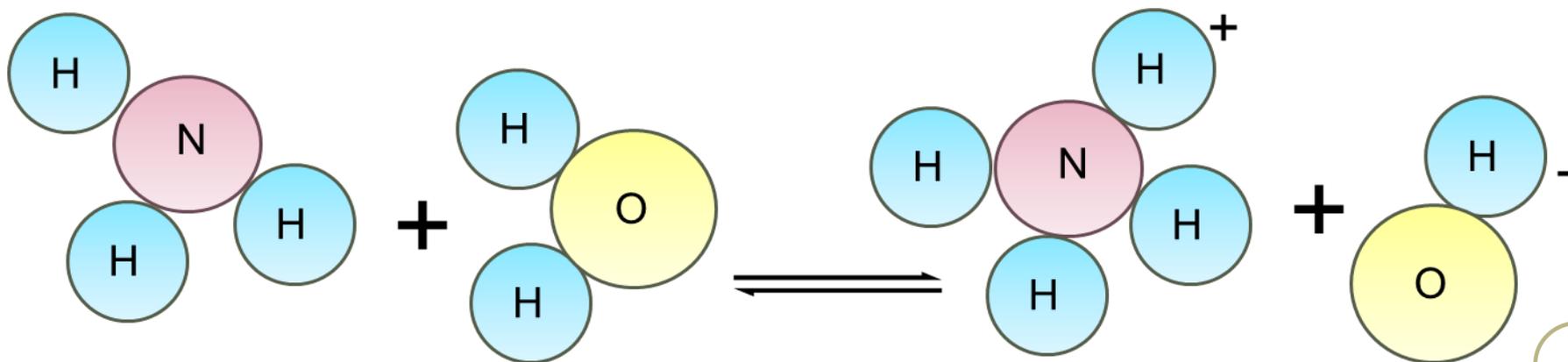
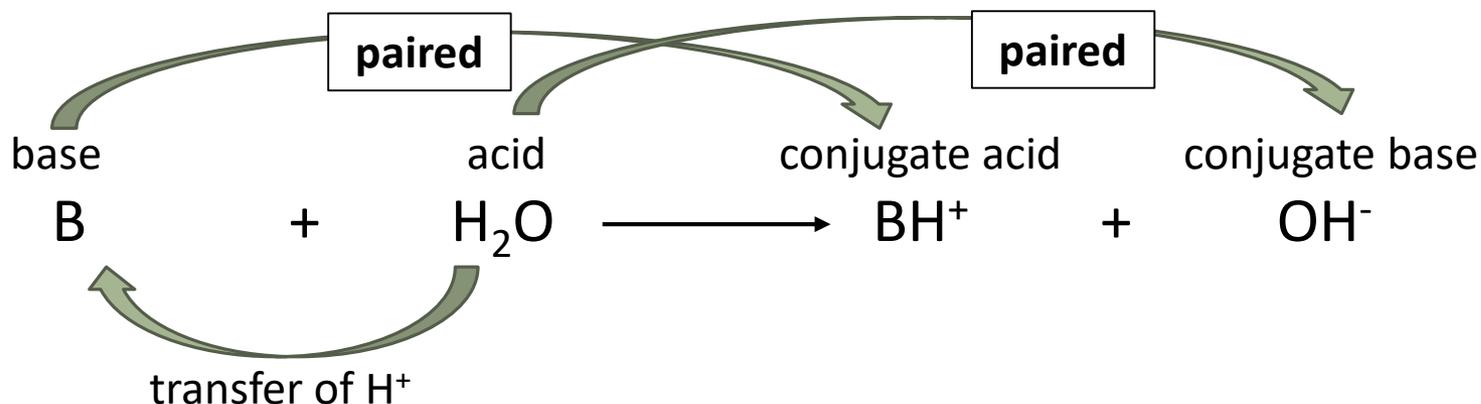
## Conjugate Acid and Base pairs (weak acid)

**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,  $\text{OH}^-$ , is the paired conjugate of the water once the  $\text{H}^+$  has been removed. Strong bases use a single direction arrow and weak bases use a double arrow.



## Conjugate Acid and Base pairs

If 2 species differ by just 1 proton they are classed as a conjugate acid-base pair. Examples of acid-base pairs are  $\text{H}_2\text{SO}_4/\text{HSO}_4^-$ , and  $\text{NH}_4^+/\text{NH}_3$ . The acid is always the species with the additional proton. It can also be said that  $\text{NH}_3$  is the conjugate base of  $\text{NH}_4^+$ .

Base		Conjugate Acid
$\text{H}_2\text{O}$	water	$\text{H}_3\text{O}^+$
$\text{SO}_4^{2-}$	sulfate ion	$\text{HSO}_4^-$
$\text{NH}_3$	ammonia	$\text{NH}_4^+$
$\text{OH}^-$	hydroxide ion	$\text{H}_2\text{O}$
$\text{HCO}_3^-$	hydrogen carbonate ion	$\text{H}_2\text{CO}_3$
$\text{CO}_3^{2-}$	carbonate ion	$\text{HCO}_3^-$

	ACID	BASE	
negligible	$\text{OH}^-$	$\text{O}^{2-}$	strong
	$\text{HS}^-$	$\text{S}^{2-}$	
weak	$\text{H}_2\text{O}$	$\text{OH}^-$	weak
	$\text{HPO}_4^{2-}$	$\text{PO}_4^{3-}$	
	$\text{HCO}_3^-$	$\text{CO}_3^{2-}$	
	$\text{NH}_4^+$	$\text{NH}_3$	
	$\text{HCN}$	$\text{CN}^-$	
	$\text{H}_2\text{PO}_4^-$	$\text{HPO}_4^{2-}$	
	$\text{HSO}_3^-$	$\text{SO}_3^{2-}$	
	$\text{H}_2\text{S}$	$\text{HS}^-$	
	$\text{H}_2\text{CO}_3$	$\text{HCO}_3^-$	
	$\text{C}_5\text{H}_5\text{NH}^+$	$\text{C}_5\text{H}_5\text{N}$	
	$\text{CH}_3\text{CO}_2\text{H}$	$\text{CH}_3\text{CO}_2^-$	
	$\text{HF}$	$\text{F}^-$	
	$\text{H}_3\text{PO}_4$	$\text{H}_2\text{PO}_4^-$	
	$\text{H}_2\text{SO}_3$	$\text{HSO}_3^-$	
	$\text{HSO}_4^-$	$\text{SO}_4^{2-}$	
strong	$\text{H}_3\text{O}^+$	$\text{H}_2\text{O}$	negligible
	$\text{HNO}_3$	$\text{NO}_3^-$	
	$\text{H}_2\text{SO}_4$	$\text{HSO}_4^-$	
	$\text{HCl}$	$\text{Cl}^-$	
	$\text{HBr}$	$\text{Br}^-$	

## Conjugate Acid and Base pairs

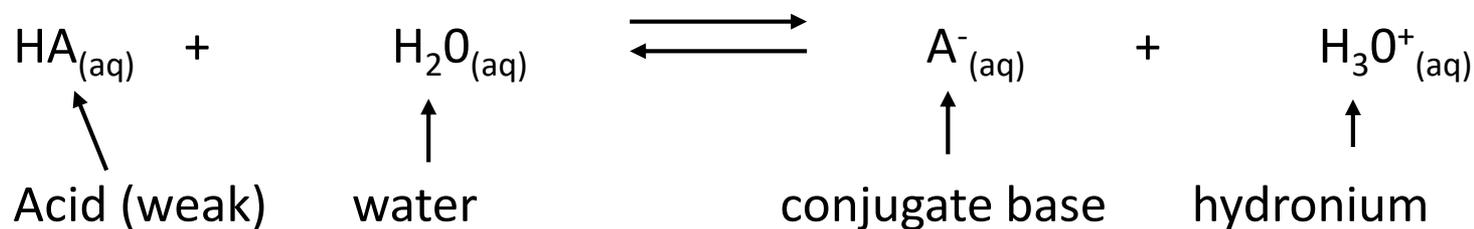
The stronger an acid, normally the weaker its conjugate base, and, conversely, the stronger a base, the weaker its conjugate acid.

A strong acid like HCl donates its proton so readily that there is essentially no tendency for the conjugate base  $\text{Cl}^-$  to reaccept a proton. Consequently,  $\text{Cl}^-$  is a very weak base. A strong base like the  $\text{H}^-$  ion accepts a proton and holds it so firmly that there is no tendency for the conjugate acid  $\text{H}_2$  to donate a proton. Hence,  $\text{H}_2$  is a very weak acid.

## Weak and strong acids

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

**Weak acid** – less than 5% dissociation



**Strong acid** – complete dissociation



Where  $c(\text{HX}) = [\text{H}_3\text{O}^+]$

Initial concentration of HX is equal to final concentration of  $\text{H}_3\text{O}^+$

so  $\text{pH} = -\log c(\text{HX})$

## 2015 dissociation equations - NCEA Case Study

Achieved  
Question

**Question: 1a: (i)** Methylammonium chloride,  $\text{CH}_3\text{NH}_3\text{Cl}$ , dissolves in water to form a weakly acidic solution.

$$K_a(\text{CH}_3\text{NH}_3^+) = 2.29 \times 10^{-11}$$

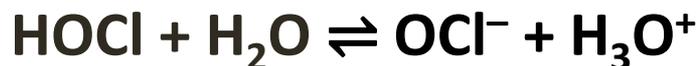
(a) (i) Write an equation to show  $\text{CH}_3\text{NH}_3\text{Cl}$  dissolving in water.



## 2014 dissociation equations - NCEA Case Study

**Question: 1a:** When chlorine gas is added to water, the equation for the reaction is:  $\text{Cl}_{2(g)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{HCl}_{(aq)} + \text{HOCl}_{(aq)}$

(i) Write an equation for the reaction of the weak acid, hypochlorous acid, HOCl, with water.



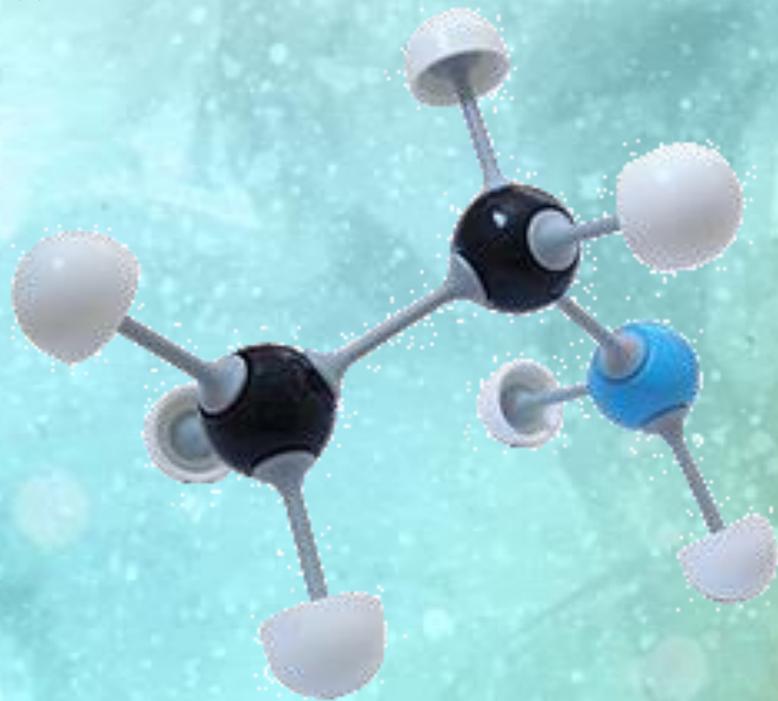
## NCEA 2016 dissociation equations

Achieved  
Question

**Question: 2a: (i)** Ethanamine,  $\text{CH}_3\text{CH}_2\text{NH}_2$ , is a weak base.

$$\text{p}K_{\text{a}}(\text{CH}_3\text{CH}_2\text{NH}_3^+) = 10.6 \quad K_{\text{a}}(\text{CH}_3\text{CH}_2\text{NH}_3^+) = 2.51 \times 10^{-11}$$

(a) Write an equation to show the reaction of ethanamine with water.



## NCEA 2017 dissociation equations

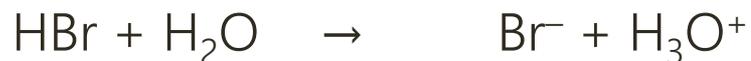
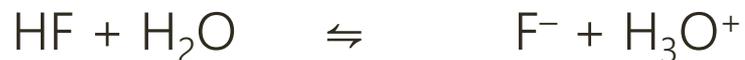
Achieved  
Question

**Question: 1a: (i)** Hydrogen fluoride, HF, and hydrogen bromide, HBr, both form acidic solutions when added to water.

(i) Write an equation for the reaction of each acid with water.

Hydrogen fluoride, HF, with water:

Hydrogen bromide, HBr, with water:



# Species in solution

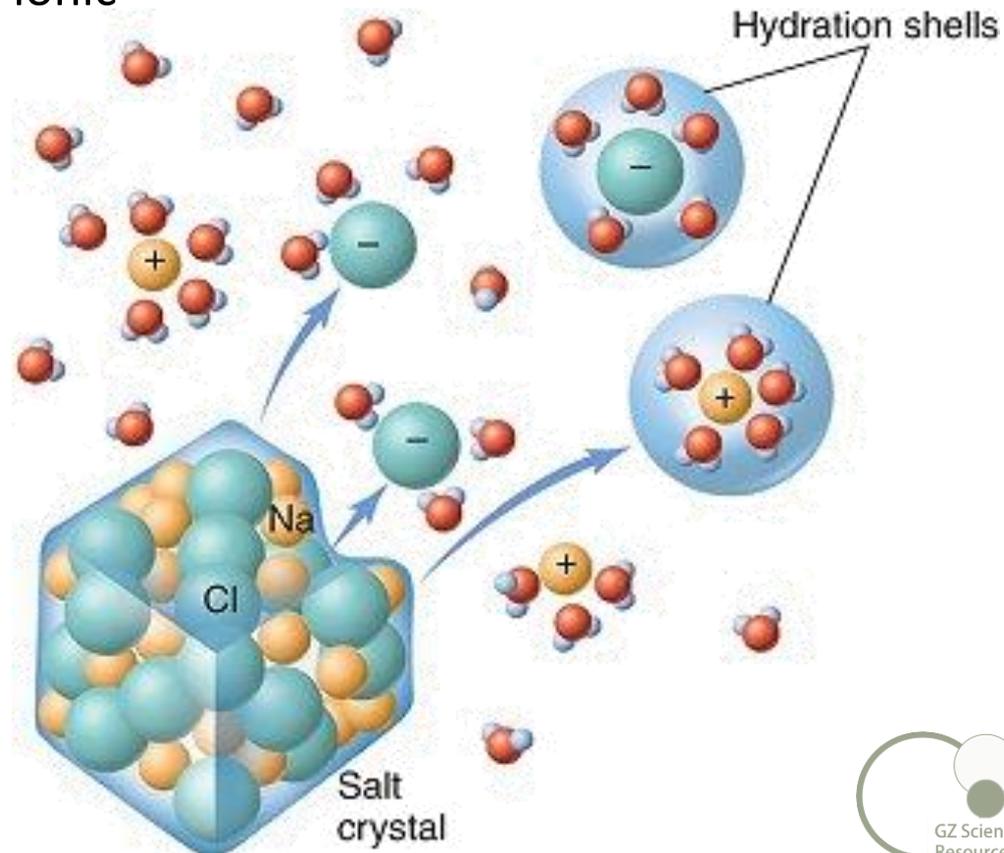
A solution is formed by mixing a **solute** (a dissolved substance) into a **solvent** (the solution that dissolves the solute).

In Aqueous Chemistry the solvent is water, and the solute can be an acid, base or ionic salt.

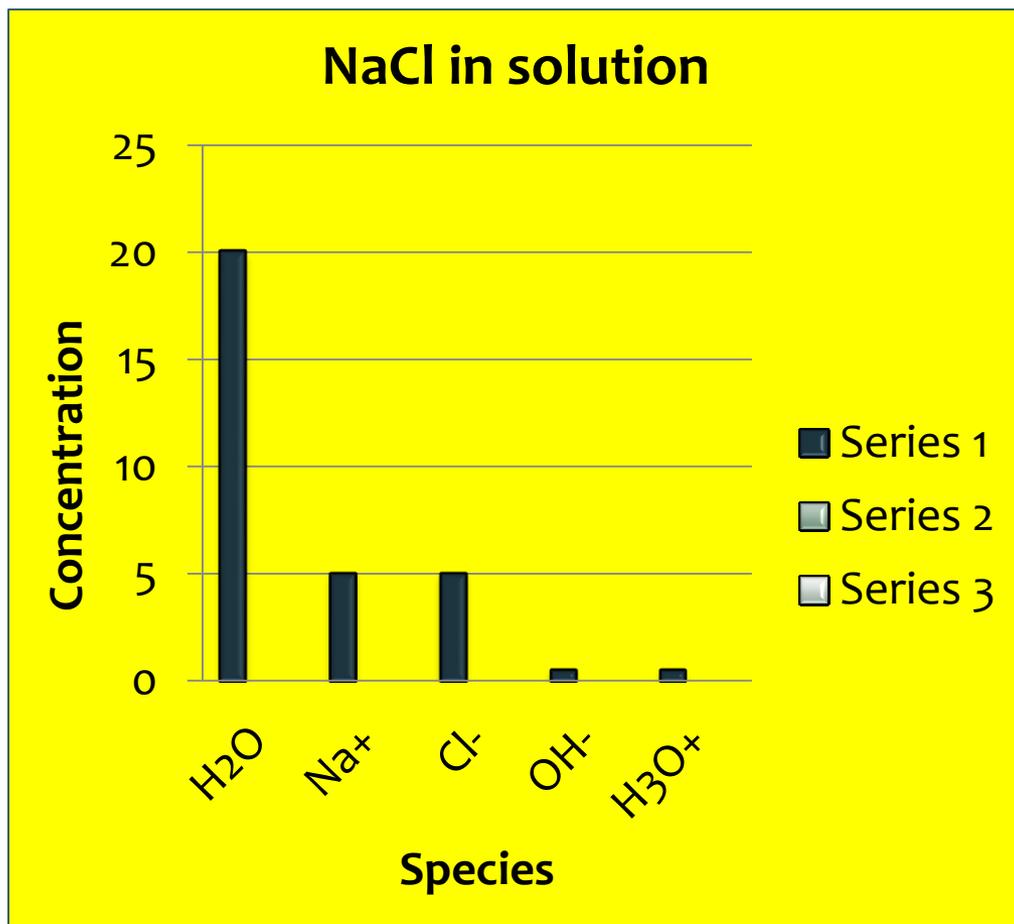
A solute dissolves by bonds being broken between solute particles (endothermic) and new bonds being formed between solute and solvent (exothermic).

A small amount of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  will always be present in water due to  $K_w = [\text{OH}^-] [\text{H}_3\text{O}^+] = 1 \times 10^{-14}$

Water will always be present in large concentrations.



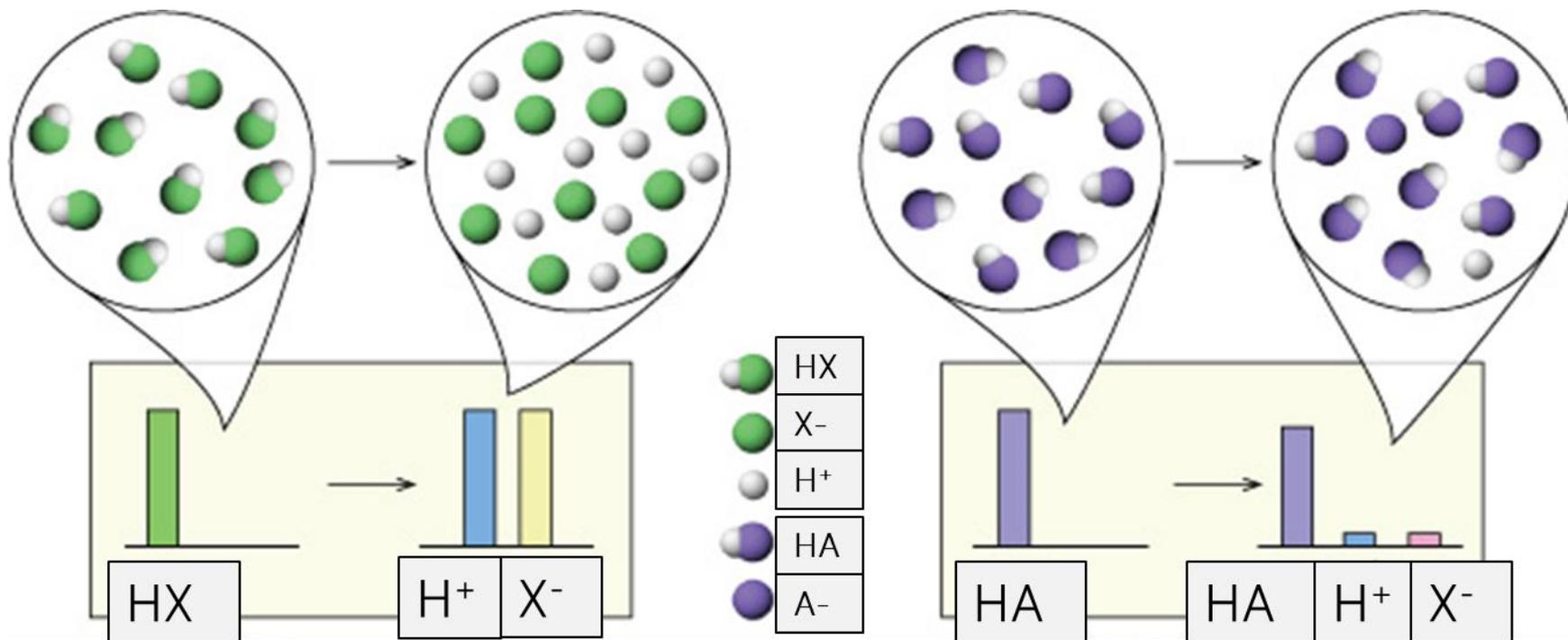
# Concentration of species in solution



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<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> will also be present, according to the  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}$
- 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.

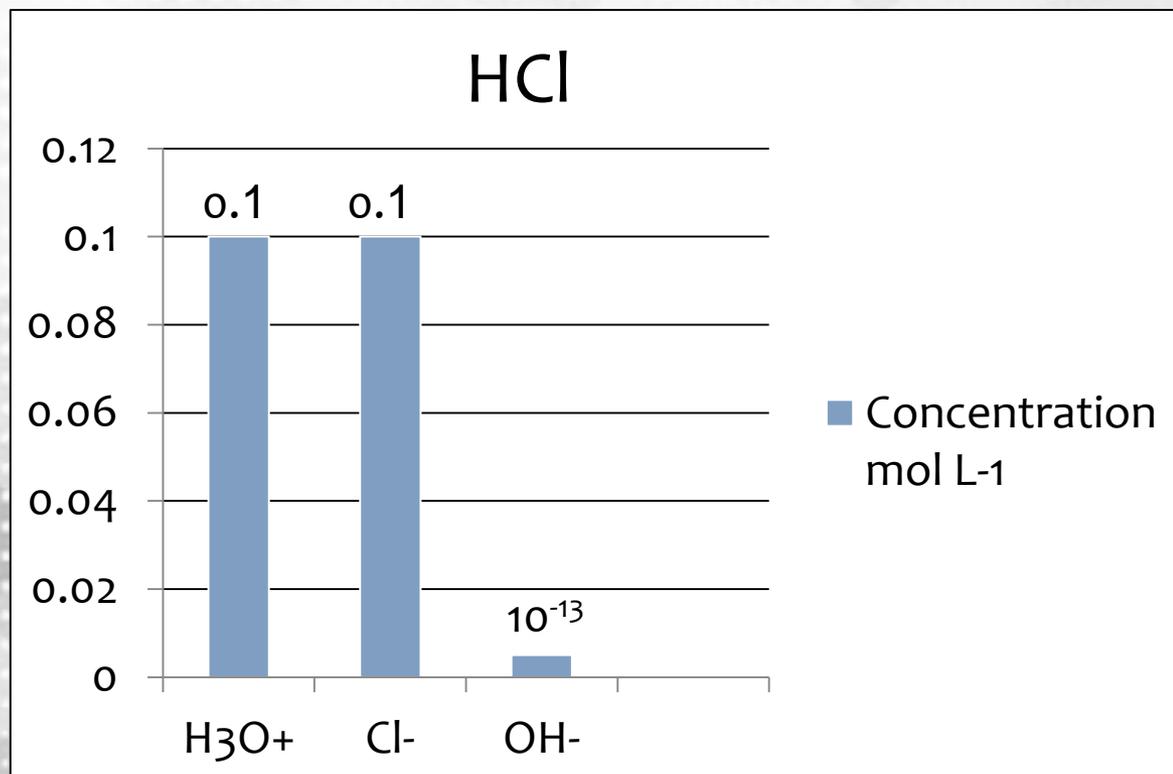
Equal quantities of conjugate base and hydronium are formed, but in small amounts

## Concentration of ions in solution – Strong Acid

Strong Acid i.e. HCl reacting with water



Strong acids will provide **good conductivity** and **pH 1-2** due to the high presence of  $\text{H}_3\text{O}^+$  ions



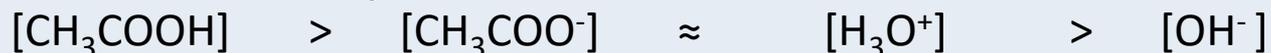
**No strong acid will be left in the final mixture.**

$\text{H}_3\text{O}^+$  and  $\text{Cl}^-$  are produced in equal concentrations – in the same concentration as the original strong acid.

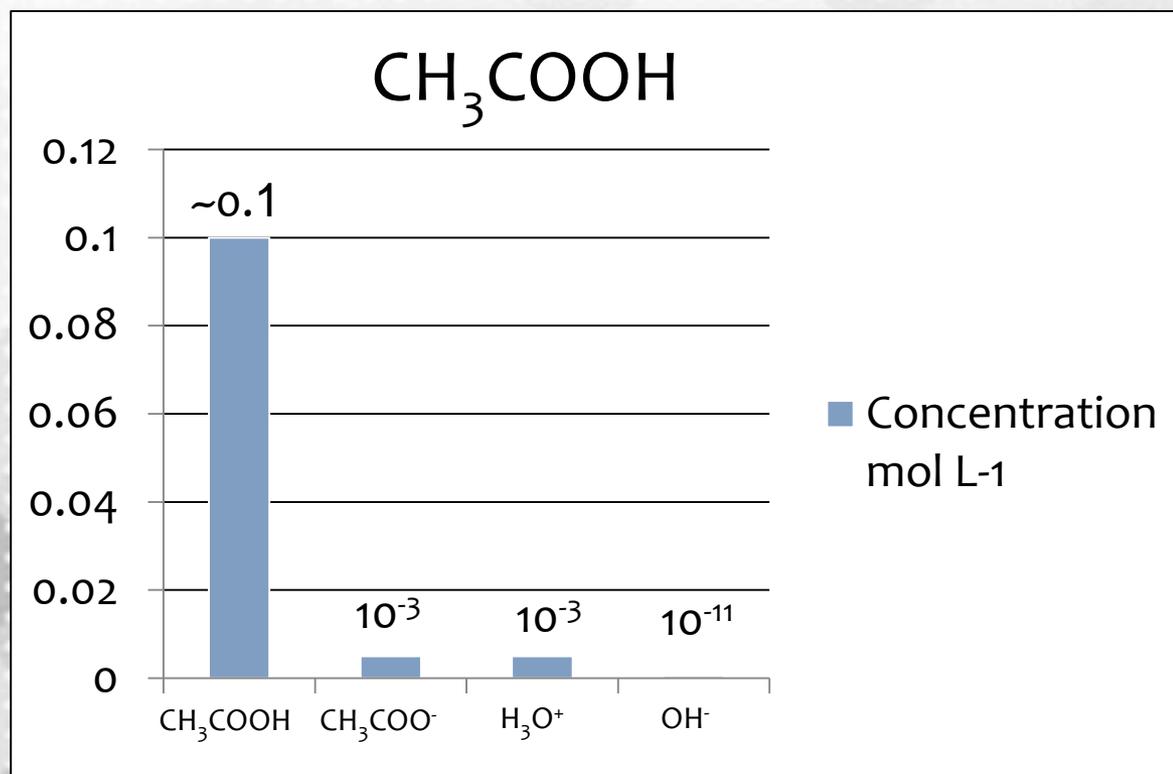
A small amount of  $\text{OH}^-$  is present as water dissociates into  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$

## Concentration of ions in solution – Weak Acid

Weak Acid i.e.  $\text{CH}_3\text{COOH}$  reacting with water



weak acids will provide **poor conductivity** and **pH 3-6** due to the low presence of  $\text{H}_3\text{O}^+$  ions (but still higher than  $\text{OH}^-$  ions)



**Most weak acid will be left in the final mixture.**

$\text{H}_3\text{O}^+$  and  $\text{CH}_3\text{COO}^-$  are produced in equal concentrations – a small amount of the weak acid had dissociated.

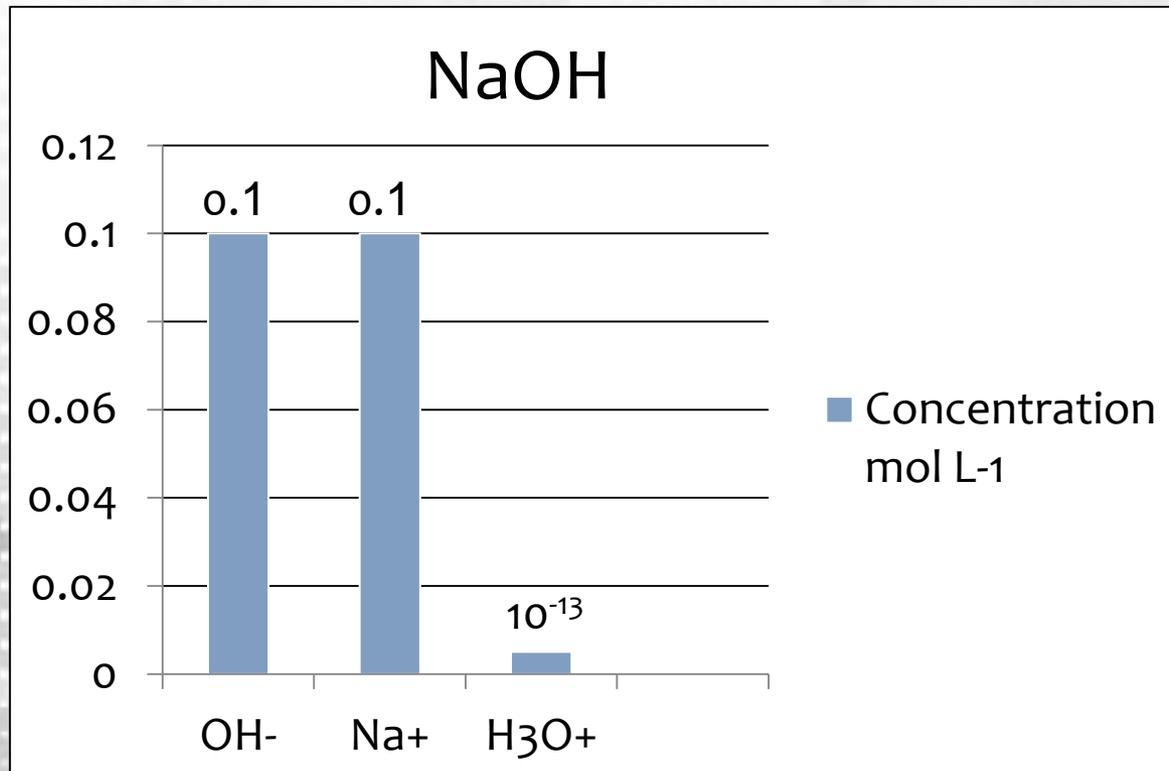
A small amount of  $\text{OH}^-$  is present as water dissociates into  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$

## Concentration of ions in solution – Strong Base

Strong Base i.e. NaOH reacting with water



Strong bases will provide **good conductivity** and **pH 12 – 14** due to the high presence of  $\text{OH}^-$  ions



**No strong base will be left in the final mixture.**

$\text{OH}^-$  and  $\text{Na}^+$  are produced in equal concentrations – in the same concentration as the original strong base.

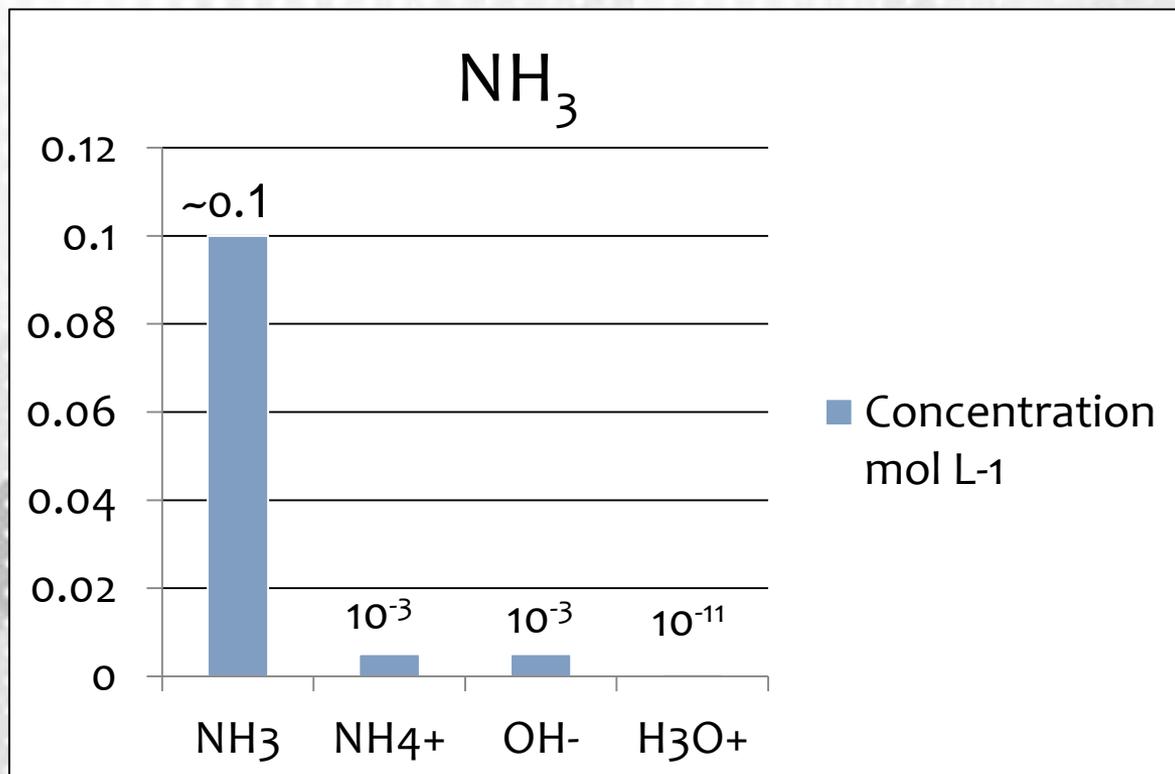
A small amount of  $\text{H}_3\text{O}^+$  is present as water dissociates into  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$

## Concentration of ions in solution – Weak Base

Weak Base i.e.  $\text{NH}_3$



weak bases will provide **poor conductivity** and **pH 8 – 11** due to the low presence of  $\text{OH}^-$  ions (but still higher than  $\text{H}_3\text{O}^+$  ions)



**Most weak base will be left in the final mixture.**

$\text{OH}^-$  and  $\text{NH}_4^+$  are produced in equal concentrations – a small amount of the weak base had dissociated.

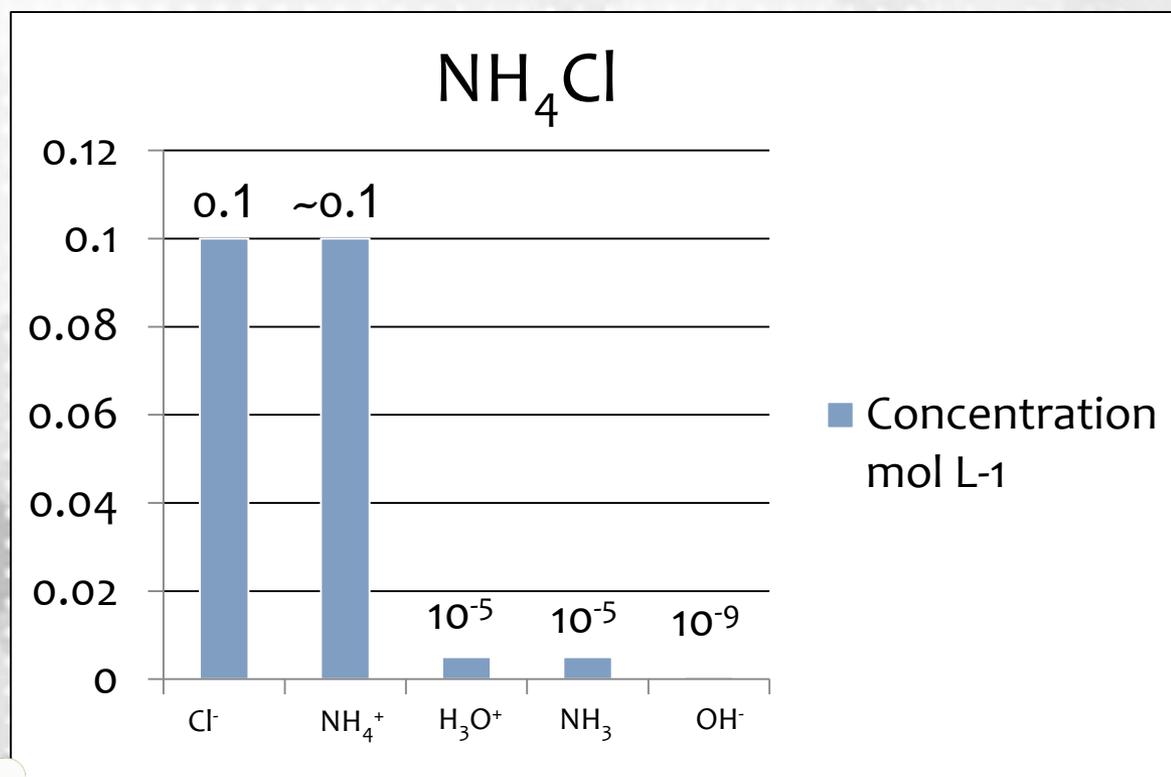
A small amount of  $\text{H}_3\text{O}^+$  is present as water dissociates into  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$

## Concentration of ions in solution – acid salt

Acid Salt i.e.  $\text{NH}_4\text{Cl}$



Acid salts will provide **good conductivity** and **pH < 7** due to the high presence of ions from dissolving and to a lesser extent  $\text{H}_3\text{O}^+$  ions



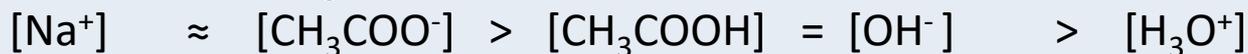
The spectator ion will be left in the highest concentration followed by the weak acid.

$\text{H}_3\text{O}^+$  and  $\text{NH}_3$  are produced in equal concentrations – a small amount of the weak acid had dissociated.

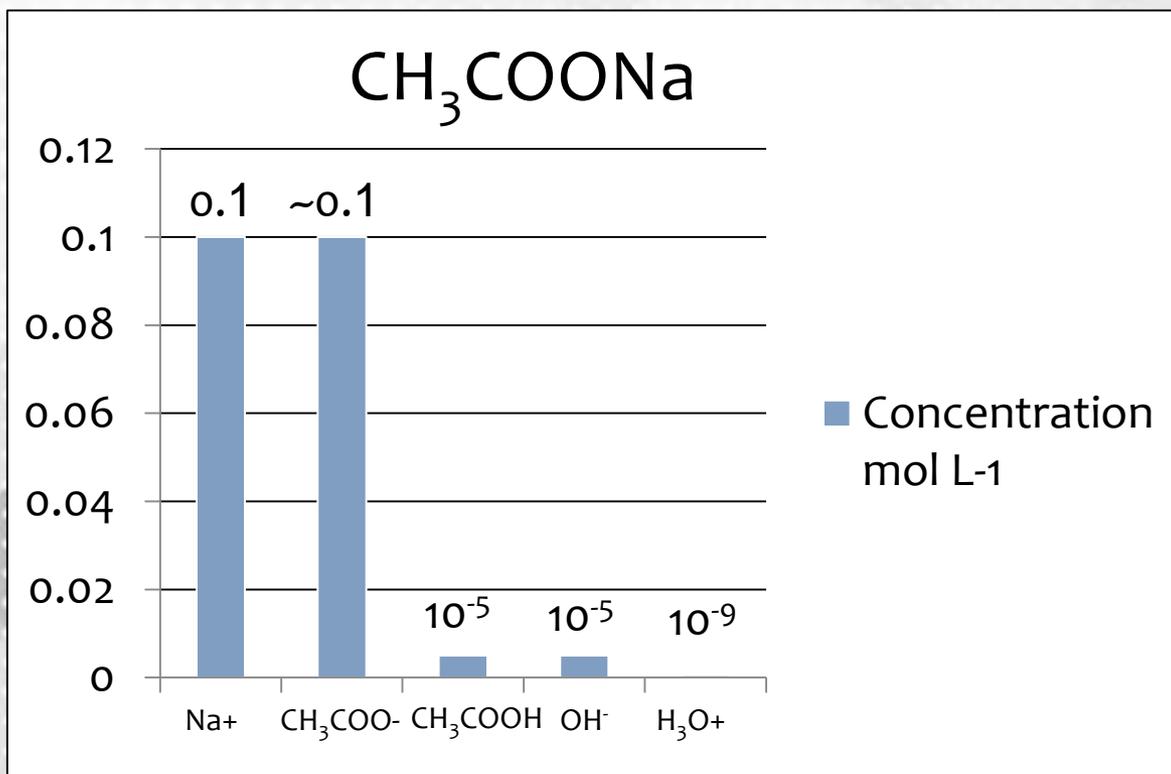
A small amount of  $\text{OH}^-$  is present as water dissociates into  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$

## Concentration of ions in solution – base salt

Base Salt i.e.  $\text{CH}_3\text{COONa}$



base salts will provide **good conductivity** and **pH > 7** due to the high presence of ions from dissolving and to a lesser extent  $\text{OH}^-$  ions



The spectator ion will be left in the highest concentration followed by the weak base.

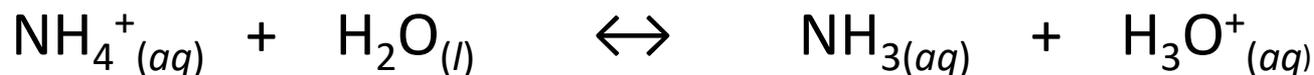
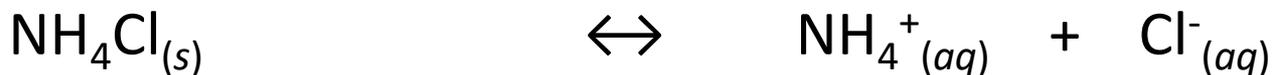
$\text{OH}^-$  and  $\text{CH}_3\text{COOH}$  are produced in equal concentrations – a small amount of the weak base had dissociated.

A small amount of  $\text{H}_3\text{O}^+$  is present as water dissociates into  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$

## 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,  $\text{NH}_4\text{Cl}$ , contains the cation  $\text{NH}_4^+$  and the anion  $\text{Cl}^-$ . The  $\text{Cl}^-$  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  $\text{NH}_4^+$  ion is the conjugate acid of the weak base  $\text{NH}_3$  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.



## NCEA 2013 Species in Solution (pH)

Excellence  
Question

**Question: 1a:** 1 mol of each of the following substances was placed in separate flasks, and water was added to these flasks to give a total volume of 1 L for each solution. In the box below, rank these solutions in order of **increasing** pH. Justify your choice and include equations where appropriate.



- HCl, a strong acid, reacts completely with water to form 1 mol L<sup>-1</sup> H<sub>3</sub>O<sup>+</sup> and hence a low pH.  $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$
- CH<sub>3</sub>NH<sub>3</sub>Cl dissociates completely in water to form CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> and Cl<sup>-</sup>. CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>, a weak acid, partially reacts with water to form less than 1 mol L<sup>-1</sup> H<sub>3</sub>O<sup>+</sup> and hence a higher pH than HCl.  $\text{CH}_3\text{NH}_3\text{Cl} \rightarrow \text{CH}_3\text{NH}_3^+ + \text{Cl}^-$   
$$\text{CH}_3\text{NH}_3^+ + \text{H}_2\text{O} \leftrightarrow \text{CH}_3\text{NH}_2 + \text{H}_3\text{O}^+$$
- CH<sub>3</sub>NH<sub>2</sub>, a weak base, partially reacts with water to form OH<sup>-</sup> ions. So there are more OH<sup>-</sup> ions than H<sub>3</sub>O<sup>+</sup> ions and the pH is thus high.



**Question: 1a:** When chlorine gas is added to water, the equation for the reaction is:  $\text{Cl}_{2(g)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{HCl}_{(aq)} + \text{HOCl}_{(aq)}$

**(ii)** List all the species present when HOCl reacts with water, in order of decreasing concentration. Justify your order.



HOCl partially dissociates, and so the equilibrium lies to the LHS/favours the reactants; therefore HOCl is present in the greatest amounts.

$\text{H}_3\text{O}^+$  and  $\text{OCl}^-$  are produced in equal amounts / there is a small contribution to  $\text{H}_3\text{O}^+$  from water therefore  $\text{H}_3\text{O}^+ > \text{OCl}^-$

Because there is a relatively high  $[\text{H}_3\text{O}^+]$ , the  $[\text{OH}^-]$  is very low (or links to  $K_w$ ).

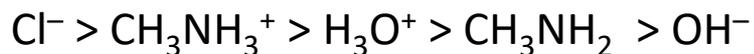
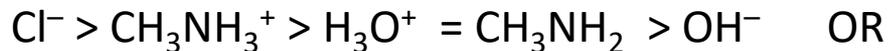
**Question: 2c:** Ethyl ammonium chloride,  $\text{CH}_3\text{CH}_2\text{NH}_3\text{Cl}$ , is a weak acid that will also react with water.

List all the species present in a solution of  $\text{CH}_3\text{CH}_2\text{NH}_3\text{Cl}$ , in order of decreasing concentration.

Do not include water.

Justify the order you have given.

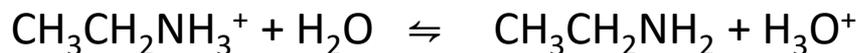
Include equations, where necessary.



$\text{CH}_3\text{CH}_2\text{NH}_3\text{Cl}$  completely dissociates.

(The chloride ion does not react further with water and so will be in the greatest concentration.)

The ethanamine ion will react further with water, but only partially, leaving it the next in the series.



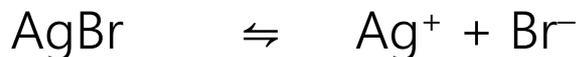
For every mole of  $\text{CH}_3\text{CH}_2\text{NH}_3^+$  that reacts with water, 1 mole of  $\text{CH}_3\text{CH}_2\text{NH}_2$  and  $\text{H}_3\text{O}^+$  are formed.

(However,  $\text{H}_3\text{O}^+$  is slightly more concentrated than  $\text{CH}_3\text{CH}_2\text{NH}_2$ , as there is a small contribution from water).

$\text{OH}^-$  is present in the lowest concentration as this comes from the dissociation of water only.

**Question: 1b:** 40.0 mL of 0.150 mol L<sup>-1</sup> HBr solution was added to 25.0 mL of a saturated silver bromide, AgBr, solution.

- (i) Write an equation for the equilibrium occurring in a saturated solution of AgBr.
- (ii) Explain the changes that occur to the concentrations of the species in the saturated solution of AgBr on the addition of the HBr solution.



Br<sup>-</sup> is a common ion / added to solution

An increase in [Br<sup>-</sup>] will result in the reverse reaction being favoured, to restore equilibrium / minimise the change.

This results in a decrease in [Ag<sup>+</sup>] (since Ag<sup>+</sup> reacts with some of the added Br<sup>-</sup> to help use it up) / AgBr becomes less soluble, (until [Ag<sup>+</sup>][Br<sup>-</sup>] is again equal to *K*<sub>s</sub>.)

Putting it all together

Blue litmus	[Orange]						[Blue]					
Red litmus	[Orange]						[Blue]					
Universal indicator	[Dark Red]	[Red]	[Orange]	[Yellow-Orange]	[Yellow]	[Light Green]	[Green]	[Light Blue]	[Blue]	[Purple-Blue]	[Purple]	[Dark Purple]
pH	<b>1-3</b>		<b>4-6</b>		<b>7</b>	<b>8-10</b>		<b>11-14</b>				
description	<b>Strong Acids</b> Readily donate all their protons when dissolved		<b>Weak Acids</b> donate only a small proportion of protons		<b>Neutral solution</b>	<b>Weak Bases</b> Accept only a small proportion of protons		<b>Strong Bases</b> Readily accept protons				
H <sub>3</sub> O <sup>+</sup> / OH <sup>-</sup> concentration	Concentration of H <sup>+</sup> ions is <b>greater</b> than that of OH <sup>-</sup> ions				Concentration of H <sup>+</sup> ions is the <b>same</b> as that of OH <sup>-</sup> ions		Concentration of H <sup>+</sup> ions is <b>less</b> than that of OH <sup>-</sup> ions					



# Conductivity of solutions

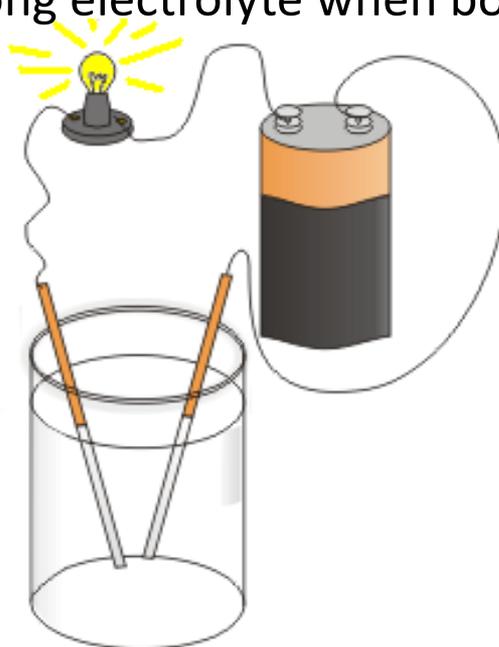
Conductivity is related to the availability of free moving charged particles.

The presence of ions in solution and the concentration of them determine conductivity.

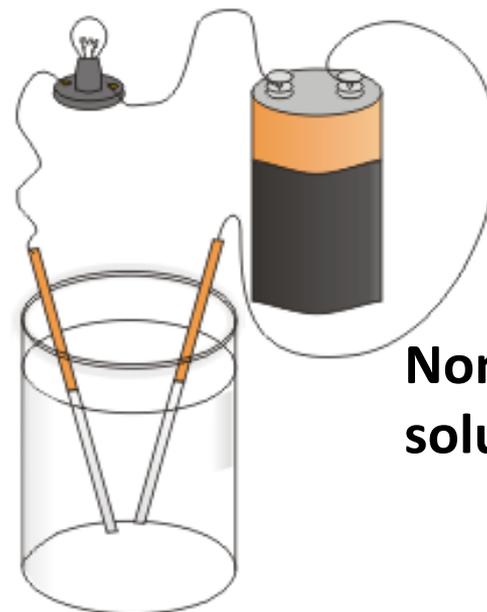
## High conductivity

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.

**Conductive  
solution**



**Non-conductive  
solution**



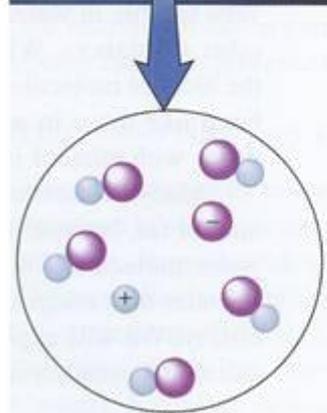
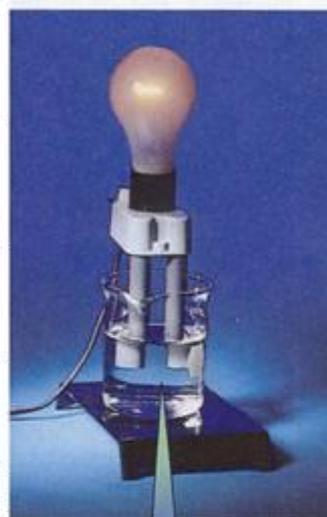
# Conductivity of solutions

## Low Conductivity

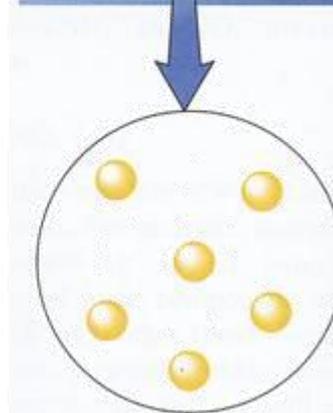
A weak electrolyte is formed from a weak acid or base that only partially dissociates. Only a small concentration of ions are created to carry charge. (such as acetic acid)

## No Conductivity

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



**ethanoic acid**



**glucose**

## NCEA 2013 Conductivity

Excellence  
Question

**Question: 1b:** The conductivity of the 1 mol L<sup>-1</sup> solutions formed in (a) can be measured. CH<sub>3</sub>NH<sub>3</sub>Cl                      CH<sub>3</sub>NH<sub>2</sub>                      HCl

Rank these solutions in order of **decreasing** conductivity. Compare and contrast the conductivity of each of the 1 mol L<sup>-1</sup> solutions, with reference to species in solution.



CH<sub>3</sub>NH<sub>3</sub>Cl and HCl will dissociate completely in water to produce 2 mol L<sup>-1</sup> ions.

CH<sub>3</sub>NH<sub>2</sub> will only partially react with water to produce less than 1 mol L<sup>-1</sup> of ions.

**Question: 1b:** The table shows the pH and electrical conductivity of three solutions. The concentrations of the solutions are the same. Compare and contrast the pH and electrical conductivity of these three solutions. Include appropriate equations in your answer.

Solution	NaOH	CH <sub>3</sub> NH <sub>2</sub>	CH <sub>3</sub> COONa
pH	13.2	11.9	8.98
Electrical conductivity	good	poor	good

The pH of a solution is calculated from its [H<sub>3</sub>O<sup>+</sup>].

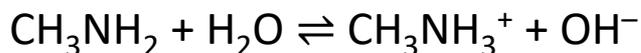
- ❑ **NaOH** is an ionic solid that is a strong base and dissociates completely to produce a high OH<sup>-</sup> concentration (low [H<sub>3</sub>O<sup>+</sup>]). Since [OH<sup>-</sup>] is high / [H<sub>3</sub>O<sup>+</sup>] is low, the pH is high.



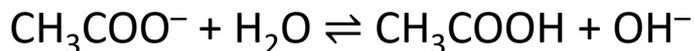
**Question: 1b:** The table shows the pH and electrical conductivity of three solutions. The concentrations of the solutions are the same. Compare and contrast the pH and electrical conductivity of these three solutions. Include appropriate equations in your answer.

Solution	NaOH	CH <sub>3</sub> NH <sub>2</sub>	CH <sub>3</sub> COONa
pH	13.2	11.9	8.98
Electrical conductivity	good	poor	good

- CH<sub>3</sub>NH<sub>2</sub> is a weak base that partially reacts / dissociates / ionises with H<sub>2</sub>O producing a lower concentration of OH<sup>-</sup>, Therefore it has a lower pH than NaOH:



- The CH<sub>3</sub>COONa is an ionic solid that dissociates completely in H<sub>2</sub>O. The CH<sub>3</sub>COO<sup>-</sup> ion is a weak base that partially reacts / dissociates / ionises with H<sub>2</sub>O producing a lower concentration of OH<sup>-</sup>.



The pH is closer to 7, showing it is the weakest base. Therefore it has a lowest pH

**Question: 1b:** The table shows the pH and electrical conductivity of three solutions. The concentrations of the solutions are the same. Compare and contrast the pH and electrical conductivity of these three solutions. Include appropriate equations in your answer.

Solution	NaOH	CH <sub>3</sub> NH <sub>2</sub>	CH <sub>3</sub> COONa
pH	13.2	11.9	8.98
Electrical conductivity	good	poor	good

### Electrical conductivity:

Electrical conductivity is determined by the concentration of ions.

- NaOH** completely dissolves to produce a high concentration of Na<sup>+</sup> and OH<sup>-</sup> ions in solution.

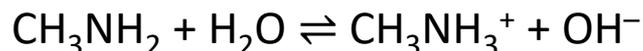
NaOH → Na<sup>+</sup> + OH<sup>-</sup> Therefore it is a good conductor.

**Question: 1b:** The table shows the pH and electrical conductivity of three solutions. The concentrations of the solutions are the same. Compare and contrast the pH and electrical conductivity of these three solutions. Include appropriate equations in your answer.

Solution	NaOH	CH <sub>3</sub> NH <sub>2</sub>	CH <sub>3</sub> COONa
pH	13.2	11.9	8.98
Electrical conductivity	good	poor	good

### Electrical conductivity:

- Since **CH<sub>3</sub>NH<sub>2</sub>** is a weak base, it only partially reacts with water to produce a low concentration of ions in solution so it is a poor electrical conductor.



- CH<sub>3</sub>COONa** is also an ionic solid. It dissolves completely to produce a high concentration of Na<sup>+</sup> and CH<sub>3</sub>COO<sup>-</sup> ions:



Therefore it is a good conductor.

**Question: 1a (ii)** : Compare and contrast the electrical conductivity of 0.150 mol L<sup>-1</sup> solutions of hydrofluoric acid, HF, and hydrobromic acid, HBr.

In your answer, you should:

- include the requirements for a solution to conduct electricity
- identify the species present AND their relative concentrations.

*No calculations are necessary.*

To conduct a current, a substance requires mobile charged particles / ions.

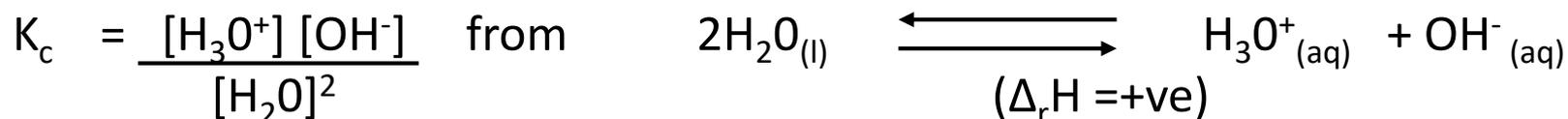
HF and HBr solutions have ions in solution, so both will conduct electricity.

HBr is a strong acid, and therefore completely dissociates to produce a high [Br<sup>-</sup>] and [H<sub>3</sub>O<sup>+</sup>]. In contrast, HF is a weak acid and therefore only partially dissociates to produce a lower [ions], i.e. F<sup>-</sup> and H<sub>3</sub>O<sup>+</sup>.

So, HF is a poorer electrical conductor / weaker electrolyte.

## K<sub>w</sub> – the ionic product for water

**K<sub>w</sub>** is ionic product for water and an equilibrium constant based on the reaction of water molecules transferring H<sup>+</sup> in an acid base reaction to create OH<sup>-</sup> and H<sub>3</sub>O<sup>+</sup> in equal quantities. The rate of reaction from reactants to products is the same as products to reactants once equilibrium is reached.



Or  $K_c \times [\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-]$

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

So  $K_c \times [\text{H}_2\text{O}]^2$  is also constant – called **K<sub>w</sub>**

As  $[\text{H}_3\text{O}^+] \times [\text{OH}^-]$  always equals  $1 \times 10^{-14}$  then so does **K<sub>w</sub>**

**Temperature increase causes an increase in K<sub>w</sub> as the reaction is endothermic this favours the forward reaction (Le Chateliers Principle)**

## Using $K_w$ to Calculate $[\text{OH}^-]$ or $[\text{H}_3\text{O}^+]$

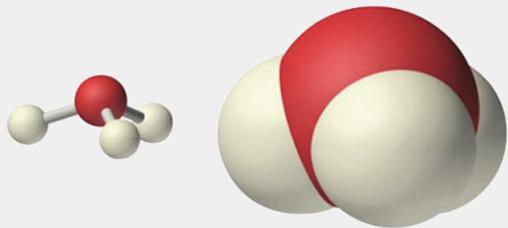
The product  $[\text{OH}^-] \times [\text{H}_3\text{O}^+]$  is a constant value (at the same temperature)

$$\text{IONIC PRODUCT} \quad K_w = [\text{OH}^-] \times [\text{H}_3\text{O}^+] = 1 \times 10^{-14}$$

e.g. If solution A has  $[\text{OH}^-] = 1 \times 10^{-1} \text{ molL}^{-1}$  find  $[\text{H}_3\text{O}^+]$

$$[\text{H}_3\text{O}^+] = \frac{1 \times 10^{-14}}{1 \times 10^{-1}} = 1 \times 10^{-13} \text{ molL}^{-1}$$

$$[\text{OH}^-] = \frac{1 \times 10^{-14}}{[\text{H}_3\text{O}^+]} \quad \text{or} \quad [\text{H}_3\text{O}^+] = \frac{1 \times 10^{-14}}{[\text{OH}^-]}$$



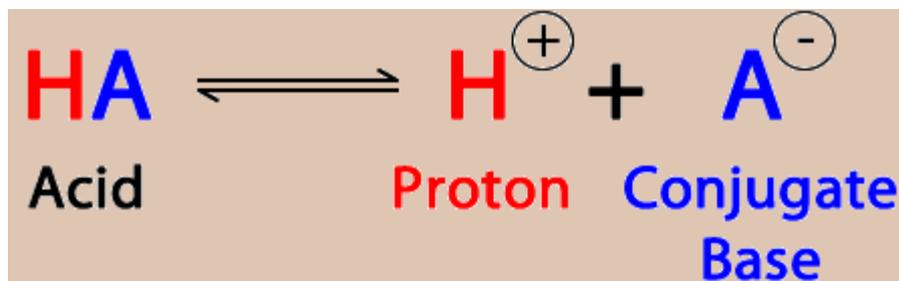
Hydronium ion,  
 $\text{H}_3\text{O}^+$

# Acidity constant

An acid dissociation constant,  $K_a$ , (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<sup>-</sup> and H<sup>+</sup> are said to be **in equilibrium** when their concentrations do not change with the passing of time.

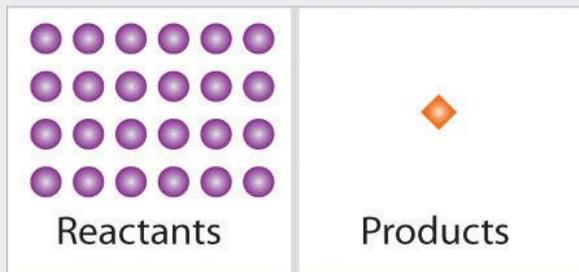
# Acidity constant

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

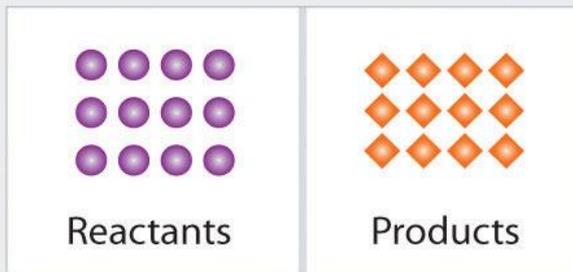
**Magnitude of K increasing** →

Small  
( $K < 10^{-3}$ )



Mostly reactants

Intermediate  
( $10^{-3} \leq K \leq 10^3$ )



Significant amounts  
of reactants and products

Large  
( $K > 10^3$ )



Mostly products

**Composition of equilibrium mixture**

# Acidity constant

From the equation:



The equilibrium constant for a weak acid can be written as:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

**We don't include H<sub>2</sub>O because in an aqueous solution it is in such high concentrations that the difference before and after dissociation is negligible.**

We can also assume that the concentration of H<sub>3</sub>O<sup>+</sup> and A<sup>-</sup> are the same, as one mole of H<sub>3</sub>O<sup>+</sup> forms every time one mole of A<sup>-</sup> 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.

# Acidity constant - assumptions

**Acidity constant** =  $K_a$

$[H_3O^+] = [A^-]$  hydronium concentration = conjugate base concentration

$$K_a = \frac{[H_3O^+]^2}{[HA]}$$

→ if  $K_a$  small then  $[H_3O^+]$  much smaller than  $[HA]$  – very little dissociation

$[HA]$  can then be assumed to be equal to  $c(HA)$

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

## Acidity constant for degree of dissociation > 1%



If degree of dissociation is >1%, then in a pH calculation the concentration of weak acid molecule present at equilibrium is significantly less than  $c(\text{HA})$ . ie  $[\text{HA}] = c(\text{HA}) - [\text{H}_3\text{O}^+]$  and this should be corrected for by solving a quadratic equation or by method of first approximation.

**For example: determine the pH of a solution made from 0.01 mole of  $\text{HNO}_2$  in 1.0 L of water.**



Initial concentration	0.01		
Equilibrium concentration	(0.01-x)	x	x

$$K_a = 10^{-3.29} = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{x^2}{(0.01-x)}$$

# Acidity constant for degree of dissociation > 1%



Initial concentration	0.01		
Equilibrium concentration	(0.01-x)	x	x

$$K_a = 10^{-3.29} = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{x^2}{(0.01-x)}$$

## Solve the quadratic equation:

$$10^{-5.29} - 10^{-3.29}x = x^2$$
$$x^2 + 10^{-3.29}x - 10^{-5.29} = 0$$
$$x = 0.002$$

$$[\text{NO}_2] = [\text{H}^+] = 2 \times 10^{-3} = (10^{0.03})(10^{-3}) = 10^{-2.7}$$
$$[\text{HNO}_2] = 8 \times 10^{-3}$$
$$\text{pH} = 2.7$$

## Solve by approximation:

Assume that  $(0.01 - x) = 0.01$

$$10^{-3.29} = \frac{x^2}{10^{-2}}$$

$$x^2 = 10^{-5.29}$$

$$x = 10^{-2.65}$$

$$\text{pH} = 2.7$$



## pH calculations – Weak acid

1. Convert  $\text{p}K_a$  to  $K_a$   
(if required)

$$K_a = 10^{-\text{p}K_a}$$

2. Calculate  $[\text{H}_3\text{O}^+]$

$$[\text{H}_3\text{O}^+] = \sqrt{K_a \times c(\text{HA})}$$

3. Calculate pH  
(start here if strong acid)

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

# pH calculations – Weak acid



$$[\text{H}_3\text{O}^+] = \sqrt{\frac{K_a}{[\text{HA}]}}$$
$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

Concentration of water is so large it is not effected – considered a constant

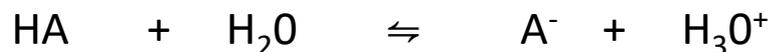
## Use when

→ given  $K_a$  (acid dissociation constant)

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

is the same

→ weak acid, HA



Use this equation to compare number of mols.

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



## NCEA 2014 pH calculations

Merit  
Question

**Question: 1a:** Hypochlorous acid has a  $pK_a$  of 7.53. Another weak acid, hydrofluoric acid, HF, has a  $pK_a$  of 3.17.

A  $0.100 \text{ mol L}^{-1}$  solution of each acid was prepared by dissolving it in water.

Compare the pHs of these two solutions.

*No calculations are necessary.*

Hydrofluoric acid is a stronger acid/more acidic/dissociates more because it has a smaller  $pK_a$  (larger  $K_a$ ) than hypochlorous acid.

So HF will therefore have a higher  $[\text{H}_3\text{O}^+]$ . As  $[\text{H}_3\text{O}^+]$  increases, the pH decreases, so HF will have a lower pH than HOCl.

(pH HF = 2.09, HOCl = 4.27)

→ **larger  $pK_a$  more reactants, the weaker the acid**

**Question: 1a: (iv)** Calculate the pH of 0.0152 mol L<sup>-1</sup> CH<sub>3</sub>NH<sub>3</sub>Cl solution.

$$K_a(\text{CH}_3\text{NH}_3^+) = 2.29 \times 10^{-11}$$

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \sqrt{K_a} \times \text{HA} \\ &= 5.90 \times 10^{-7} \end{aligned}$$

$$\text{pH} = 6.23$$

$$\begin{aligned} [\text{H}_3\text{O}^+] &= 5.90 \times 10^{-7} \text{ mol L}^{-1} \\ \text{pH} &= -\log 5.90 \times 10^{-7} = 6.23 \end{aligned}$$

$$K_a = 10^{-\text{p}K_a}$$

$$[\text{H}_3\text{O}^+] = \sqrt{K_a \times c(\text{HA})}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

## NCEA 2016 pH calculations

Excellence  
Question

**Question: 2b:** Calculate the pH of a  $0.109 \text{ mol L}^{-1}$  solution of ethanamine.

$$pK_a(\text{CH}_3\text{CH}_2\text{NH}_3^+) = 10.6$$

$$[\text{H}_3\text{O}^+] = \sqrt{K_a \times K_w \div [\text{CH}_3\text{CH}_2\text{NH}_2]}$$

$$[\text{H}_3\text{O}^+] = \sqrt{2.51 \times 10^{-11} \times 1.00 \times 10^{-14} \div 0.109}$$

$$[\text{H}_3\text{O}^+] = 1.52 \times 10^{-12} \text{ mol L}^{-1}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = 11.8$$

$$K_b = 1 \times 10^{-14} / K_a$$

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

$$[\text{H}_3\text{O}^+] = 1 \times 10^{-14} / [\text{OH}^-]$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

## NCEA 2017 pH calculations

Excellence  
Question

Question: 2a: Ammonia,  $\text{NH}_3$ , is a weak base.

$$\text{p}K_a(\text{NH}_4^+) = 9.24 \quad K_a(\text{NH}_4^+) = 5.75 \times 10^{-10}$$

(i) Calculate the pH of a  $0.105 \text{ mol L}^{-1}$   $\text{NH}_3$  solution.

$$[\text{H}_3\text{O}^+] = \sqrt{K_a \times K_w \div [\text{NH}_3]}$$

$$[\text{H}_3\text{O}^+] = \sqrt{5.75 \times 10^{-10} \times 1.00 \times 10^{-14} \div 0.105}$$

$$[\text{H}_3\text{O}^+] = 7.40 \times 10^{-12} \text{ mol L}^{-1}$$

$$\text{pH} = -\log(7.40 \times 10^{-12}) = 11.1$$

$$K_b = 1 \times 10^{-14} / K_a$$

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

$$[\text{H}_3\text{O}^+] = 1 \times 10^{-14} / [\text{OH}^-]$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

# $\text{pK}_a$

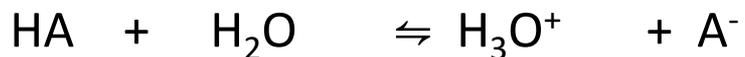
$$\text{pK}_a = -\log K_a$$

→ larger  $\text{pK}_a$  more reactants

→ negative for strong acids (HX)

→ gets larger (3 – 13) as acids get weaker – less dissociation

Weaker acid = stronger conjugate base

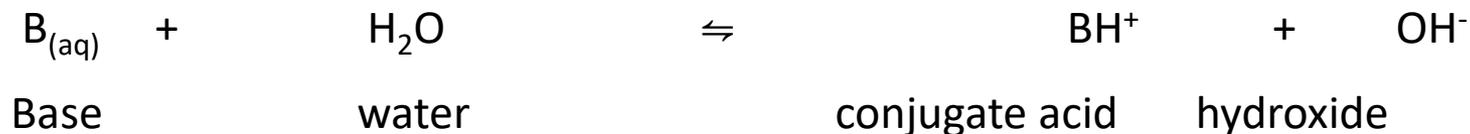


reactants

products

$$K_a = 10^{-\text{pK}_a}$$

# Bases



**Strong base** – completely dissociates (accepts all  $\text{H}^+$  ions)

$$\text{pH} = -\log[\text{H}_3\text{O}^+] \quad [\text{H}_3\text{O}^+] = 1 \times 10^{-14} / [\text{OH}^-]$$

Strong bases will have a conjugate weak acid

**Weak base** – partly dissociates (accepts few  $\text{H}^+$  ions)

[B] assumed to be same as  $c(\text{B})$  – initial concentration

$K_b$  – base dissociation constant

$$K_b = 1 \times 10^{-14} / K_a$$

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

**$K_b$  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**

# pH calculations – Weak base

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{K_w \times K_a}{[\text{A}^-]}}$$



$$K_w = K_c \times [\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+] \times [\text{OH}^-]$$

Because the concentration of water is considered constant

$$[\text{H}_3\text{O}^+] \times [\text{OH}^-] = 1 \times 10^{-14}$$

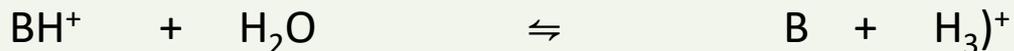
$$K_w = 1 \times 10^{-14}$$

## Use when

→ given  $K_a$  of conjugate acid (acid dissociation constant)

→ given concentration of reactant

→ weak base, B (replace  $[\text{A}^-]$ )



Use this equation to compare number of mols.

## pH calculations – Weak base

1. Convert  $K_a$  to  $K_b$

$$K_b = 1 \times 10^{-14} / K_a$$

2. Calculate  $[\text{OH}^-]$

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

3. Convert  $[\text{OH}^-]$  to  $[\text{H}_3\text{O}^+]$   
(start here if Strong Base)

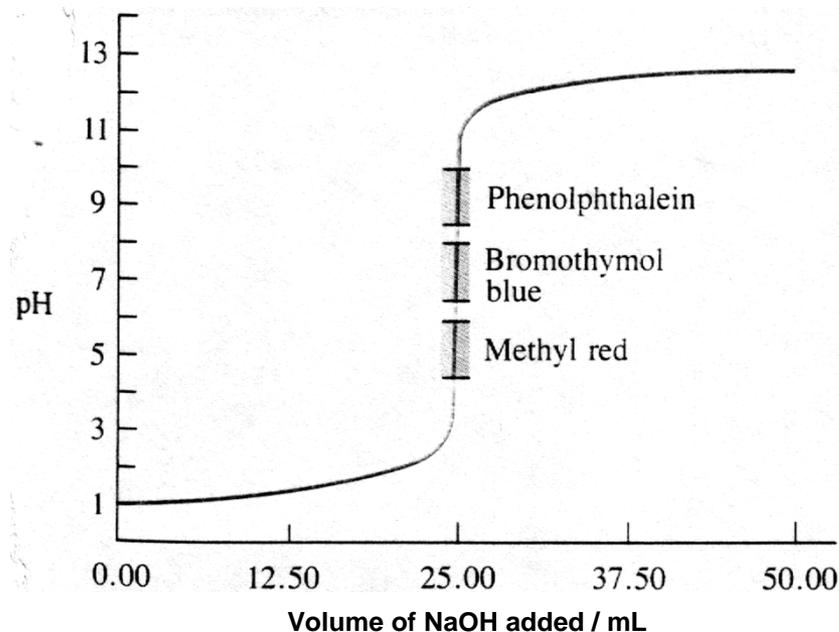
$$[\text{H}_3\text{O}^+] = 1 \times 10^{-14} / [\text{OH}^-]$$

4. Calculate pH

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

# Acid – base titration curves

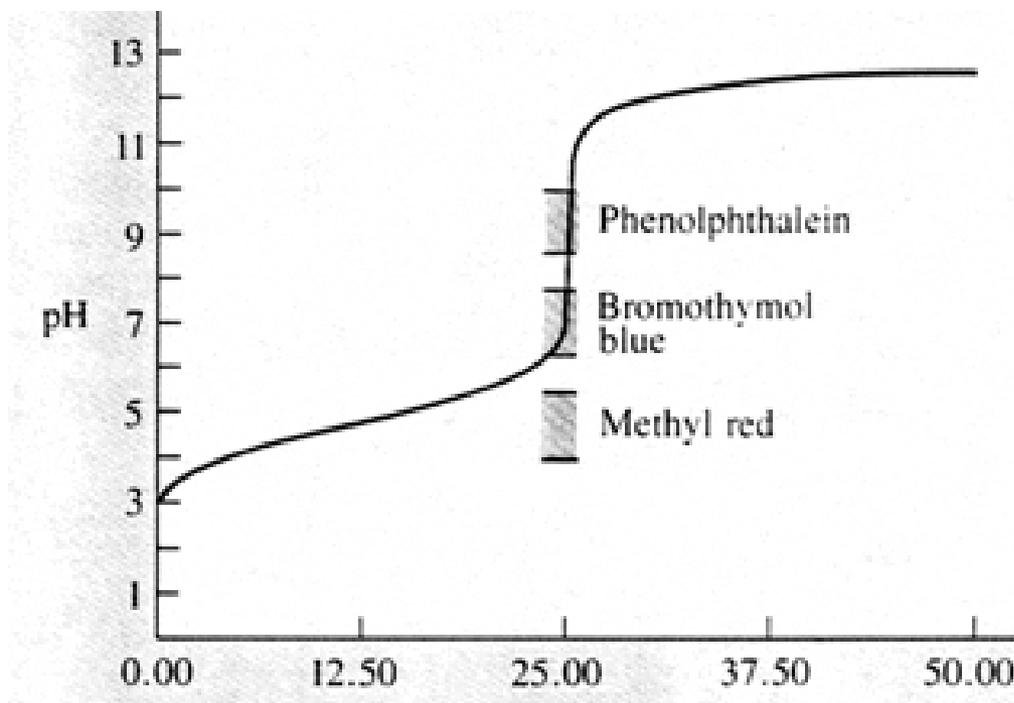
A plot of the pH of an acid solution against the volume of added base (or vice-versa) produces what is called a **pH titration curve**. The example below shows how the pH (measured using a pH meter) changes when a strong acid is added to a strong base. There are characteristic points on the curve that 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  $pK_a$  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.**

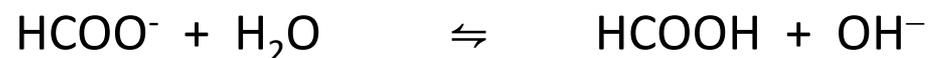
# Acid – base titration curves

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.



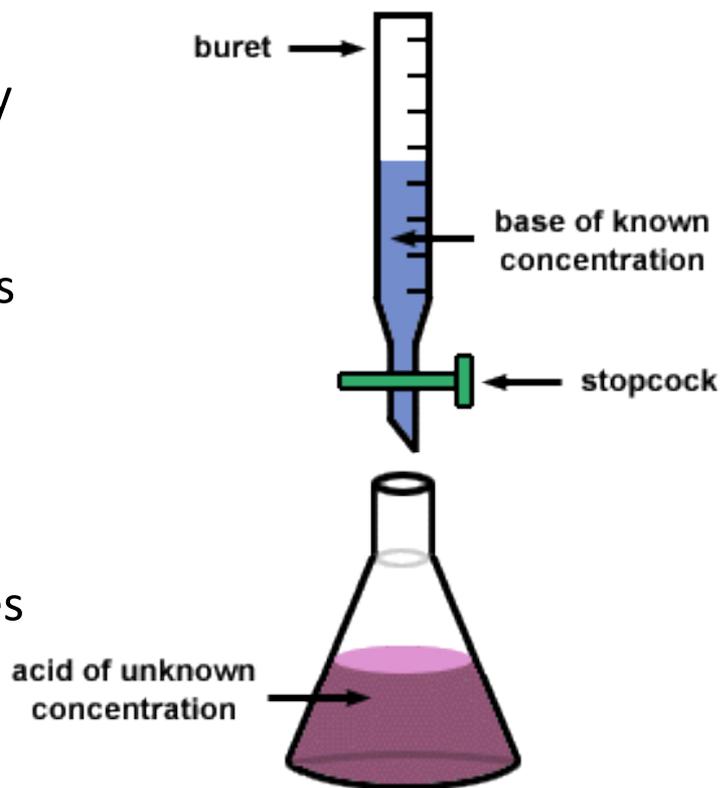
The equivalence point is at a pH greater than 7 so only indicators with a  $pK_a$  about 8-9 will change colour at the correct pH and be useful

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:



# 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.**

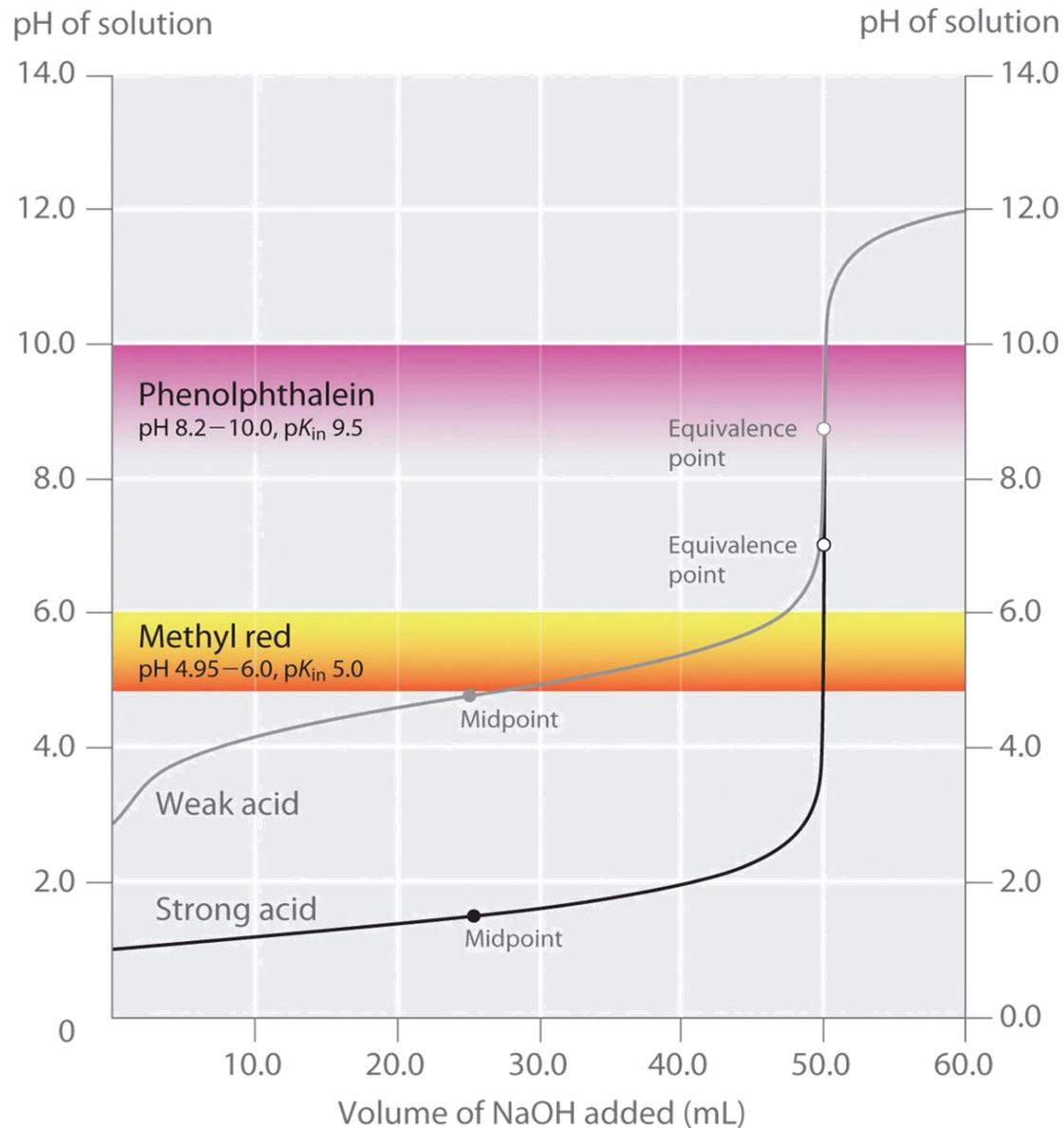


# Neutralisation of acids

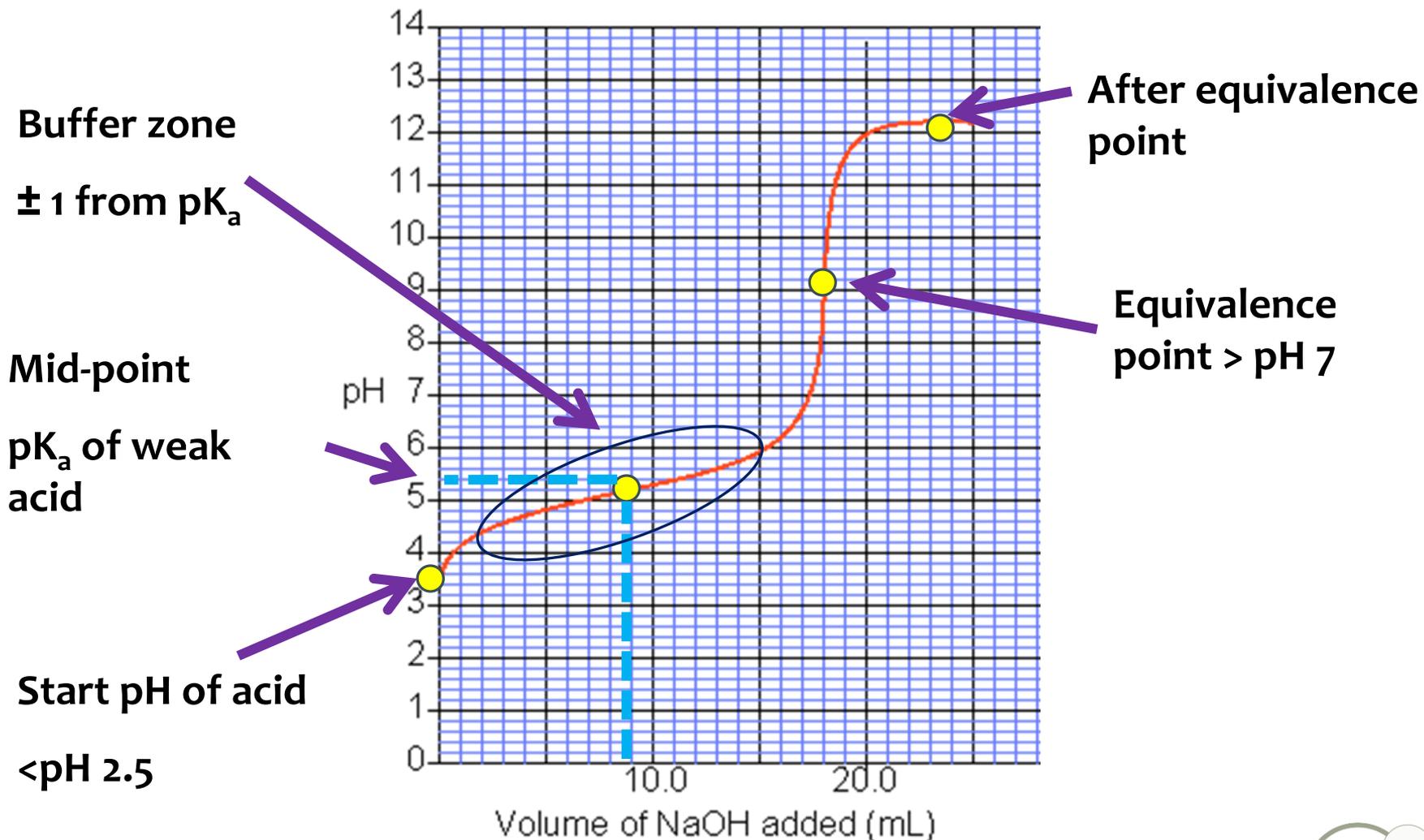
The pH of the equivalence point will determine the choice of indicator used.



methyl red



# Features of a titration curve – strong base/weak acid

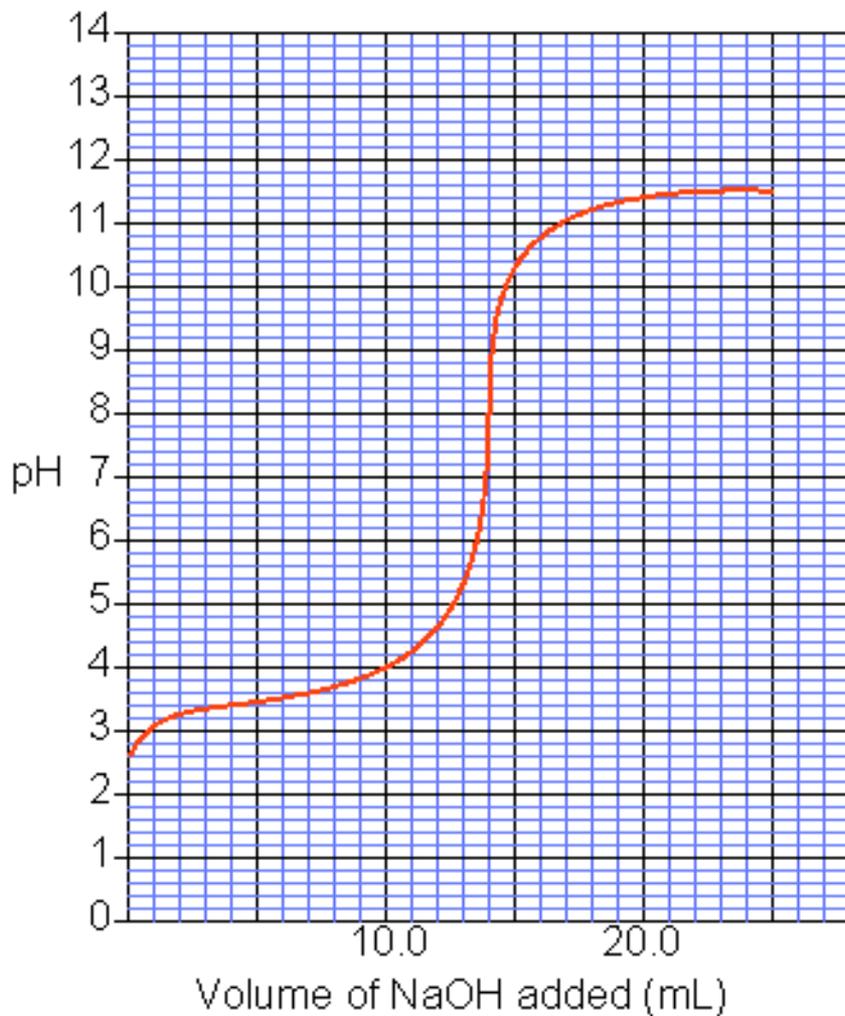


## Features of a titration curve – strong base/weak acid

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  $\text{p}K_a$  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.

# Acid – base titration curves

## Strong Base added to Strong Acid



### Characteristics

Start point below pH 3

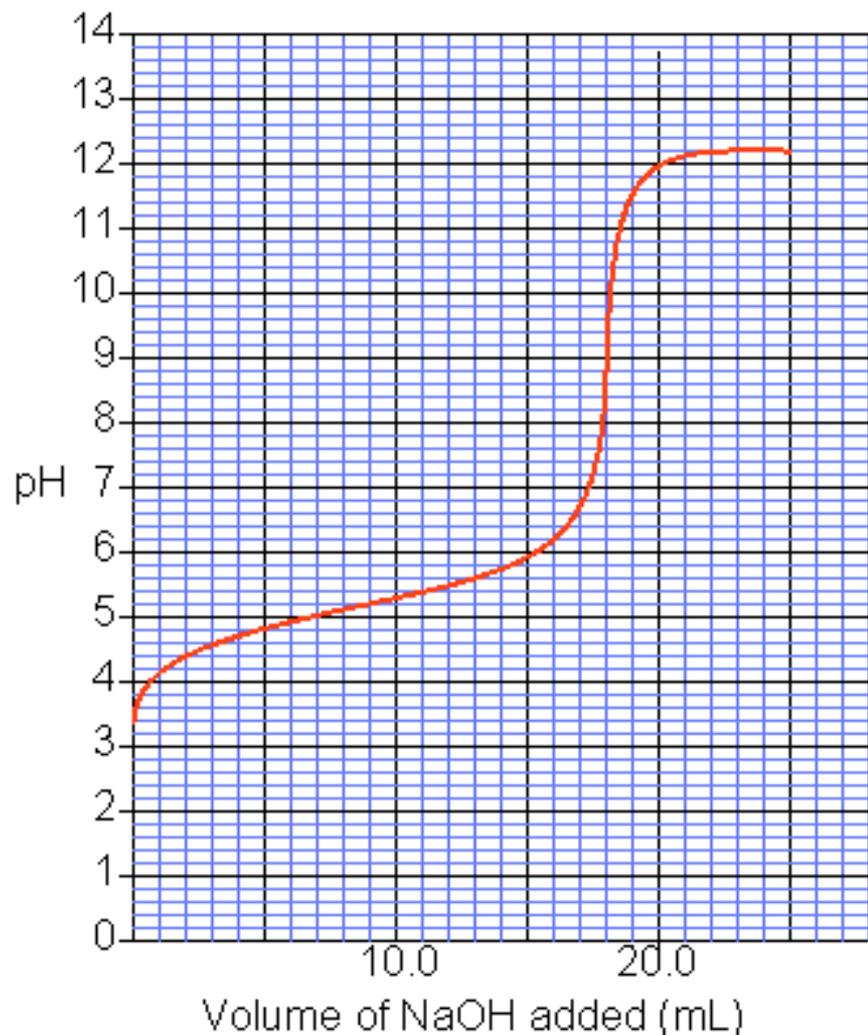
Equivalence point at 7

End of titration below pH12

Symmetrical shape

# Acid – base titration curves

## Strong Base added to Weak Acid



### Characteristics

Start point above pH 3

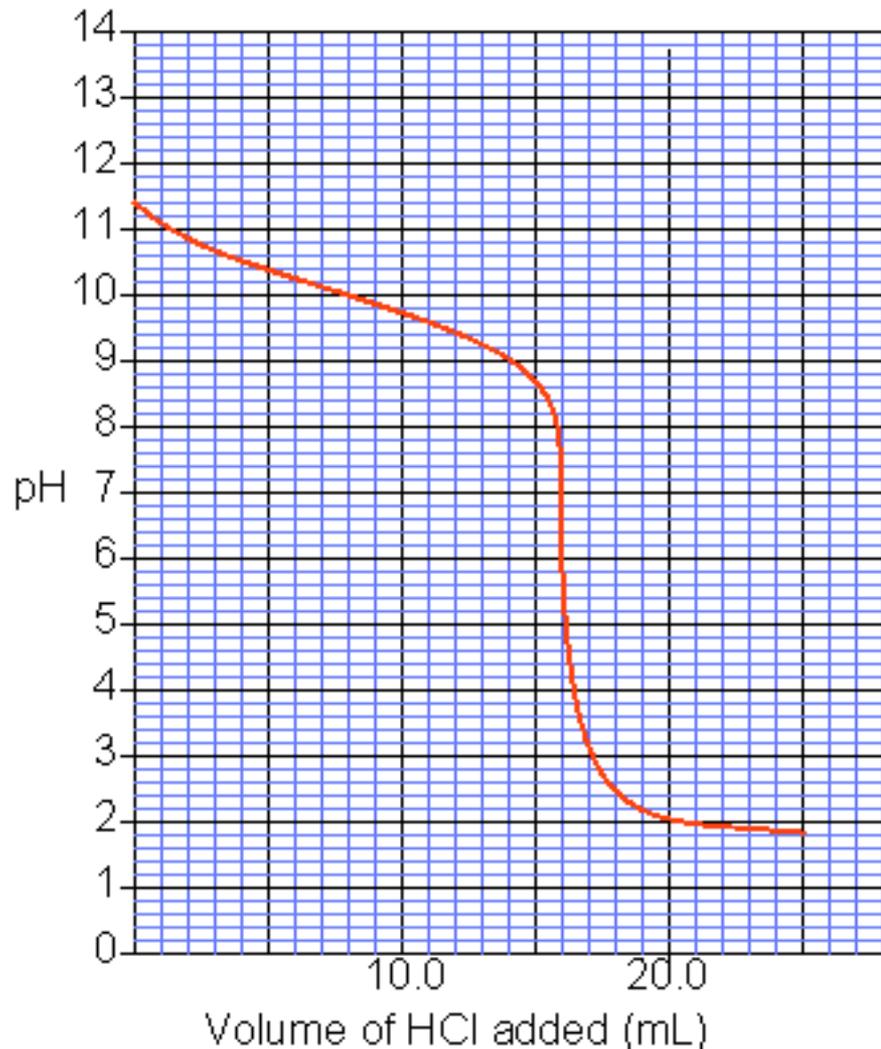
Equivalence point above 7

End of titration above pH12

Unsymmetrical shape

# Acid – base titration curves

## Strong Acid added to Weak Base



## Characteristics

Start point below pH 12

Equivalence point below 7

End of titration below pH 3

Unsymmetrical shape

Steps to drawing a titration curve

**Question:**

20.0 mL of 0.0896 mol L<sup>-1</sup> ethanoic acid is titrated with 0.100 mol L<sup>-1</sup> sodium hydroxide up to a total of 30mL  
pKa (CH<sub>3</sub>COOH) = 4.76

In order to graph a titration curve there are a number of points that need to be calculated in their specific order

1. The pH before any base is added
2. The volume of the base at equivalence point
3. The volume of base when pH = pKa
4. The pH at equivalence point
5. The pH after all of the base 30mL has been added

# Drawing titration curves

**Step One:** Calculate the start pH (in flask)

$$\text{Weak acid } [\text{H}_3\text{O}^+] = \sqrt{K_a \times c(\text{HA})}$$

$$K_a = 10^{-\text{p}K_a}$$

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

$$K_b = \frac{K_w}{K_a}$$

**Assumptions:**

$$[\text{HA}] = c(\text{HA})$$

**H<sub>2</sub>O concentration is the same before and after**

$$[\text{H}_3\text{O}^+] = [\text{conj base}]$$

Step One:  
Start pH

Find the pH of:

0.0896 molL<sup>-1</sup>

of

CH<sub>3</sub>COOH<sub>(aq)</sub>

pK<sub>a</sub> = 4.76



$$K_a = \frac{[\text{CH}_3\text{COO}^-] [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 10^{-\text{pK}_a}$$

$$= 10^{-4.76}$$

$$= 1.74 \times 10^{-5}$$

Assume

1. [CH<sub>3</sub>COO<sup>-</sup>] = [H<sub>3</sub>O<sup>+</sup>]

2. [CH<sub>3</sub>COOH] = 0.0896 molL<sup>-1</sup>

**Step One:**  
Start pH

Equilibrium  
expression of acid  
dissociation in water

$K_a =$



$$1.74 \times 10^{-5}$$

$=$

$$0.0896 \text{ mol L}^{-1}$$

Rearrange:

$$\sqrt{1.74 \times 10^{-5} \times 0.0896 \text{ mol L}^{-1}} = [\text{H}_3\text{O}^+]$$

$$1.25 \times 10^{-3} \text{ mol L}^{-1}$$

$$= [\text{H}_3\text{O}^+]$$

$$= -\log (1.25 \times 10^{-3} \text{ mol L}^{-1})$$

Could also use  
 $10^{-\text{p}K_a}$  in  
formula

$$\text{pH} = 2.90$$

# Drawing titration curves

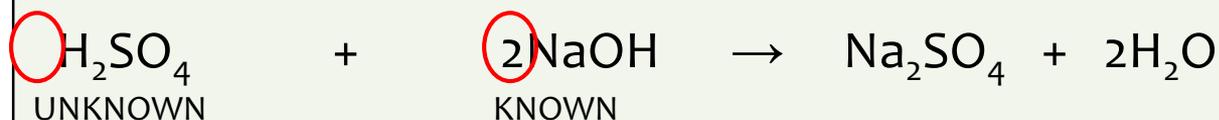
**Step Two:** Calculate the volume at equivalence point

a) Calculate the number of moles of known acid or base (the substance where the concentration has been given)

b) Multiply the number of moles by U/K

$$n = c \times v$$

Example – if concentration given for NaOH and you are calculating the concentration for H<sub>2</sub>SO<sub>4</sub>



$$\text{Moles Unknown} = \text{Moles known} \times \text{U/K} = \text{Mole Known} \times 1/2$$

c) Rearrange equation to calculate volume

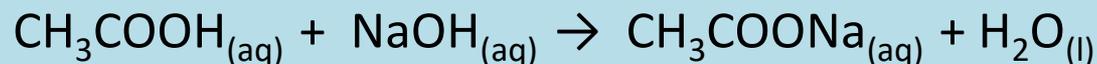
$$v = n / c$$

v = volume (L) c = concentration (molL<sup>-1</sup>)

**Step Two:**  
Volume of equivalence

Calculate the volume of **NaOH** at the endpoint.

Titration reaction is:



$$n(\text{CH}_3\text{COOH}) = cV$$

$$= 0.0896 \text{ mol L}^{-1} \times 0.0200\text{L}$$

$$= 1.79 \times 10^{-3} \text{ mol}$$

$$n(\text{NaOH}) = n(\text{CH}_3\text{COOH})$$

$$= 1.79 \times 10^{-3} \text{ mol}$$

Volume of acid at start

$$V(\text{NaOH}) = \frac{n}{c}$$

$$V(\text{NaOH}) = \frac{1.79 \times 10^{-3} \text{ mol}}{0.100 \text{ mol L}^{-1}}$$

$$\mathbf{V(\text{NaOH}) = 17.9\text{mL}}$$

From equation  
1 mol acid = 1  
mole base

## Drawing titration curves

**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

### Why is $pK_a = pH$ 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  $\rightleftharpoons$  conjugate base +  $H_3O^+$**

$$\text{So } K_a = \frac{[\text{conjugate base}][H_3O^+]}{[\text{acid}]}$$

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

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

**Step Three:**  
Mid-point of Buffer

Calculate the volume of **NaOH** when  
 $\text{pH} = \text{pKa}$

The volume of **NaOH** at equivalence  
point is **17.9mL**

$$17.9\text{mL} / 2 = 8.96\text{mL} \quad (\text{x})$$

$$\text{pKa} = 4.76 \quad (\text{y})$$

These points  
intersect on  
the graph

The  $\text{pH} = \text{pKa}$  when **8.96 mL** of **NaOH** has been added

The buffer zone will be 1 pH point above and below  $\text{pH}$  **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.

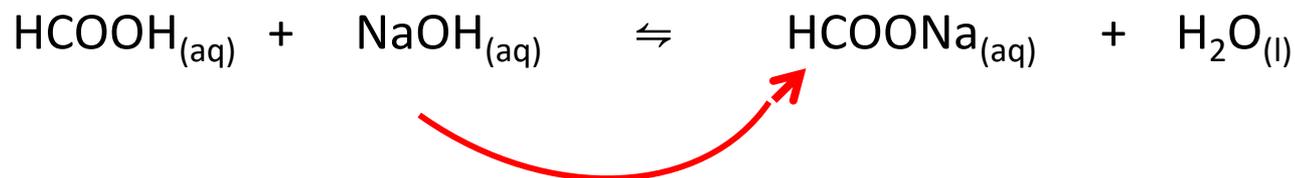
## Drawing titration curves

**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



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

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{k_a \times k_w}{c(\text{conjugate base})}}$$

**Step Four:**  
pH of equivalence

Calculate the pH at equivalence point.  
At the Equivalence point we will have:

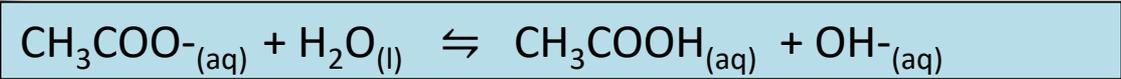
$1.79 \times 10^{-3} \text{ mol}$  of  $\text{CH}_3\text{COONa}$  in  
( $20\text{mL} + 17.9\text{mL} = 37.9\text{mL}$ ) of solution

$$\begin{aligned} C(\text{CH}_3\text{COONa}) &= \frac{1.79 \times 10^{-3} \text{ mol}}{0.0379\text{L}} && \leftarrow c = n/V \\ &= 0.0472 \text{ molL}^{-1} \end{aligned}$$

We need to calculate the pH of a solution of  $\text{CH}_3\text{COONa}$   
with this concentration:  $0.0472 \text{ molL}^{-1}$

Use same mol of conjugate base as base  
calculated from step 2. as they are  
produced 1 mol = 1 mol

**Step Four:**  
pH of equivalence



$$K_b = \frac{1 \times 10^{-14}}{K_a}$$

$$K_b = \frac{1 \times 10^{-14}}{1.74 \times 10^{-5}}$$

$$K_b = 5.75 \times 10^{-10}$$

$$K_b = \frac{[\text{CH}_3\text{COOH}] [\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

Assume

1  $[\text{CH}_3\text{COOH}] = [\text{OH}^-]$

2  $[\text{CH}_3\text{COO}^-] = 0.0472 \text{ molL}^{-1}$

Concentration calculated from previous step  $c=n/v$

**Step Four:**  
pH of equivalence

$$K_b = \frac{[\text{OH}^-]^2}{c(\text{conj base})}$$



$$5.75 \times 10^{-10}$$

$$= \frac{[\text{OH}^-]^2}{0.0472 \text{ molL}^{-1}}$$

$$\sqrt{5.75 \times 10^{-10} \times 0.0472}$$

$$= [\text{OH}^-]$$

$$5.21 \times 10^{-6} \text{ molL}^{-1}$$

$$= [\text{OH}^-]$$

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-]$$

$$[\text{H}_3\text{O}^+] = 1 \times 10^{-14} / 5.21 \times 10^{-6} \text{ molL}^{-1}$$

$$[\text{H}_3\text{O}^+] = 1.92 \times 10^{-9} \text{ molL}^{-1}$$

$$\text{pH} = -\log (1.92 \times 10^{-9} \text{ molL}^{-1})$$

$$\text{pH} = 8.72$$

## Drawing titration curves

**Step Five:** Calculate pH after the equivalence point

$$[\text{OH}^-] = \frac{\text{start concentration} \times \text{volume added **after** equivalence}}{\text{total volume acid} + \text{base}}$$

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

Although the  $\text{CH}_3\text{COONa}$  formed hydrolyses slightly in water, the  $[\text{OH}^-]$  from this reaction is very small compared to the  $[\text{OH}^-]$  from the NaOH so we assume all  $[\text{OH}^-]$  comes from NaOH

$$\text{Total volume of solution} = 20\text{mL} + 30\text{mL} = 50\text{mL}$$

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

Original concentration

$$= 0.0242\text{molL}^{-1}$$

This is a dilution calculation

$$(30\text{mL} - 17.9\text{mL} = 12.1\text{mL})$$

New concentration after dilution

**Step Five:**  
Final pH

NaOH is a strong base

Assume  $[\text{OH}^-] = c(\text{NaOH})$

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

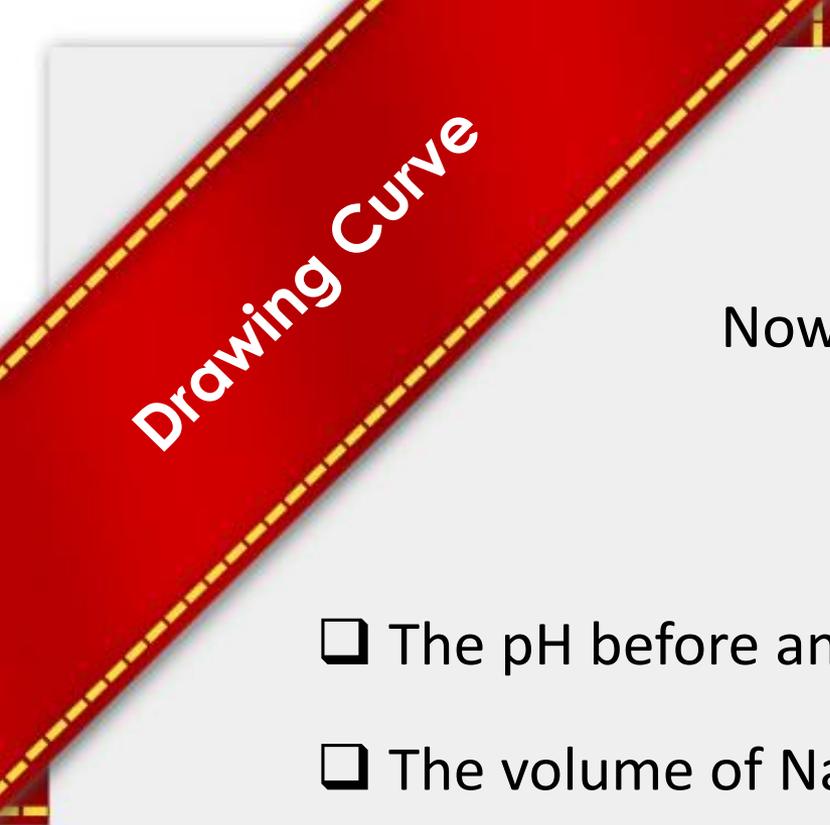
$$[\text{H}_3\text{O}^+] = K_w / 0.0242 \text{ molL}^{-1}$$

$$[\text{H}_3\text{O}^+] = 1 \times 10^{-14} / 0.0242 \text{ molL}^{-1}$$

$$[\text{H}_3\text{O}^+] = 4.13 \times 10^{-13} \text{ molL}^{-1}$$

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

$$\text{pH} = 12.4$$



# 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

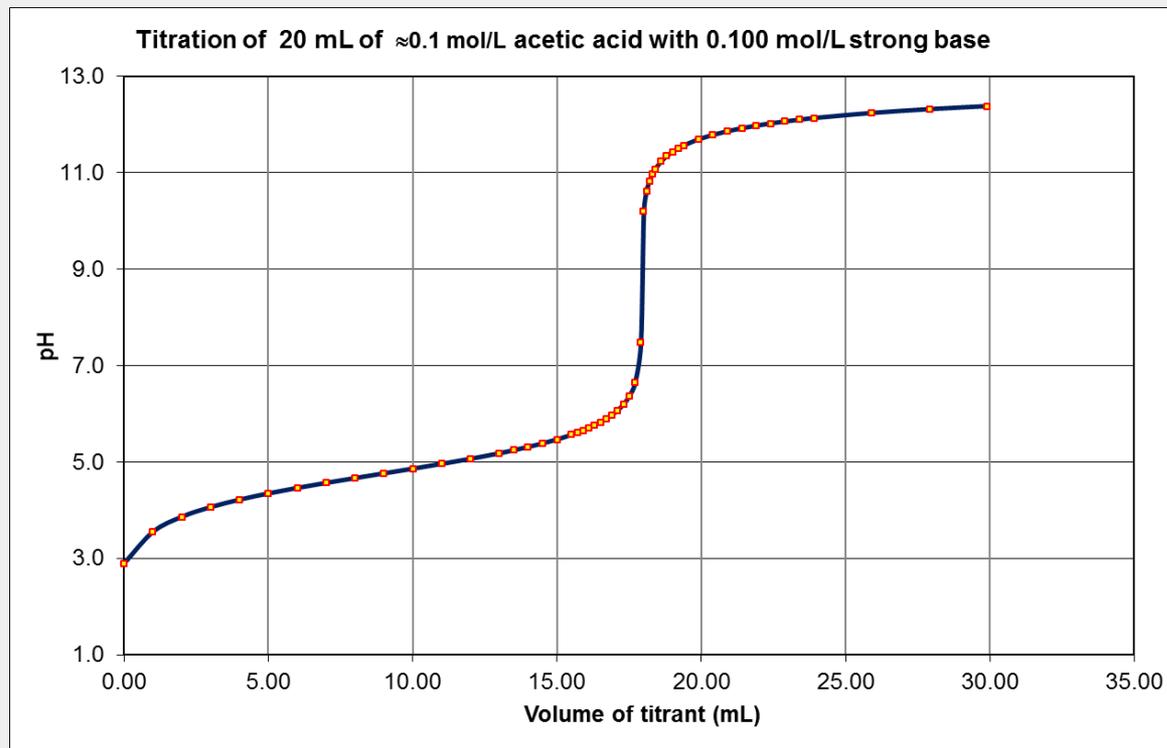
volume      pH

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

# Drawing R.I.C.E Charts to track concentrations



for weak acid + strong base identify “**limiting**” reagent

e.g in 20 mL 0.10 mol L<sup>-1</sup> CH<sub>3</sub>COOH + 15 mL 0.20 mol L<sup>-1</sup> NaOH



n	[CH <sub>3</sub> COOH]	[NaOH]	[CH <sub>3</sub> COO <sup>-</sup> ]
Initial	n = 0.1 x 0.02 = 0.002 mol	n = 0.2 x 0.015 = 0.003 mol	0 = 0 mol
Change	- 0.002 mol	- 0.002 mol	+ 0.002 mol
Equilibrium	≈ 0	= 0.001 mol	0.002 mol

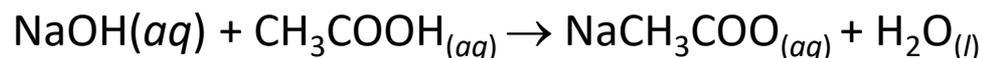
**Strong base determines pH** i.e. [OH<sup>-</sup>] = 0.001 mol / 0.035 L

Then pH = -log (1 x 10<sup>-14</sup>) / [OH<sup>-</sup>] = 12.5

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

**Sample question:** 20.0 mL of 0.0896 mol L<sup>-1</sup> ethanoic acid is titrated with 0.100 mol L<sup>-1</sup> sodium hydroxide. pK<sub>a</sub> (CH<sub>3</sub>COOH) = 4.76

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



$$n(\text{CH}_3\text{COOH at start}) = 0.0896 \times (20 \times 10^{-3}) = 1.79 \times 10^{-3} \text{ mol}$$

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

After 5 mL NaOH added: (total 25mL)

$$n(\text{CH}_3\text{COOH}) = 1.29 \times 10^{-3} \text{ mol}$$

$$n(\text{CH}_3\text{COO}^-) = 5 \times 10^{-4} \text{ mol}$$

$$[\text{CH}_3\text{COOH}] = 0.0516 \text{ mol L}^{-1}$$

$$[\text{CH}_3\text{COO}^-] = 0.0200 \text{ mol L}^{-1}$$

$$\text{pH} = 4.35$$

Calculate the number of moles of 20ml acid

$$n = c \times v$$

Calculate the number of moles of 5ml base

Subtract moles of base from acid

$$(n(\text{CH}_3\text{COOH}) - n(\text{NaOH}) \text{ after 5mL})$$

$$c = n/v$$

Volume is 25ml total

$$\text{pH} = \text{pK}_a + \log \left( \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \right)$$

## NCEA 2013 Titration Curve - (PART ONE)

Excellence  
Question

**Question: 3a:** 20.0 mL of 0.0896 mol L<sup>-1</sup> ethanoic acid is titrated with 0.100 mol L<sup>-1</sup> sodium hydroxide. pK<sub>a</sub> (CH<sub>3</sub>COOH) = 4.76

(a) Calculate the pH of the ethanoic acid before any NaOH is added.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$\bullet \text{ pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \sqrt{1.74 \times 10^{-5} \times 0.0896} \text{ mol L}^{-1} \\ &= 1.25 \times 10^{-3} \text{ mol L}^{-1} \end{aligned}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 2.90$$

Alternative  
equation

## NCEA 2013 Titration Curve - (PART TWO)

Excellence  
Question

**Question: 3b:** Halfway to the equivalence point of the titration, the  $\text{pH} = \text{pK}_a$  of the ethanoic acid.

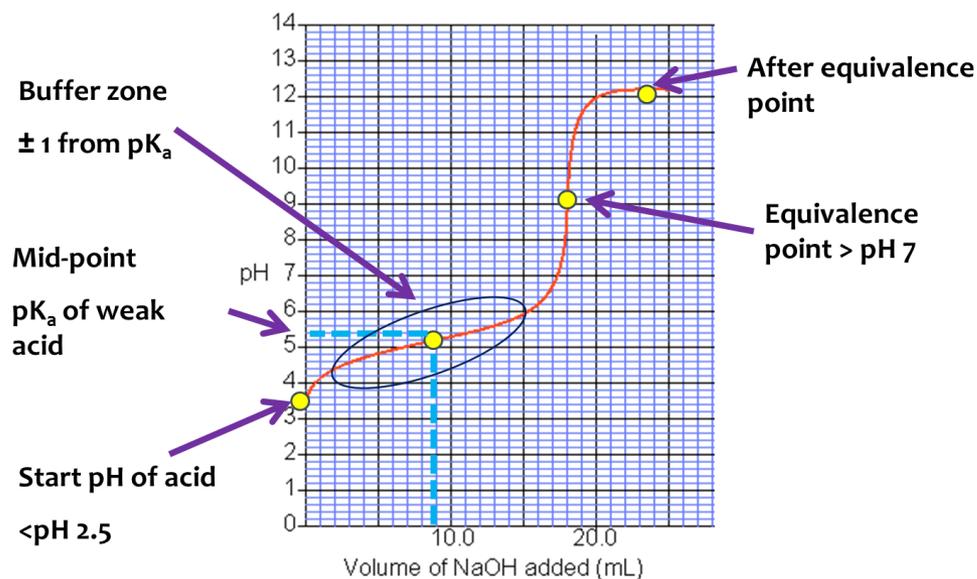
Discuss the reason for this.

Halfway to equivalence point, half of the ethanoic acid has been used up. There are now equimolar quantities of ethanoic acid and sodium ethanoate.

According to the equation when  $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$

then  $K_a = [\text{H}_3\text{O}^+]$

So  $\text{pK}_a = \text{pH}$



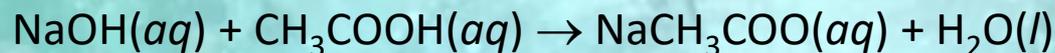
## NCEA 2013 Titration Curve - (PART THREE)

Excellence  
Question

**Question: 3c:** (i) Discuss the change in the concentration of species in solution, as the first 5.00 mL of NaOH is added to the 20.0 mL of ethanoic acid.

Your answer should include chemical equations.

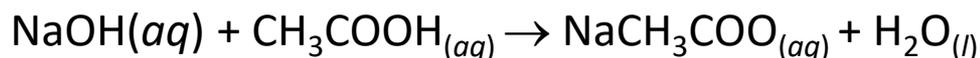
No calculations are required.



- $[\text{CH}_3\text{COO}^-]$  increases as it is formed in reaction
- $[\text{Na}^+]$  increases as NaOH is added
- $[\text{CH}_3\text{COOH}]$  decreases as it reacts with NaOH
- $[\text{H}_3\text{O}^+]$  decreases because  $[\text{CH}_3\text{COO}^-] / [\text{CH}_3\text{COOH}]$  increases and  $K_a$  is a constant.
- $[\text{OH}^-]$  increases because  $[\text{H}_3\text{O}^+]$  decreases and  $[\text{H}_3\text{O}^+][\text{OH}^-]$  is constant.

**Question: 3c:** 20.0 mL of 0.0896 mol L<sup>-1</sup> ethanoic acid is titrated with 0.100 mol L<sup>-1</sup> sodium hydroxide. pKa (CH<sub>3</sub>COOH) = 4.76

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



$$n(\text{CH}_3\text{COOH at start}) = 0.0896 \times (20 \times 10^{-3}) = 1.79 \times 10^{-3} \text{ mol} \quad \mathbf{n = c \times v}$$

$$n(\text{NaOH added}) = 0.1 \times (5 \times 10^{-3}) = 5 \times 10^{-4} \text{ mol} \quad \mathbf{n = c \times v}$$

After 5 mL NaOH added: (total 25mL)

$$n(\text{CH}_3\text{COOH}) = 1.29 \times 10^{-3} \text{ mol}$$

(n(CH<sub>3</sub>COOH – n(NaOH) after 5mL)

$$n(\text{CH}_3\text{COO}^-) = 5 \times 10^{-4} \text{ mol}$$

$$[\text{CH}_3\text{COOH}] = 0.0516 \text{ mol L}^{-1} \quad \mathbf{c = n / v}$$

$$[\text{CH}_3\text{COO}^-] = 0.0200 \text{ mol L}^{-1} \quad \mathbf{c = n / v}$$

$$[\text{H}_3\text{O}^+] = 4.48 \times 10^{-5} \text{ mol L}^{-1}$$

$$\text{pH} = 4.35$$

**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



b) Calculate c (conjugate base) using  $c = n/v$

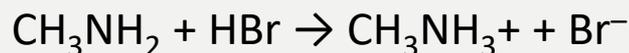
V = initial volume in flask + volume added during titration to reach equivalence

c) Use pH equations

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{k_a \times k_w}{c(\text{conjugate base})}}$$

**Question: 3a:** A titration was carried out by adding hydrobromic acid, HBr, to 20.0 mL of aqueous methylamine, CH<sub>3</sub>NH<sub>2</sub>, solution.

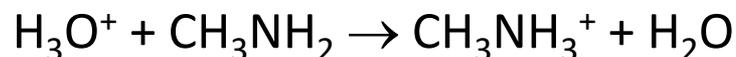
The equation for the reaction is:



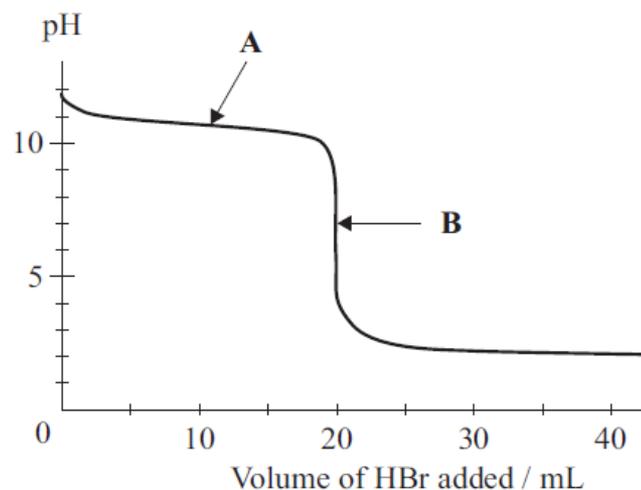
$$K_a(\text{CH}_3\text{NH}_3^+) = 2.29 \times 10^{-11}$$

Explain why the pH does not change significantly between the addition of 5 to 15 mL of HBr (around point **A** on the curve).

At point A, [CH<sub>3</sub>NH<sub>2</sub>] ≈ [CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>]. So the solution has buffering properties in the proximity of point A. When HBr is added, the H<sub>3</sub>O<sup>+</sup> is consumed:



Since the H<sub>3</sub>O<sup>+</sup> is removed from the solution (neutralised), the pH does not change significantly.



**Question: 3b:** A titration was carried out by adding hydrobromic acid, HBr, to 20.0 mL of aqueous methylamine, CH<sub>3</sub>NH<sub>2</sub>, solution.

The equation for the reaction is: CH<sub>3</sub>NH<sub>2</sub> + HBr → CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> + Br<sup>-</sup>

$$K_a(\text{CH}_3\text{NH}_3^+) = 2.29 \times 10^{-11}$$

The aqueous methylamine, CH<sub>3</sub>NH<sub>2</sub>, solution has a pH of 11.8 before any HBr is added.

Show by calculation that the concentration of this solution is 0.0912 mol L<sup>-1</sup>.

$$[\text{H}_3\text{O}^+] = 10^{-11.8} = 1.58 \times 10^{-12}$$

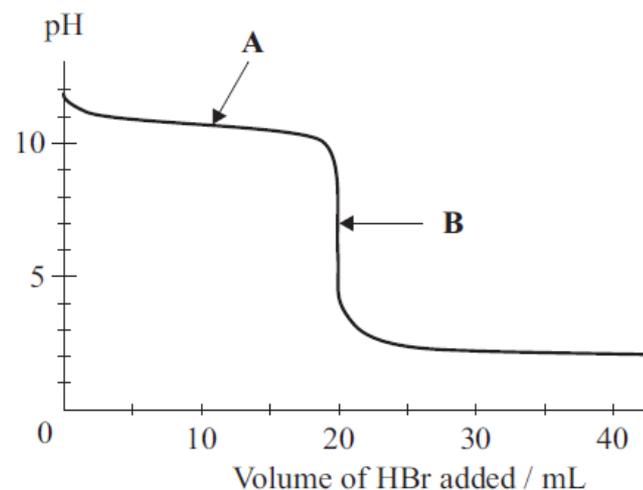
$$K_a = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+]}$$

$$= \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{OH}^-]}$$

$$2.29 \times 10^{-11} = \frac{[\text{CH}_3\text{NH}_2] \times (10^{-11.8})^2}{1 \times 10^{-14}}$$

$$[\text{CH}_3\text{NH}_2] = \frac{(2.29 \times 10^{-11}) \times (1 \times 10^{-14})}{(10^{-11.8})^2}$$

$$= 0.0912 \text{ mol L}^{-1}$$



## NCEA 2014 Titration Curve - (PART THREE)

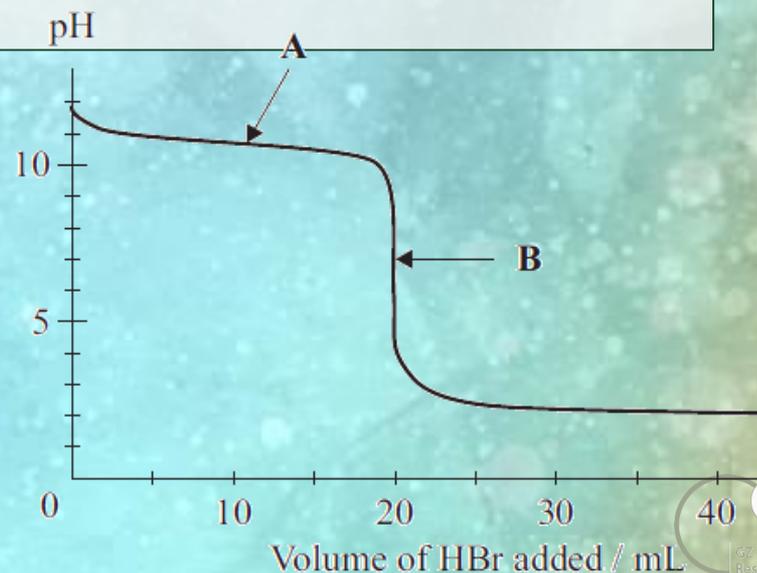
Excellence  
Question

**Question: 3c:** Write the formulae of the four chemical species, apart from water and  $\text{OH}^-$ , that are present at the point marked **B** on the curve.

(ii) Compare and contrast the solution at point **B** with the initial aqueous methylamine solution.

In your answer you should include:

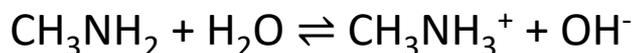
- a comparison of species present AND their relative concentrations
- a comparison of electrical conductivity linked to the relevant species present in each solution
- equations to support your answer.



**Question: 3c:** (ii) Compare and contrast the solution at point **B** with the initial aqueous methylamine solution.

At the start, before addition of HBr there is a solution of weak base ( $\text{CH}_3\text{NH}_2$ ) which only partially reacts with water to produce a relatively low concentration of ions.

As a result, the initial  $\text{CH}_3\text{NH}_2$  solution will be a poor electrical conductor.

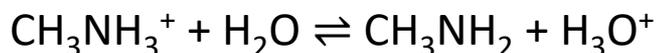


Therefore species present are  $\text{CH}_3\text{NH}_2 > \text{OH}^- \geq \text{CH}_3\text{NH}_3^+ > \text{H}_3\text{O}^+$

At point B, there is a solution of the salt  $\text{CH}_3\text{NH}_3\text{Br}$  present which is dissociated completely into ions. Therefore there is a relatively high concentration of ions ( $\text{CH}_3\text{NH}_3^+$  and  $\text{Br}^-$ ) present in the solution, so it will be a good electrical conductor / electrolyte.



$\text{CH}_3\text{NH}_3^+$  reacts with water according to the equation



Species present are  $\text{Br}^- > \text{CH}_3\text{NH}_3^+ > \text{H}_3\text{O}^+ \geq \text{CH}_3\text{NH}_2 > (\text{OH}^-)$

## NCEA 2015 Titration Curves - (PART ONE)

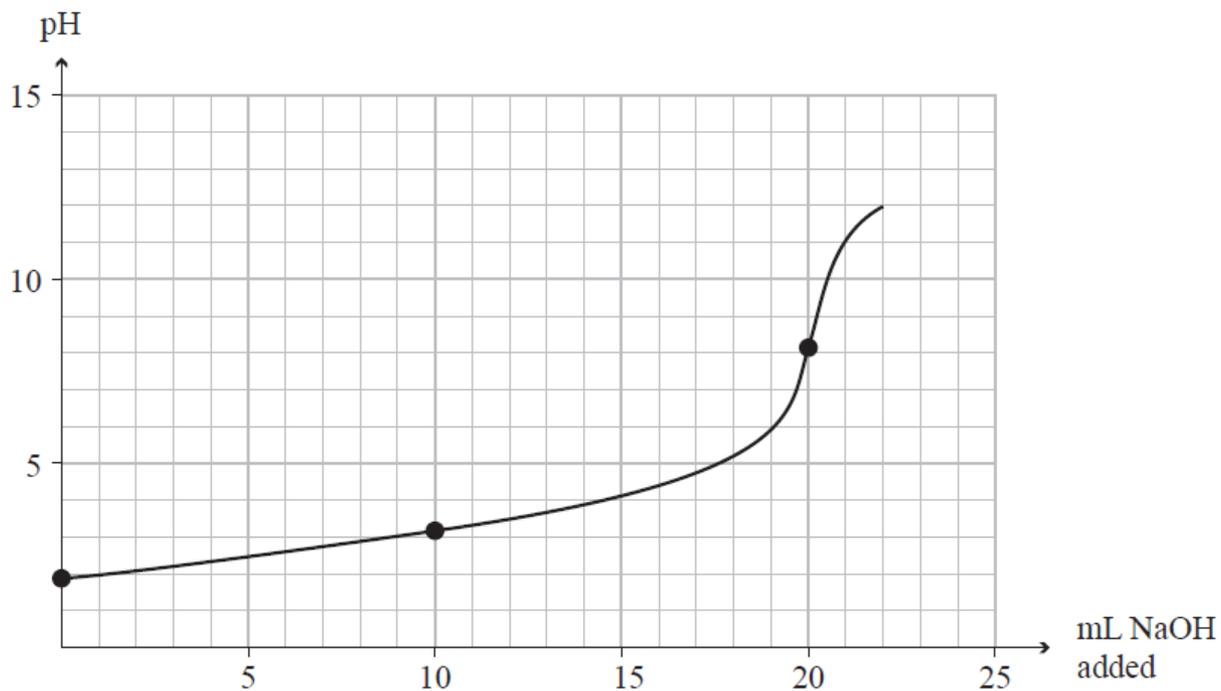
Achieved  
Question

**Question: 3a:** 20.0 mL of 0.258 mol L<sup>-1</sup> hydrofluoric acid, HF, solution is titrated with a sodium hydroxide, NaOH, solution.

The equation for the reaction is:



(i) Identify the species in solution at the equivalence point.

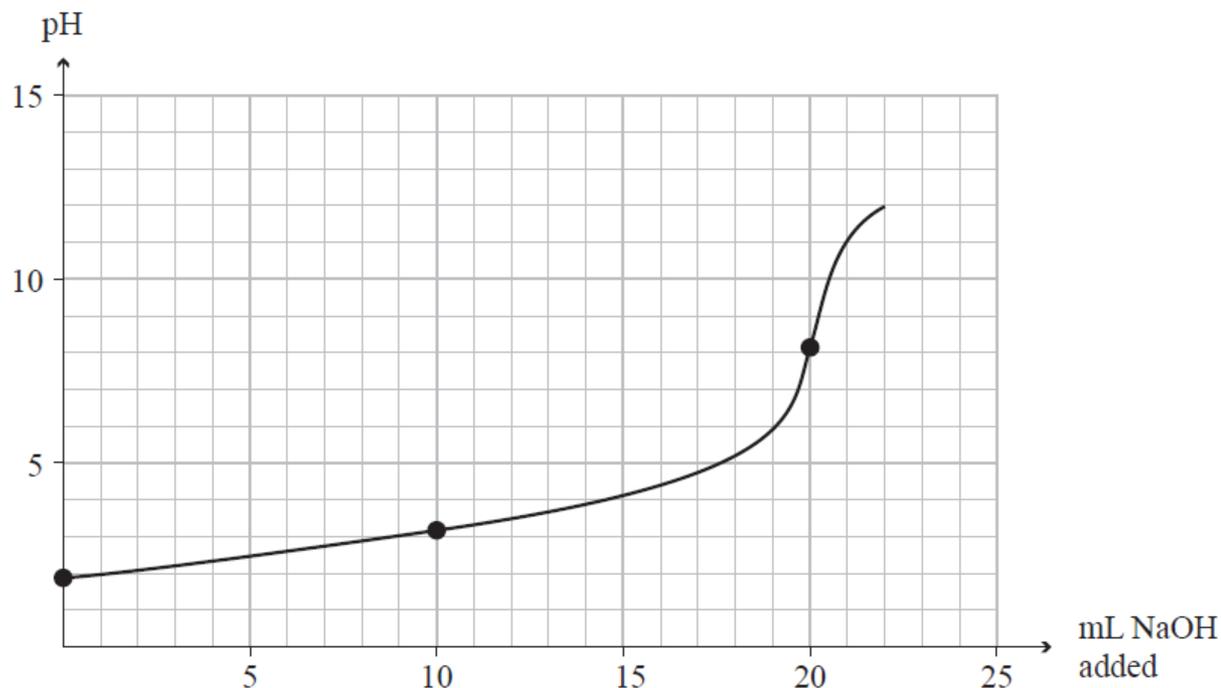


**Na<sup>+</sup>, F<sup>-</sup>, H<sub>2</sub>O,  
HF, OH<sup>-</sup>,  
H<sub>3</sub>O<sup>+</sup>.**

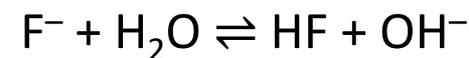
## NCEA 2015 Titration Curves - (PART TWO)

Merit  
Question

**Question: 3a:** (ii) Explain why the pH at the equivalence point is greater than 7. Include an equation in your answer.



A weak base,  $F^-$ , is present at the equivalence point:



This increase in  $[OH^-]$  causes the pH to be greater than 7.

**Question: 3a:** 20.0 mL of 0.258 mol L<sup>-1</sup> hydrofluoric acid, HF, solution is titrated with a sodium hydroxide, NaOH, solution.



(iii) After a certain volume of NaOH solution has been added, the concentration of HF in the solution will be twice that of the F<sup>-</sup>.

Calculate the pH of this solution, and evaluate its ability to function as a buffer.

$$[\text{H}_3\text{O}^+] = 2 \times 10^{-3.17} = 1.35 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{pH} = -\log (1.35 \times 10^{-3}) = 2.87.$$

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log [\text{F}^-] / [\text{HF}] \\ &= 3.17 + \log 0.5 \\ &= 2.87 \end{aligned}$$

**Alternative  
method**

Since there are significant concentrations of the weak acid and its conjugate base the solution can resist added acid or base.

However, since the pH of the buffer solution is less than the pK<sub>a</sub>, / [HF] > [F<sup>-</sup>], it is more effective against added base than acid.

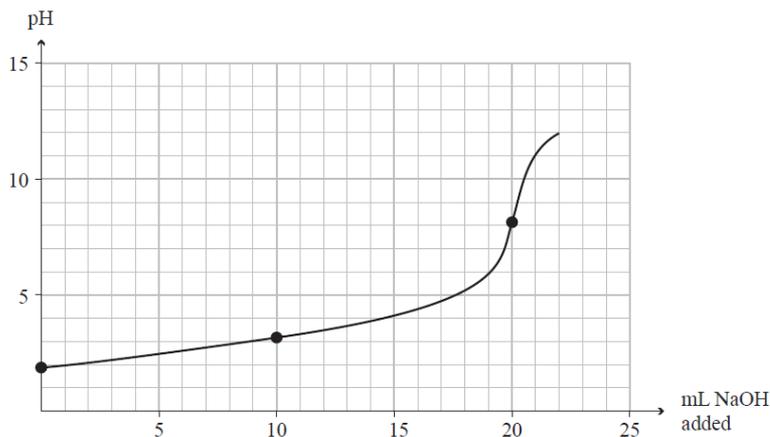
## NCEA 2015 Titration Curves - (PART FOUR)

Excellence  
Question

**Question: 3a:** 20.0 mL of 0.258 mol L<sup>-1</sup> hydrofluoric acid, HF, solution is titrated with a sodium hydroxide, NaOH, solution.



(iv) Determine by calculation, the pH of the solution after 24.0 mL of 0.258 mol L<sup>-1</sup> NaOH solution has been added. .



$$n(\text{NaOH}) = cv = 0.258 \cdot \frac{24 - 20}{1000} = 1.032 \cdot 10^{-3} \text{ mol}$$

$$c(\text{NaOH}) = \frac{n}{v} = \frac{1.032 \cdot 10^{-3}}{\frac{44}{1000}} = 0.0235 \text{ mol L}^{-1}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1 \cdot 10^{-14}}{0.0235} = 4.26 \cdot 10^{-13} \text{ mol L}^{-1}$$

$$\text{pH} = -\log 4.26 \cdot 10^{-13} = 12.4$$

**Question: 3b:** In a second titration, a  $0.258 \text{ mol L}^{-1}$  ethanoic acid,  $\text{CH}_3\text{COOH}$ , solution was titrated with the NaOH solution.

Contrast the expected pH at the equivalence point with the HF titration.

$\text{pK}_a(\text{CH}_3\text{COOH}) = 4.76$       No calculations are necessary.

→ **larger pKa more reactants**

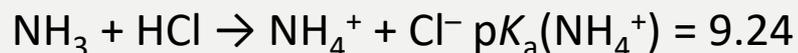
Since  $\text{CH}_3\text{COOH}$  has a higher  $\text{pK}_a$ , it is a weaker acid than HF. Therefore its conjugate base,  $\text{CH}_3\text{COO}^-$ , will be a stronger base than  $\text{F}^-$ . This means  $[\text{OH}^-]$  will be higher at the equivalence point for the  $\text{CH}_3\text{COOH}$  vs NaOH titration, so the equivalence point pH will be higher.

## NCEA 2016 Titration Curves - (PART ONE)

Merit  
Question

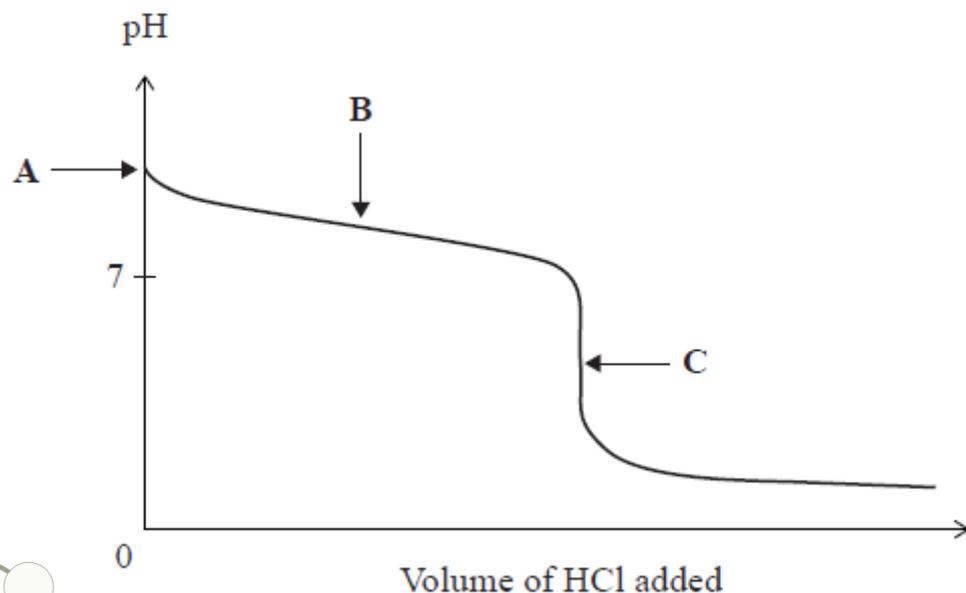
**Question: 3a:** 20.00 mL of 0.320 mol L<sup>-1</sup> ammonia, NH<sub>3</sub>, is titrated with 0.640 mol L<sup>-1</sup> hydrochloric acid, HCl.

The equation for this reaction is:

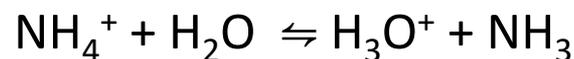


The curve for this titration is given below.

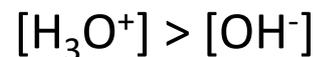
Explain why the pH at the equivalence point (point C) is not 7.



(Ammonium chloride) is acidic



So therefore



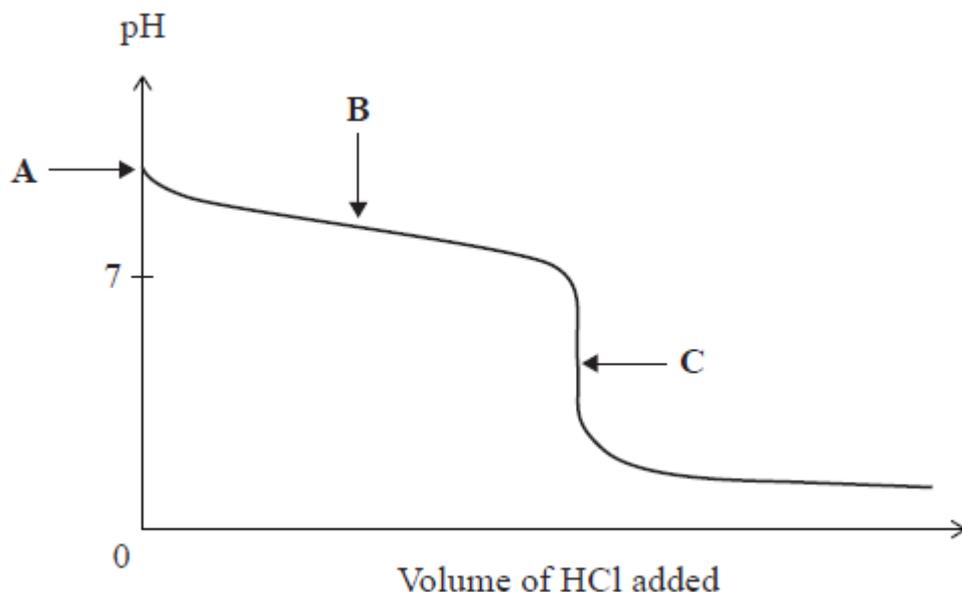
**When considering pH think about which ion, H<sub>3</sub>O<sup>+</sup> or OH<sup>-</sup>, will be at the higher concentration**

## NCEA 2016 Titration Curves - (PART TWO)

Excellence  
Question

**Question 3c:** 20.00 mL of 0.320 mol L<sup>-1</sup> ammonia, NH<sub>3</sub>, is titrated with 0.640 mol L<sup>-1</sup> hydrochloric acid, HCl.  $pK_a(\text{NH}_4^+) = 9.24$

Show, by calculation, that the pH at the equivalence point (point C) is 4.96.



Since B is half way to the equivalence point,  $[\text{NH}_4^+] = [\text{NH}_3]$ .

OR

$$pK_a = \text{pH} + \log [\text{acid}] \div [\text{c.base}]$$

$$\text{so } K_a = [\text{H}_3\text{O}^+]$$

therefore  $pK_a = \text{pH}$ .

## NCEA 2016 Titration Curves - (PART THREE)

Excellence  
Question

**Question 3b:** 20.00 mL of 0.320 mol L<sup>-1</sup> ammonia, NH<sub>3</sub>, is titrated with 0.640 mol L<sup>-1</sup> hydrochloric acid, HCl. pK<sub>a</sub>(NH<sub>4</sub><sup>+</sup>) = 9.24

Explain, in terms of the species present, why the pH at B (half way to the equivalence point) is 9.24.

$$[\text{NH}_4^+] = 0.320 \times 20 / 30 = 0.213 \text{ molL}^{-1}$$

$$(K_a = 10^{-9.24} = 5.75 \times 10^{-10})$$

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \sqrt{(5.75 \times 10^{-10} \times 0.213)} \\ &= 1.11 \times 10^{-5} \text{ molL}^{-1} \end{aligned}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

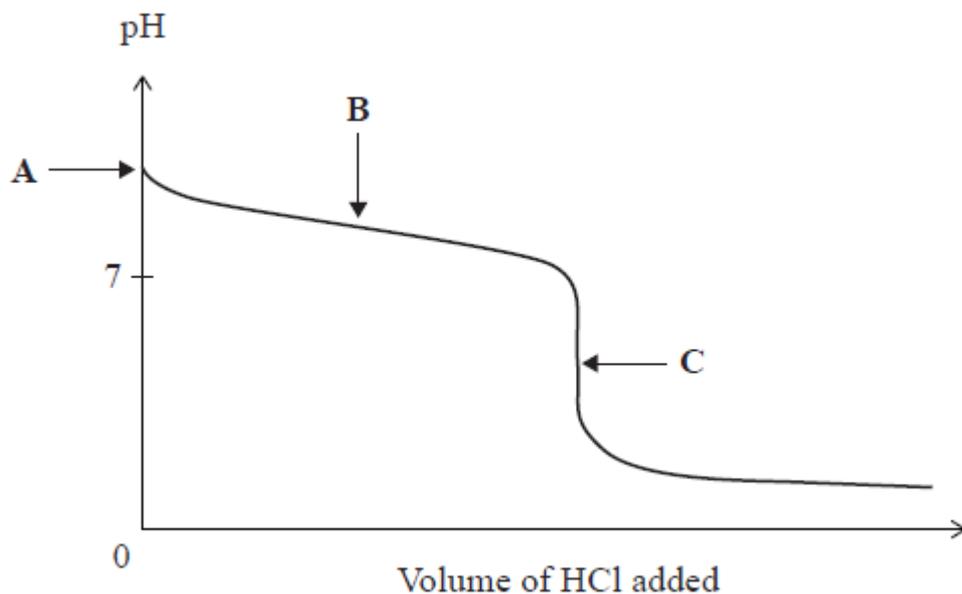
$$\text{pH} = 4.96$$

## NCEA 2016 Titration Curves - (PART FOUR)

Merit  
Question

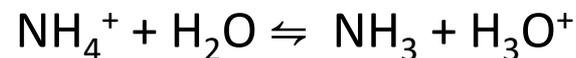
**Question 3d:** 20.00 mL of 0.320 mol L<sup>-1</sup> ammonia, NH<sub>3</sub>, is titrated with 0.640 mol L<sup>-1</sup> hydrochloric acid, HCl. pK<sub>a</sub>(NH<sub>4</sub><sup>+</sup>) = 9.24

Explain, in terms of the species present, why the pH of the solution at point C is 4.96.



The solution at the equivalence point is NH<sub>4</sub>Cl.

NH<sub>4</sub><sup>+</sup> solution is acidic since,

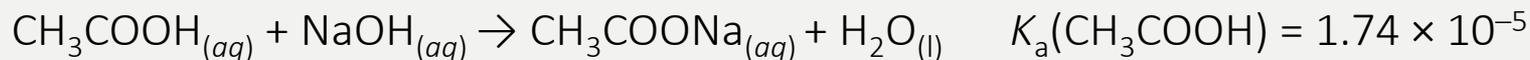


## NCEA 2017 Titration Curves - (PART ONE)

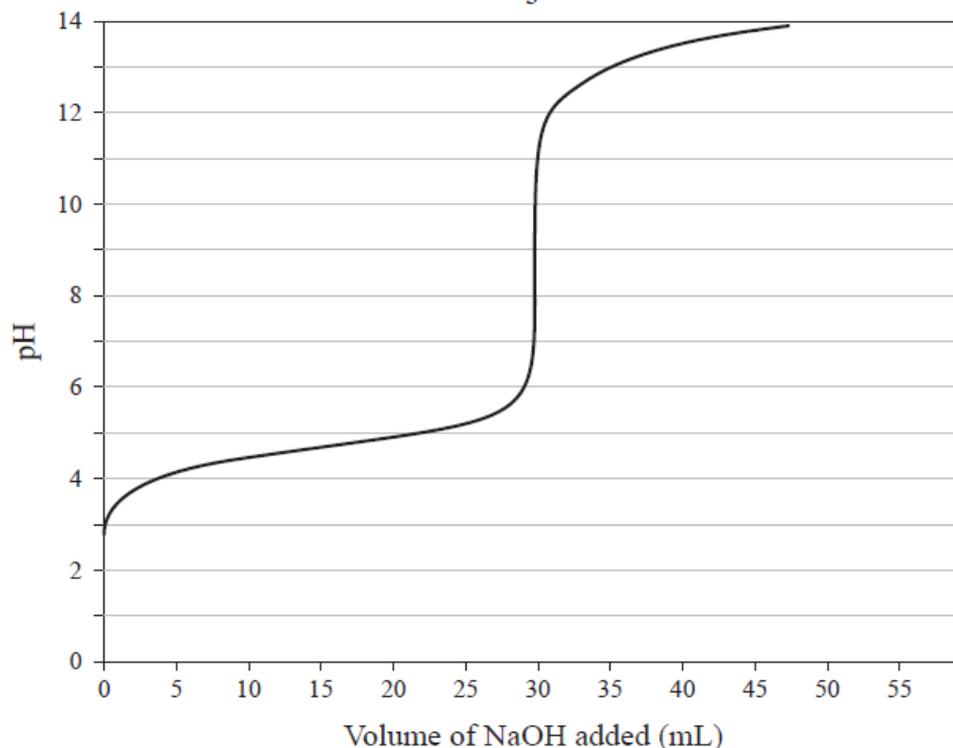
Achieved  
Question

**Question 3a:** A titration was carried out by adding  $0.112 \text{ mol L}^{-1}$  sodium hydroxide solution,  $\text{NaOH}_{(aq)}$ , to  $20.0 \text{ mL}$  of ethanoic acid solution,  $\text{CH}_3\text{COOH}_{(aq)}$ .

The equation for the reaction is:



**Titration curve for  $\text{CH}_3\text{COOH}$  versus  $\text{NaOH}$**



**(a)** With reference to the titration curve above, put a tick next to the indicator most suited to identify the equivalence point.

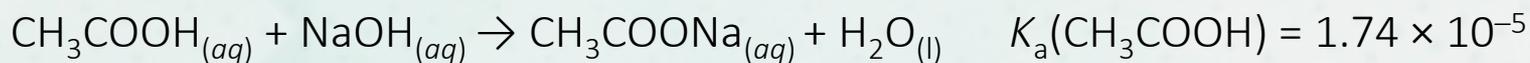
Indicator	$\text{p}K_a$	Tick ONE box below
Methyl yellow	3.1	<input type="checkbox"/>
Bromocresol purple	6.3	<input type="checkbox"/>
Phenolphthalein	9.6	<input checked="" type="checkbox"/>

## NCEA 2017 Titration Curves - (PART TWO)

Merit  
Question

**Question 3b (i)** : The ethanoic acid solution,  $\text{CH}_3\text{COOH}_{(aq)}$ , has a pH of 2.77 before any NaOH is added.

Show by calculation that the concentration of the  $\text{CH}_3\text{COOH}$  solution is  $0.166 \text{ mol L}^{-1}$ .



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

$$1.74 \times 10^{-5} = \frac{(10^{-2.77})^2}{[\text{CH}_3\text{COOH}]}$$

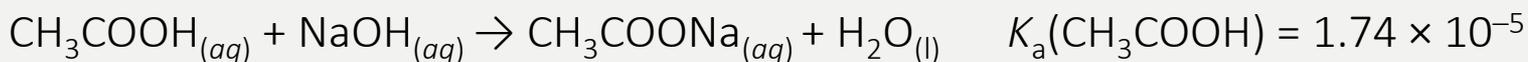
$$[\text{CH}_3\text{COOH}] = 0.166 \text{ mol L}^{-1}$$

## NCEA 2017 Titration Curves - (PART THREE)

Excellence  
Question

Question 3b (ii) :

Calculate the pH of the solution in the flask after 10.0 mL of 0.112 mol L<sup>-1</sup> NaOH has been added to 20.0 mL of ethanoic acid solution, CH<sub>3</sub>COOH<sub>(aq)</sub>.



$$n(\text{NaOH}) \text{ added} = 0.112 \text{ mol L}^{-1} \times 0.01 \text{ L}$$

$$= 1.12 \times 10^{-3} \text{ mol}$$

$$\text{Initial } n(\text{CH}_3\text{COOH}) = 0.166 \text{ mol L}^{-1} \times 0.02 \text{ L}$$

$$= 3.32 \times 10^{-3} \text{ mol}$$

$$n(\text{CH}_3\text{COOH}) \text{ remaining in 30 mL}$$

$$= 3.32 \times 10^{-3} \text{ mol} - 1.12 \times 10^{-3} \text{ mol}$$

$$= 2.2 \times 10^{-3} \text{ mol}$$

$$n(\text{CH}_3\text{COO}^-) \text{ in 30 mL} = 1.12 \times 10^{-3} \text{ mol}$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]_i}$$

$$1.74 \times 10^{-5} = \frac{\left(\frac{1.12 \times 10^{-3}}{0.03}\right)[\text{H}_3\text{O}^+]}{\frac{2.2 \times 10^{-3}}{0.03}}$$

$$[\text{H}_3\text{O}^+] = 3.42 \times 10^{-5}$$

$$\text{pH} = -\log 3.42 \times 10^{-5}$$

$$\text{pH} = 4.47$$

### Question 3c:

The equivalence point pH for the titration of ethanoic acid with sodium hydroxide is 8.79.

(i) Identify the chemical species present at the equivalence point, other than water.

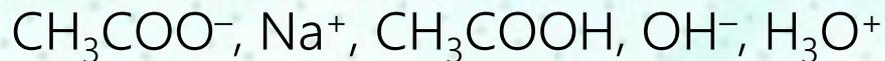
(ii) In a second titration, a  $0.166 \text{ mol L}^{-1}$  methanoic acid solution,  $\text{HCOOH}_{(aq)}$ , is titrated with the NaOH solution. The equivalence point pH for this titration is 8.28.

The equivalence point pH for the  $\text{CH}_3\text{COOH}$  titration is 8.79.

Compare and contrast the pH values at the equivalence point for both titrations.

$$K_a(\text{HCOOH}) = 1.82 \times 10^{-4} \quad K_a(\text{CH}_3\text{COOH}) = 1.74 \times 10^{-5}$$

*No calculations are necessary.*



### Question 3c: (ii)

Compare and contrast the pH values at the equivalence point for both titrations.

$$K_a(\text{HCOOH}) = 1.82 \times 10^{-4} \quad K_a(\text{CH}_3\text{COOH}) = 1.74 \times 10^{-5}$$

*No calculations are necessary.*

Both titrations produce a basic salt at the equivalence point because  $[\text{OH}^-] > [\text{H}_3\text{O}^+]$  /  $\text{pH} > 7$  / equations.

At the equivalence point the ethanoic acid is converted into the ethanoate ion and the methanoic acid is converted into the methanoate ion.

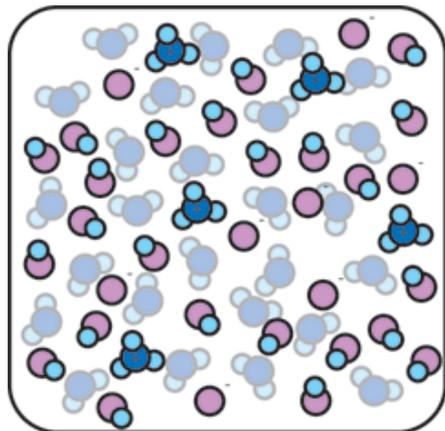
The methanoic acid titration has a lower pH than the ethanoic acid titration at the equivalence point because: methanoate ions are a weaker base / produce fewer  $\text{OH}^-$  ions than ethanoate ions

OR  $\text{HCOOH}$  has a larger  $K_a$  than  $\text{CH}_3\text{COOH}$ , as it is a stronger acid. As a result, its conjugate base,  $\text{HCOO}^-$ , is weaker than  $\text{CH}_3\text{COO}^-$ , so the pH will be lower at the equivalence point.

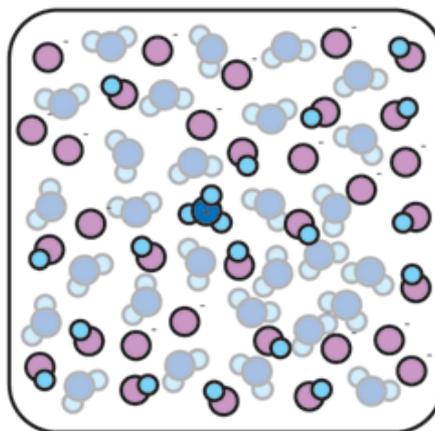
# Buffer solutions

The pH of aqueous solutions is controlled by the transfer of protons between ions and water molecules. The pH of blood, for example, is normally 7.4, and if it falls more than 0.4 from this value (as a result 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.

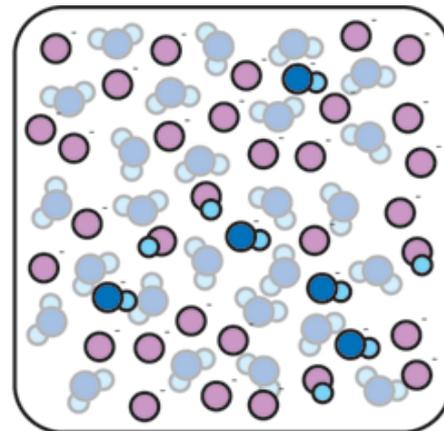
A buffer solution consists of a **weak acid** (to supply protons to any added strong base) and its **conjugate weak base** (to receive protons from any added strong acid). A buffer solution is a solution that resists changes in pH when small amounts of acid or base are added.



8 A<sup>-</sup>  
24 HA  
pH < pK<sub>a</sub>



16 A<sup>-</sup>  
16 HA  
pH = pK<sub>a</sub>



28 A<sup>-</sup>  
4 HA  
pH > pK<sub>a</sub>

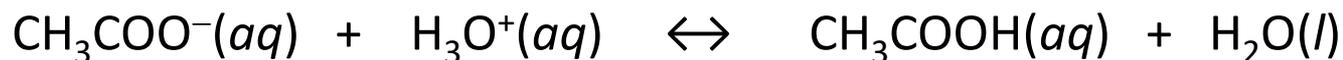
## Buffer solutions

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

An example of a buffer solution would be one containing a mixture of ethanoic acid and sodium ethanoate. If base ( $\text{OH}^-$ ) ions are added they will react with the ethanoic acid.



If acid ( $\text{H}_3\text{O}^+$ ) ions are added they will react with the ethanoate ions.



These reactions show that any added acid ( $\text{H}_3\text{O}^+$ ) or base ( $\text{OH}^-$ ) are largely consumed and the pH of the solution therefore hardly changes.

**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



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

**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**

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

# Buffer calculations for monoprotic acids

## Buffer calculations

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{weak acid}]}{[\text{conjugate base}]} \quad \text{OR} \quad \text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

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

**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.

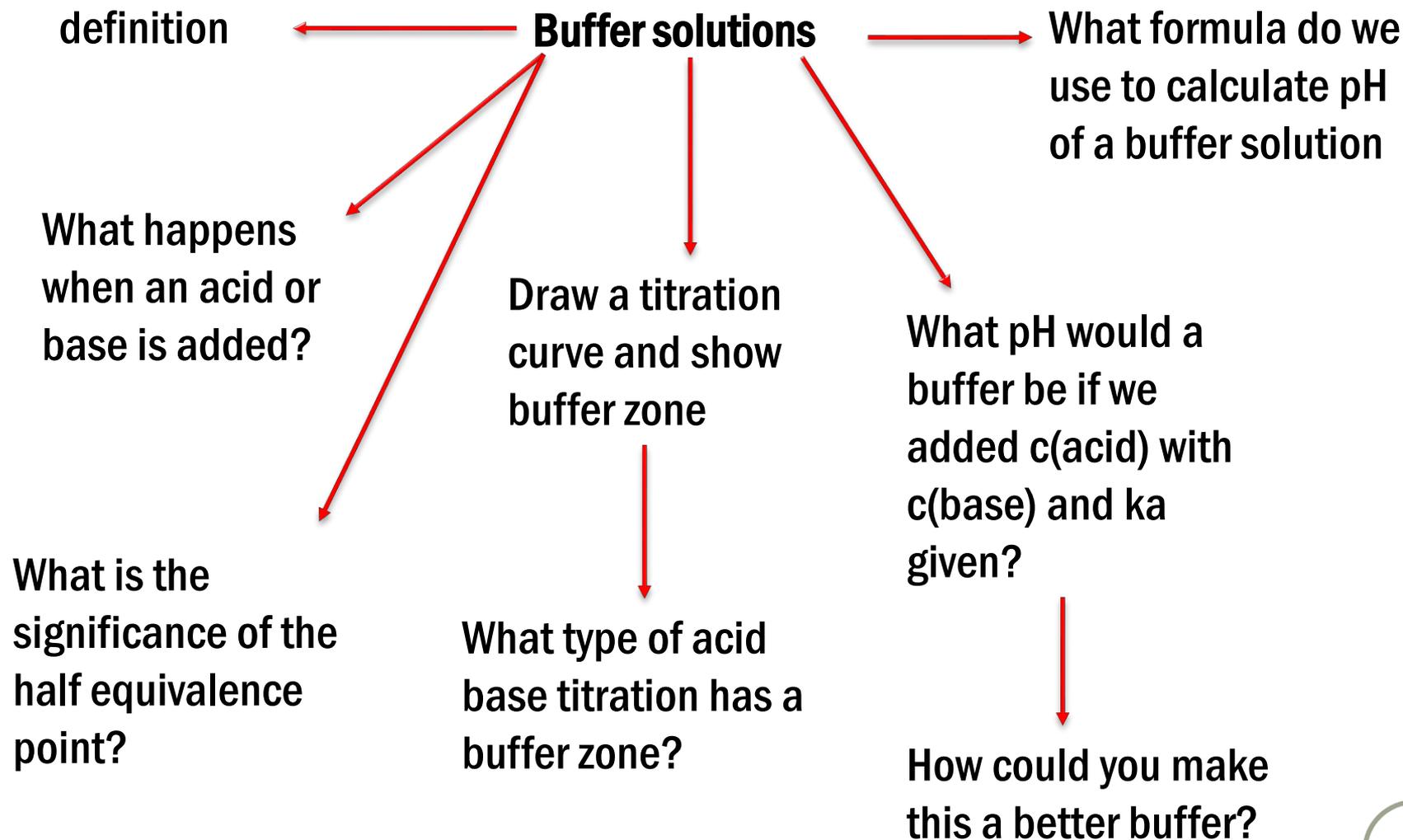
**If [weak base] = [weak acid] in a buffer solution, then pH = pKa.**

## Example

If a buffer solution is made up of 0.050 mol L<sup>-1</sup> benzoic acid and 0.050 mol L<sup>-1</sup> sodium benzoate, show that the pH of the solution = 4.19, given that pK<sub>a</sub>(benzoic acid) = 4.19.

$$\begin{aligned} \text{pH} &= \text{pK}_a + \log^{10} \frac{[\textit{benzoate ion}]}{[\textit{benzoic acid}]} \\ &= 4.19 + \log^{10} \frac{0.050}{0.050} \\ &= 4.19 + \log_{10} 1.0 = 4.19 \end{aligned}$$

# Buffer Key Questions



## NCEA 2013 Buffers

Excellence  
Question

**Question: 1c:** (i) The following two solutions from part (a) are mixed to form a buffer solution:

20.0 mL of 1 mol L<sup>-1</sup> CH<sub>3</sub>NH<sub>3</sub>Cl and 30.0 mL of 1 mol L<sup>-1</sup> CH<sub>3</sub>NH<sub>2</sub>

Calculate the pH of the resultant buffer solution. pK<sub>a</sub> (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>) = 10.64

$$K_a = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+]}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad \text{to} \quad [\text{H}_3\text{O}^+] = \frac{K_a \times [\text{HA}]}{[\text{A}^-]}$$

$$[\text{H}_3\text{O}^+] = \frac{K_a [\text{CH}_3\text{NH}_3^+]}{[\text{CH}_3\text{NH}_2]}$$

20mL in a 50mL total

30mL in a 50mL total

$$[\text{CH}_3\text{NH}_2] = \frac{30 \times 10^{-3} \times 1}{50 \times 10^{-3}} = 0.600 \text{ mol L}^{-1}$$

$$[\text{CH}_3\text{NH}_3^+] = \frac{20 \times 10^{-3} \times 1}{50 \times 10^{-3}} = 0.400 \text{ mol L}^{-1}$$

$$[\text{H}_3\text{O}^+] = 1.52705 \times 10^{-11} \text{ mol L}^{-1}$$

$$\text{pH} = 10.8$$

## NCEA 2013 Buffers

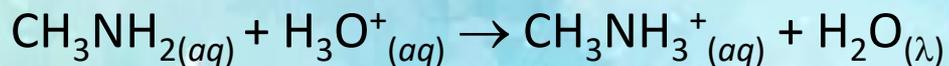
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(ii) Explain the effect on the solution formed in (i) when a small amount of acid is added.

When a small amount of acid (H<sub>3</sub>O<sup>+</sup>) ions are added, they will react with the CH<sub>3</sub>NH<sub>2(aq)</sub> molecules to form CH<sub>3</sub>NH<sub>3<sup>+</sup>(aq)</sub> ions.



The added acid (H<sub>3</sub>O<sup>+</sup>), is mostly consumed, and the pH of the solution changes very little.

**Question: 1c:** An aqueous solution containing a mixture of HF and sodium fluoride, NaF, can act as a buffer solution.

**Calculate the mass** of NaF that must be added to 150 mL of 0.0500 mol L<sup>-1</sup> HF to give a buffer solution with a pH of 4.02.

Assume there is no change in volume.

$M(\text{NaF}) = 42.0 \text{ g mol}^{-1}$   $\text{p}K_{\text{a}}(\text{HF}) = 3.17$

$$K_{\text{a}} = \frac{[\text{F}^{-}][\text{H}_3\text{O}^{+}]}{[\text{HF}]}$$

$$10^{-3.17} = \frac{[\text{F}^{-}] \times 10^{-4.02}}{0.0500}$$

$$[\text{F}^{-}] = 0.354 \text{ mol L}^{-1}$$

$$n(\text{NaF}) = 0.354 \text{ mol L}^{-1} \times 0.150 \text{ L} = 0.0531 \text{ mol}$$

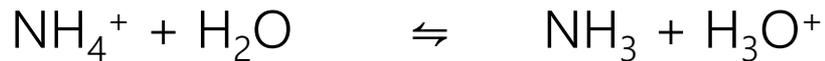
$$m(\text{NaF}) = 0.0531 \text{ mol} \times 42.0 \text{ g mol}^{-1} = 2.23 \text{ g}$$

$$n = c \times V$$

$$m = n \times M$$

**Question 2a (ii)** : Dilute hydrochloric acid, HCl, is added to the NH<sub>3</sub> solution until the ratio of NH<sub>3</sub> to NH<sub>4</sub><sup>+</sup> in the solution is 5:1.

Determine the pH of this solution, and evaluate its ability to resist a change in pH when small volumes of strong acid or base are added.



$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

$$10^{-9.24} = 5 \times \frac{[\text{H}_3\text{O}^+]}{1}$$

$$[\text{H}_3\text{O}^+] = 1.15 \times 10^{-10}$$

$$\text{pH} = 9.94$$

$$\text{p}K_a = 9.24$$

The solution will function as a buffer (*as it contains a weak base and conjugate acid in a 5:1 ratio / within a 1:10 ratio / within a pH range of 8.24 – 10.24*).

Since the [NH<sub>3</sub>] > [NH<sub>4</sub><sup>+</sup>] / pH > pK<sub>a</sub>, the buffer will be more effective at neutralising added strong acid.

## Definitions

**Acid:** A solution that has an excess of  $\text{H}^+$  ions.

**Alkali:** A base in solution that has an excess of  $\text{OH}^-$  ions.

**Amphiprotic:** A substance that can act as either an acid or a base.

**Aqueous:** A solution that is mainly water.

**Base:** A substance that accepts  $\text{H}^+$  ions.

**Neutral:** A solution that has a pH of 7. It is neither acidic nor basic.

**Strong Acid:** An acid that has a very low pH (0-4). The  $\text{H}^+$  ions completely dissociates in solution

**Strong Base:** A base that has a very high pH (10-14). A substance that readily accepts all  $\text{H}^+$  ions.

**Weak Acid:** An acid that only partially ionizes in an aqueous solution. That means not every molecule breaks apart. They usually have a pH close to 7 (3-6).

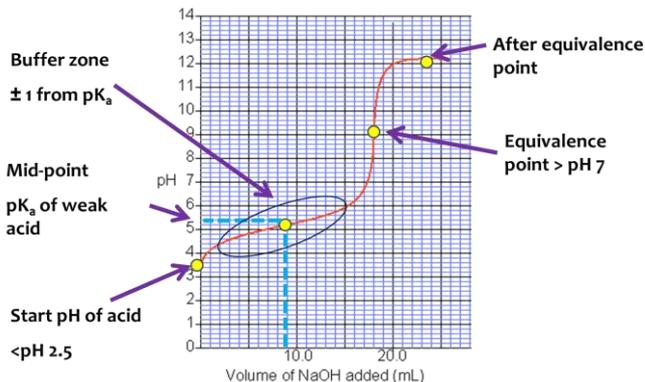
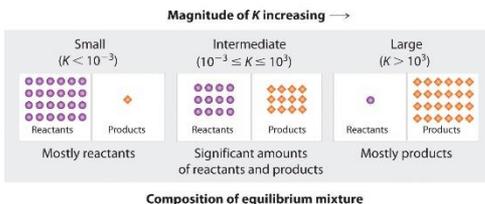
**Weak Base:** A base that only partially ionizes in an aqueous solution. That means not every molecule breaks apart. They usually have a pH close to 7 (8-10).



# Acid/Base Key concepts

$$pK_a = -\log K_a$$

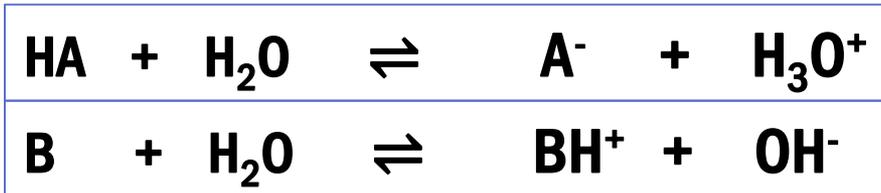
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$



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

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

## $K_a$ and $pK_a$



## titration curves

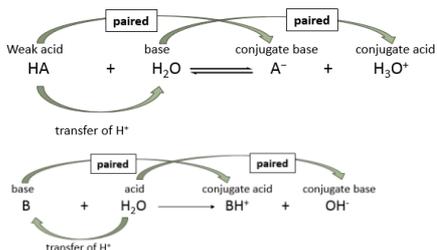
## pH calculations

## buffers

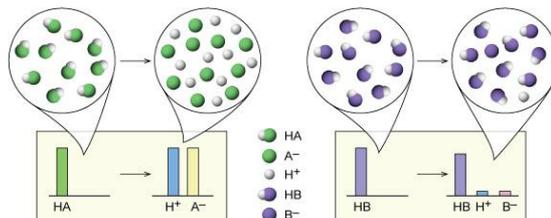
$$[H_3O^+] = K_a \times \frac{[\text{weak acid}]}{[\text{conjugate base}]} \quad \text{OR} \quad pH = pK_a + \log \frac{[A^-]}{[HA]}$$

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

## conjugate acid/base



## species in solution



## conductivity

Universal indicator pH	1 - 2	3 - 6	7	8 - 12	13 - 14
description	<b>Strong Acids</b> Readily donate all their protons when dissolved	<b>Weak Acids</b> Donate only a small proportion of protons	<b>Neutral solution</b>	<b>Weak Bases</b> Accept only a small proportion of protons	<b>Strong Bases</b> Readily accept protons
$H_3O^+ / OH^-$ concentration	Concentration of $H^+$ ions is greater than that of $OH^-$ ions		Concentration of $H^+$ ions is the same as that of $OH^-$ ions		Concentration of $H^+$ ions is less than that of $OH^-$ ions
conductivity	High conductivity	Low conductivity	High conductivity if ionic salt	Low conductivity	High conductivity