

With 2018 NCEA
Exam included

2020
Version

Chemistry AS 91392

C3.6 Aqueous Systems

Achievement Criteria - Solubility

AS 91392

C3.6

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, A₂B and AB₂ types where neither of the ions A nor B reacts further with water.

Candidates are expected to recognise common strong acids (HCl, HBr, HNO₃, H₂SO₄); strong bases (KOH, NaOH); weak acids (HF, CH₃COOH, and NH₄⁺); weak bases (NH₃, CH₃NH₂, and CH₃COO⁻). 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

Demonstrate understanding of equilibrium principles in aqueous systems

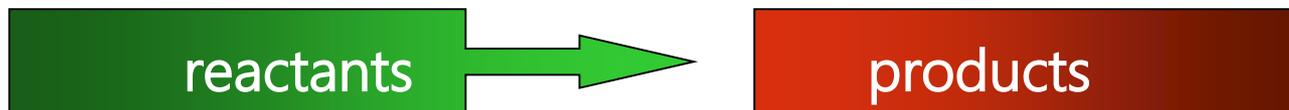
Aqueous systems are limited to those involving acidic and basic solutions (in which proton transfer occurs).

- 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).

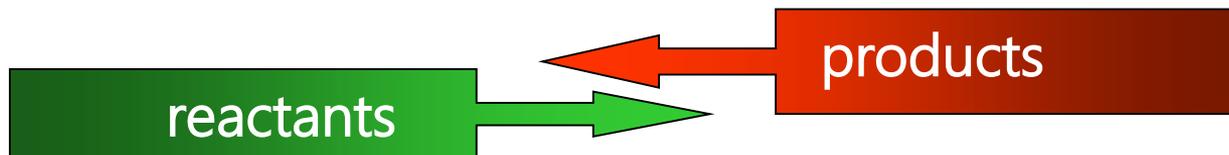
Equilibrium

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.

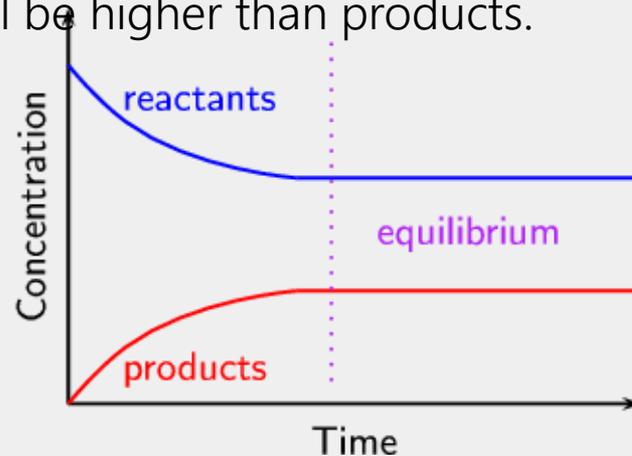
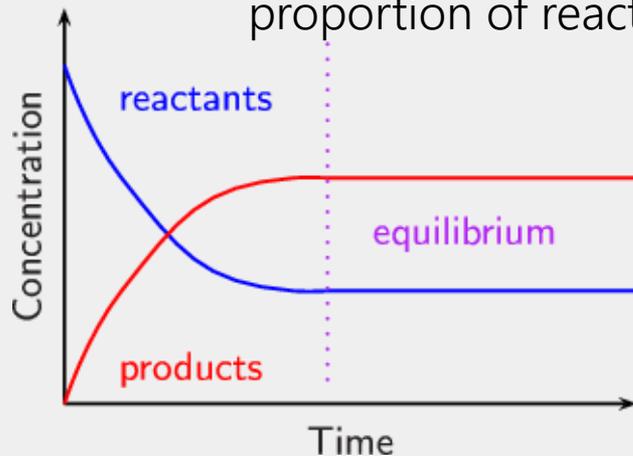
However, both the forward and reverse reactions are continuing

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.



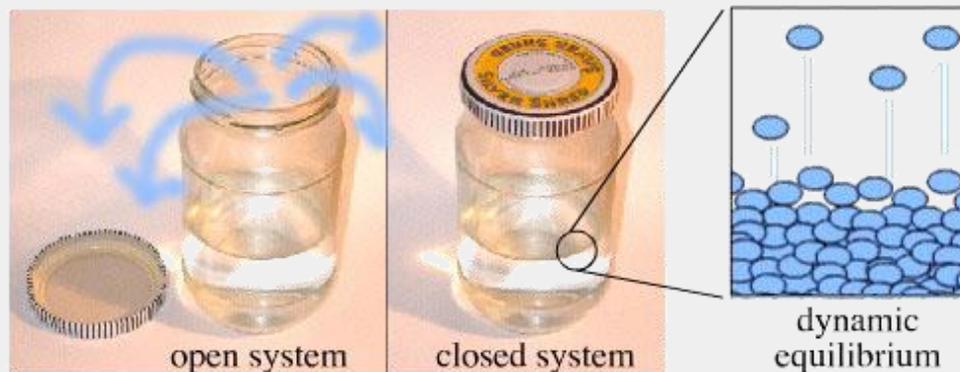
Equilibrium – Evaporation case study

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.

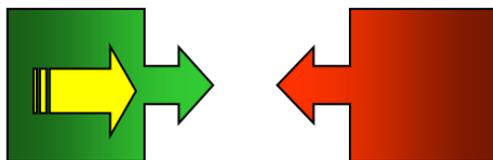
In a closed system, where the lid prevents the gas escaping, the proportion of liquid to gas will become fixed at a dynamic equilibrium. Liquid will evaporate into gas at the same rate that gas condenses into a liquid.



Changes in Equilibrium

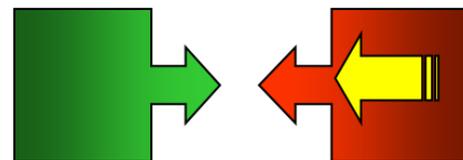
A system stays in equilibrium unless a change is made
A change made to a system in equilibrium will **either**

Increase the rate of the
forward reaction



OR

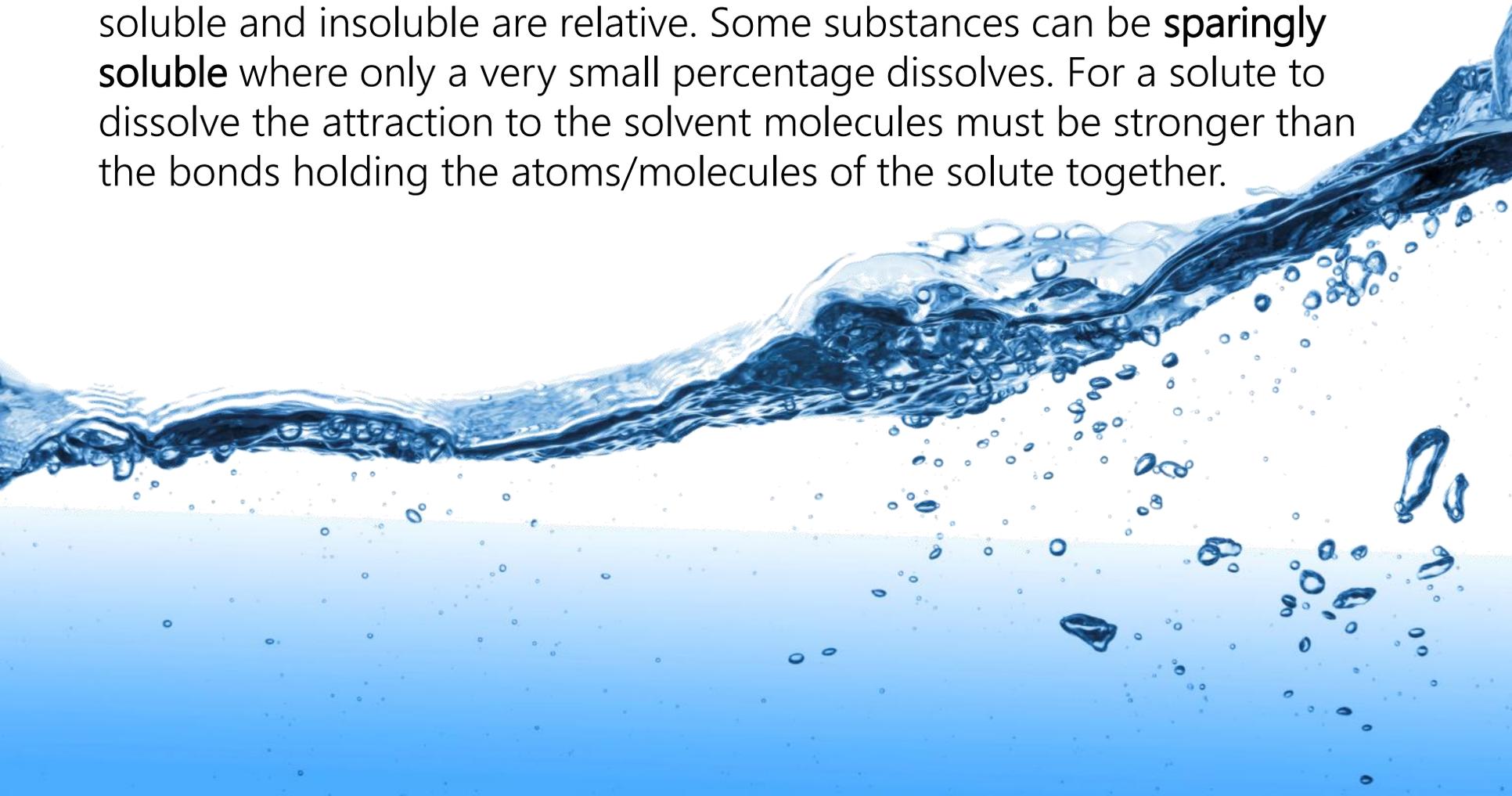
Increase the rate of the **reverse**
reaction



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

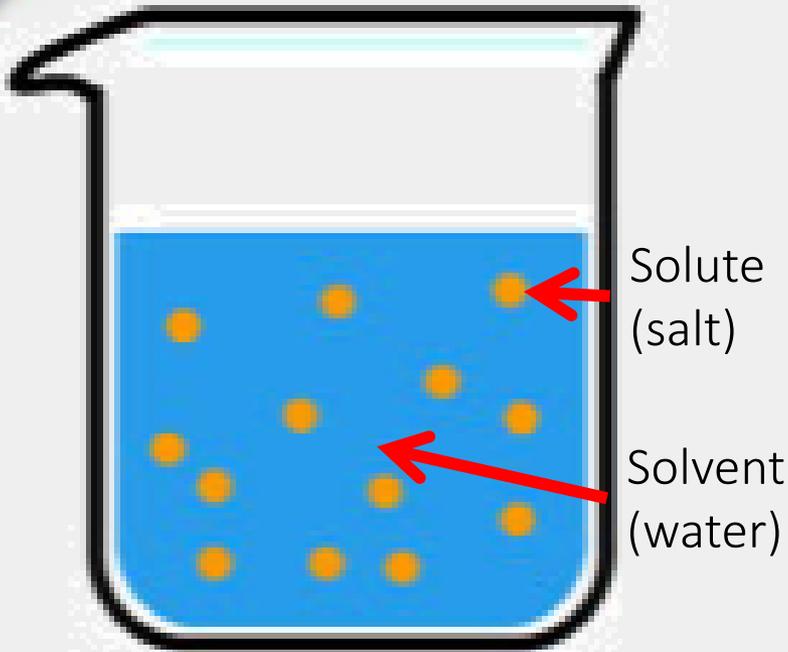
Solubility

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**.



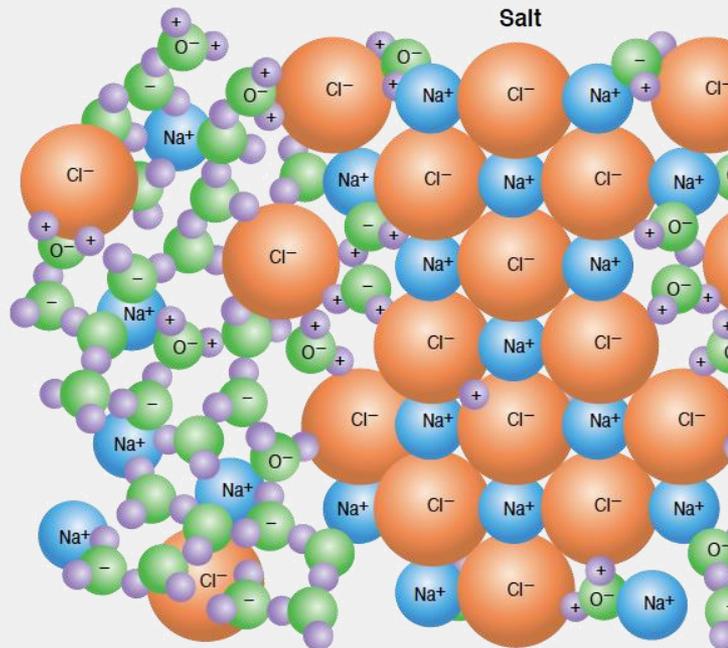
Solution
(saltwater)

Background Knowledge



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.



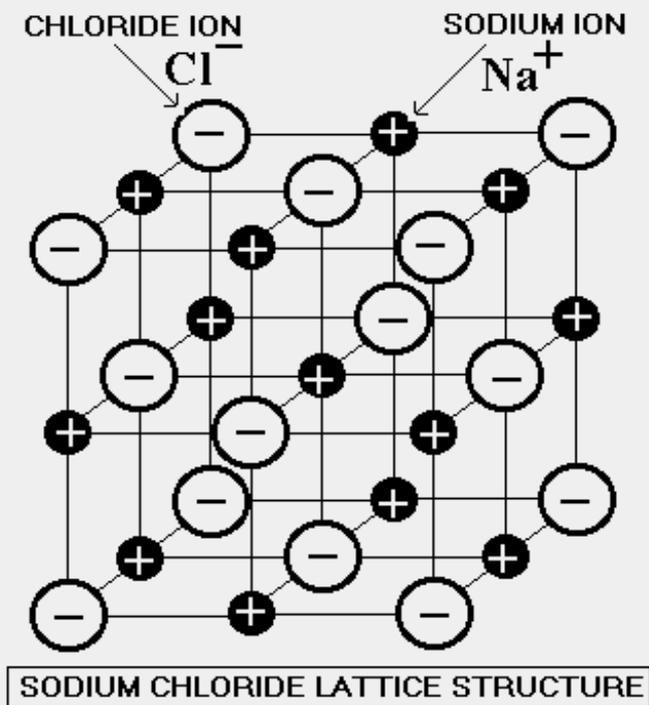
For a solute to dissolve, the solvent particles must form bonds with the solute particles that are of similar strength, to the bonds between the solute particles.

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

The structure of Ionic Solids

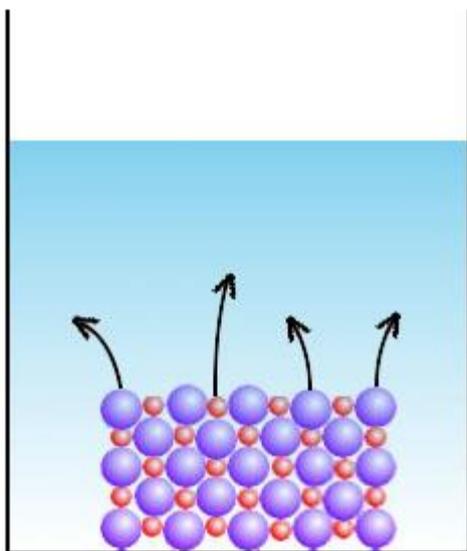
Metal + Non-Metal

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.

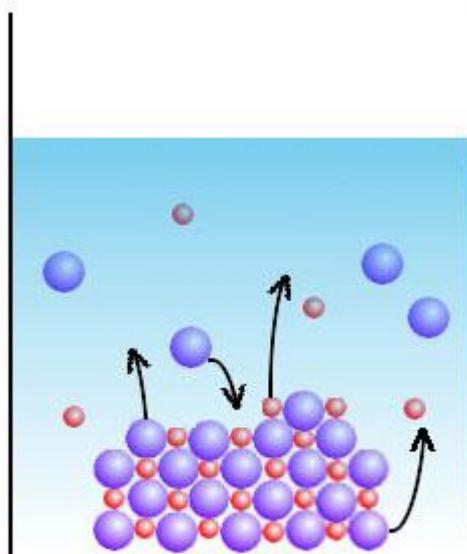


Equilibrium of solutions

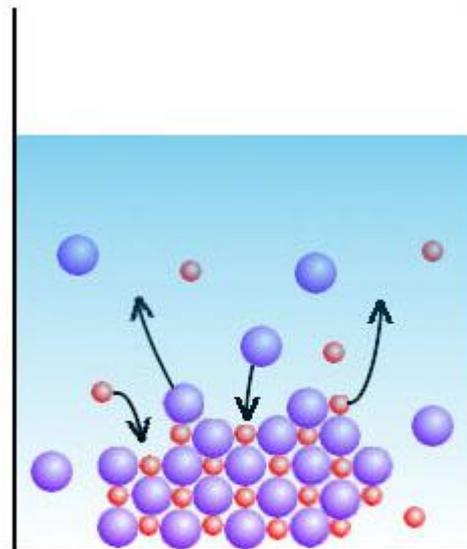
A system reaches **equilibrium** when the rate the solid dissociates into ions matches the rate that the ions precipitate into solids. The equilibrium can be changed permanently by adjusting the system temperature (or temporarily - pressure or adding/removing reactants/product)



Salt is initially put into the water and begins dissolving.



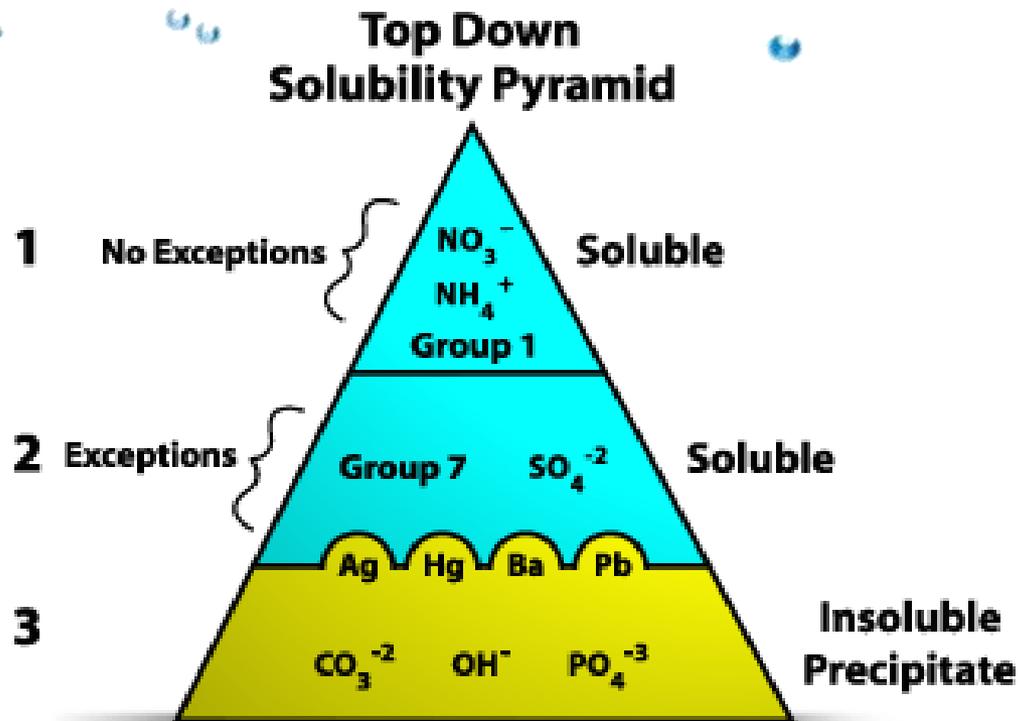
Salt continues to dissolve; however, dissolved ions will also precipitate. Because the salt dissolves faster than its ions precipitate, the net movement is towards dissolution.



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

Sparingly Soluble Equilibrium Equations

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

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

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



Water is not included in the equation because the very large concentration before and after means there is negligible change

Solubility [s] and Concentration

[] indicates
concentration

At room temperature the solubility of silver chromate, Ag_2CrO_4 , is $6.5 \times 10^{-5} \text{ mol L}^{-1}$.

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

Start with the equation for the dissolving process.

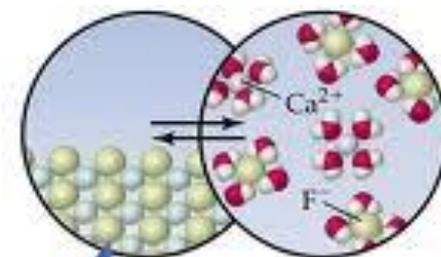


The equation shows that for every mole of dissolved solid there are **2 moles of Ag^+ ions** and **1 mole of CrO_4^{2-} ions**. Therefore

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

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

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⁻¹ to gL⁻¹

Example question: What is the solubility [s] of Ag₂CrO₄ in g L⁻¹?

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 **$m = n \times M$** .

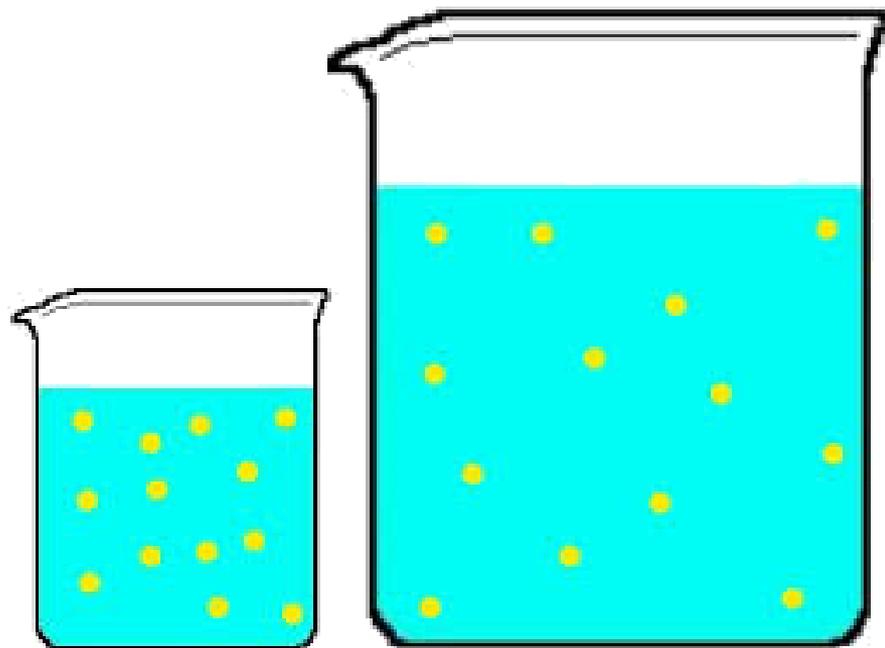
$$s = 6.5 \times 10^{-5} \text{ mol L}^{-1}$$

Since there is 6.5×10^{-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 g L⁻¹.



Equilibrium Constant: K_c

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

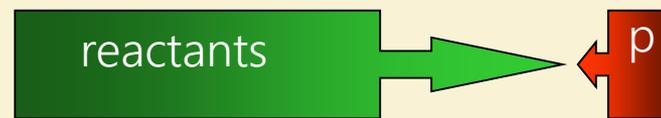
Large K value eg $K=10000$

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 molL⁻¹ at equilibrium

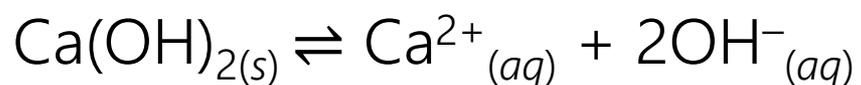
e.g. $K_c = \frac{[NH_3]^2}{[N_2] \times [H_2]^3}$

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

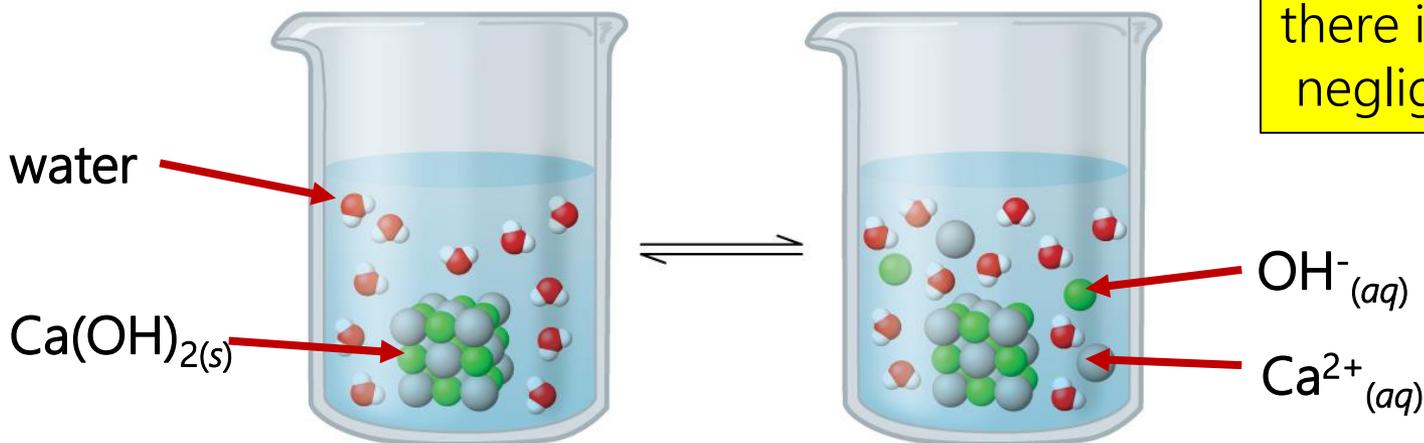
Solubility product K_s

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 Ca(OH)_2 . For this equilibrium, we have the solubility product expression:



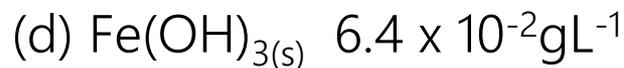
$$K_s (\text{Ca(OH)}_2) = [\text{Ca}^{2+}] [\text{OH}^{-}]^2$$



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 [Ks]**.



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

[] = concentration in 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 BaSO_4 is given as $1.05 \times 10^{-5} \text{ mol L}^{-1}$ at 25°C . Calculate the value of K_s .



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

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

$$= 1.10 \times 10^{-10}$$

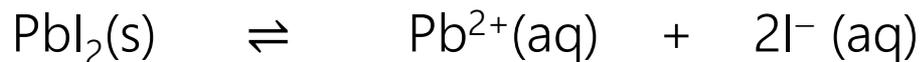
$$K_s = s^2$$

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

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

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

$$K_s = 4s^3$$

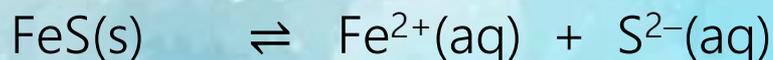
NOTE: because $[2s]^2$ means everything inside the brackets is squared then expanding it out becomes $2^2 \times s^2 = 4s^2$. The other ion $[s]$ then is multiplied so the whole expression becomes $4s^3$ (cubed)

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

$$s = \sqrt{K_s}$$

$$\therefore K_s (\text{FeS}) = s^2 \quad \text{and} \quad s = \sqrt{6.3 \times 10^{-18}} = 2.51 \times 10^{-9} \text{ mol L}^{-1}$$

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.

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

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

Converting Mass to s(and K_s) and K_s to Mass

Some questions will provide the **mass** of a sparingly soluble salt and the **volume** of water that it is dissolved into. The **molar mass** of the salt will also be provided. You may need to calculate the solubility or K_s.

1. Write the ionic equation and expression
2. Calculate concentration (in molL⁻¹) Use $n = m/M$ and then $c = n/v$
(remember volume = L and Mass =g) Assume concentration (c) = s
3. Calculate K_s 1:1 salt $K_s = [s][s]$ (or s^2) 2:1 salt $K_s = [2s]^2[s]$ (or $4s^3$)

Other questions may require you to calculate mass (of salt) given K_s or s. For example:

Silver carbonate, Ag₂CO₃, 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 Ag₂CO₃ that will dissolve in 50 mL of water to make a saturated solution at 25°C.

1. Write the ionic equation and expression
2. Calculate s 1:1 $s = \sqrt{K_s}$ 2:1 $s = \sqrt[3]{K_s/4}$ Assume s = concentration (c)
3. Calculate Mass use $n = c.v$ and $m = n/M$

Summary of solubility calculations

Question: Calculate K_s

Starting information:

Mass, Molar mass and Volume

Calculate c

$$n = m/M \text{ and then } c = n/v$$

Question: Calculate mass

Starting information:

K_s and Molar Mass

Calculate s

$$1:1 \quad s = \sqrt{K_s} \quad 2:1 \quad s = \sqrt[3]{K_s/4}$$

Assume concentration (c) = s

Calculate K_s

$$1:1 \text{ salt } K_s = [s][s] \text{ (or } s^2)$$

$$2:1 \text{ salt } K_s = [2s]^2[s] \text{ (or } 4s^3)$$

Calculate Mass

$$\text{use } n = c.v$$

$$\text{then } m = n/M$$

Mass (g)

concentration (molL^{-1})

answers to 3 sgf.

Effects of Acid on Solubility

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



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 Ag^+ which reacts with NH_3 or OH^- to produce a complex ion such as $[\text{Ag}(\text{NH}_3)_2]^+$

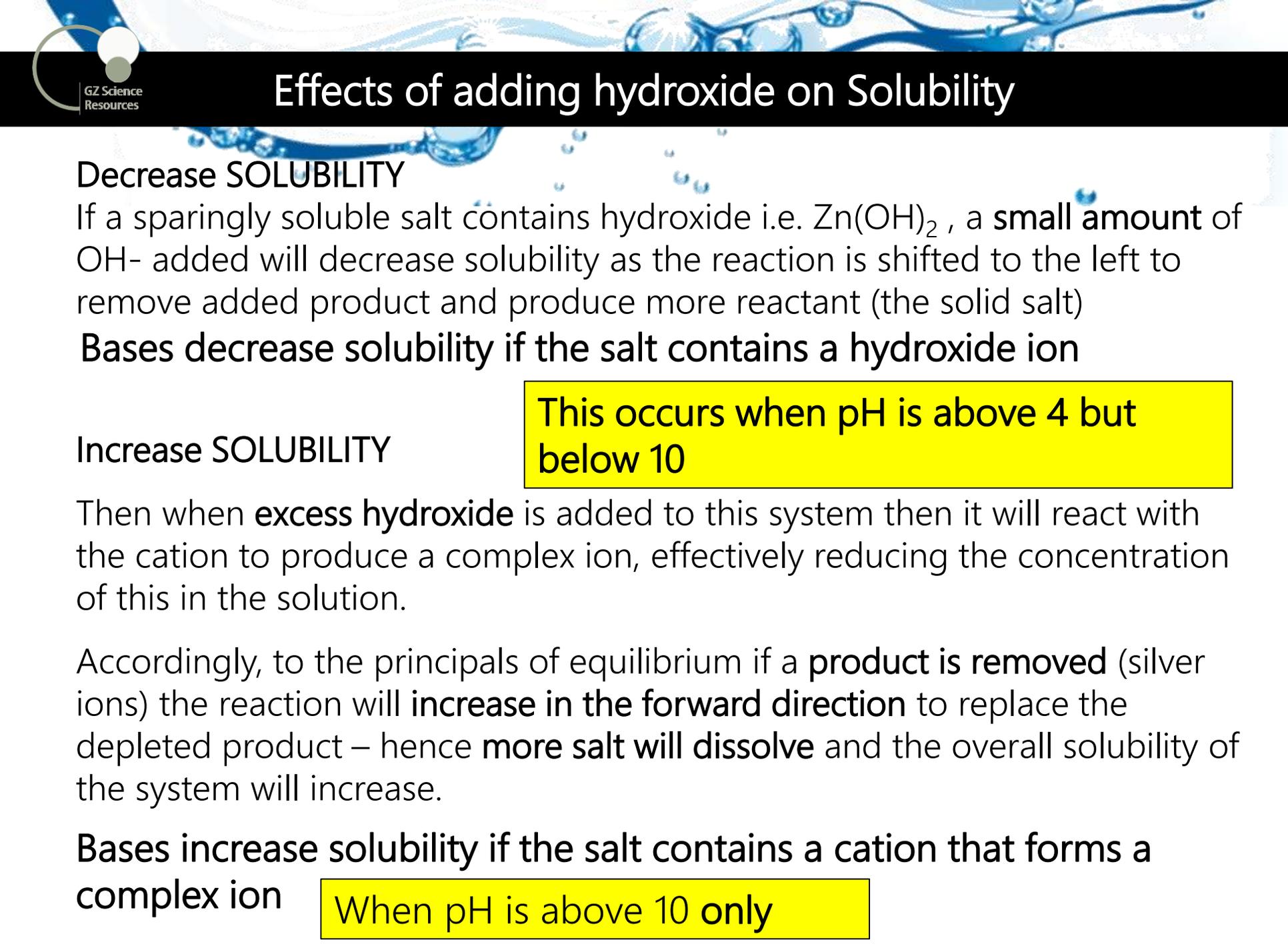
Base “locks up” many cations into complex ions

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 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

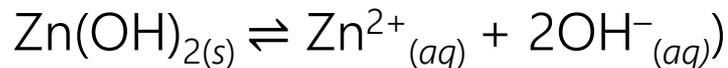
Then when **excess hydroxide** is added to this system then it will react with the cation to produce a complex ion, effectively reducing the concentration of this in the solution.

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.

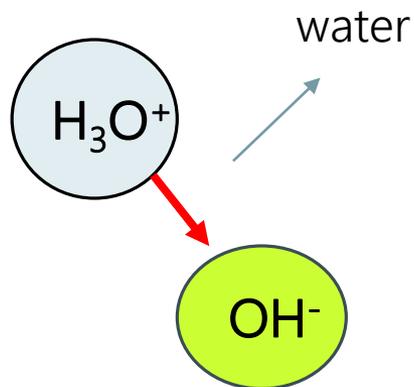
Bases increase solubility if the salt contains a cation that forms a complex ion

When pH is above 10 only

Summary of Equilibrium changes in Solubility



pH is below 4



Hydronium ions in acid solution **neutralise** OH⁻, and removing as product.

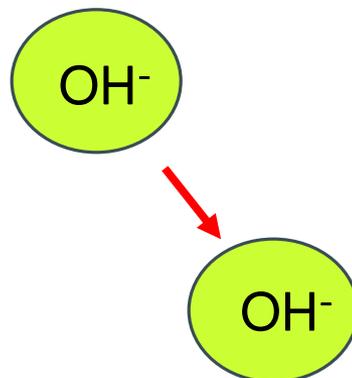
Forward reaction increases

Solubility increases



pH is above 4 but below 10

Adding few drops OH⁻



Total OH⁻ concentration increases, therefore more product.

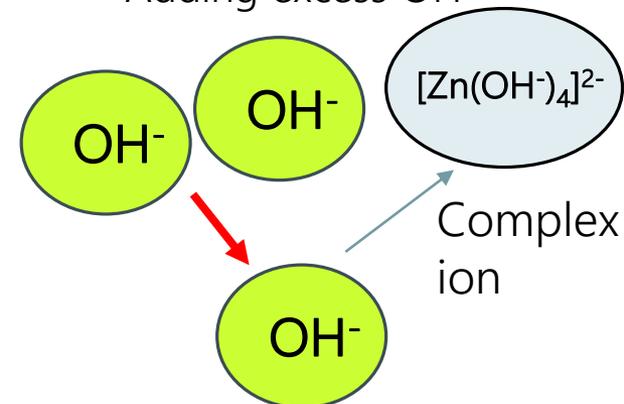
Reverse reaction increases

Solubility decreases



pH is above 10

Adding excess OH⁻



Complex ion forms, and removes product., by removing Zn²⁺ ions.

Forward reaction increases

Solubility increases



Remove product – solubility increases.

Add to product – solubility decreases

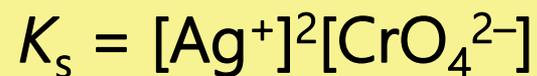
NCEA 2013 solubility

Achieved
Question

Question: 2a: In an experiment, a saturated solution was made by dissolving 1.44×10^{-3} g of Ag_2CrO_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 $\text{Ag}_2\text{CrO}_{4(s)}$.



NCEA 2013 solubility

Excellence
Question

Question: 2b: In an experiment, a saturated solution was made by dissolving 1.44×10^{-3} g of Ag_2CrO_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 $K_s(\text{Ag}_2\text{CrO}_4)$.

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

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

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

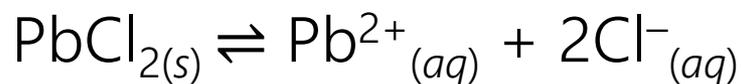
$$[\text{CrO}_4^{2-}] = 8.67 \times 10^{-5} \text{ mol L}^{-1}$$

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

NCEA 2014 solubility

Achieved
Question

Question: 2a: A flask contains a saturated solution of PbCl_2 in the presence of undissolved PbCl_2 . (i) Write the equation for the dissolving equilibrium in a saturated solution of 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⁻¹) of lead(II) chloride in water at 25°C, and give the [Pb²⁺] and [Cl⁻] in the solution.

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

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

$$2x$$

$$K_s = 4x^3$$

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

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

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

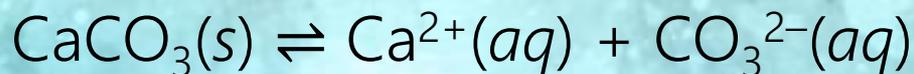
$$[\text{Pb}^{2+}] = 1.62 \times 10^{-2} \text{ mol L}^{-1}$$

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

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

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 CaCO_3 .



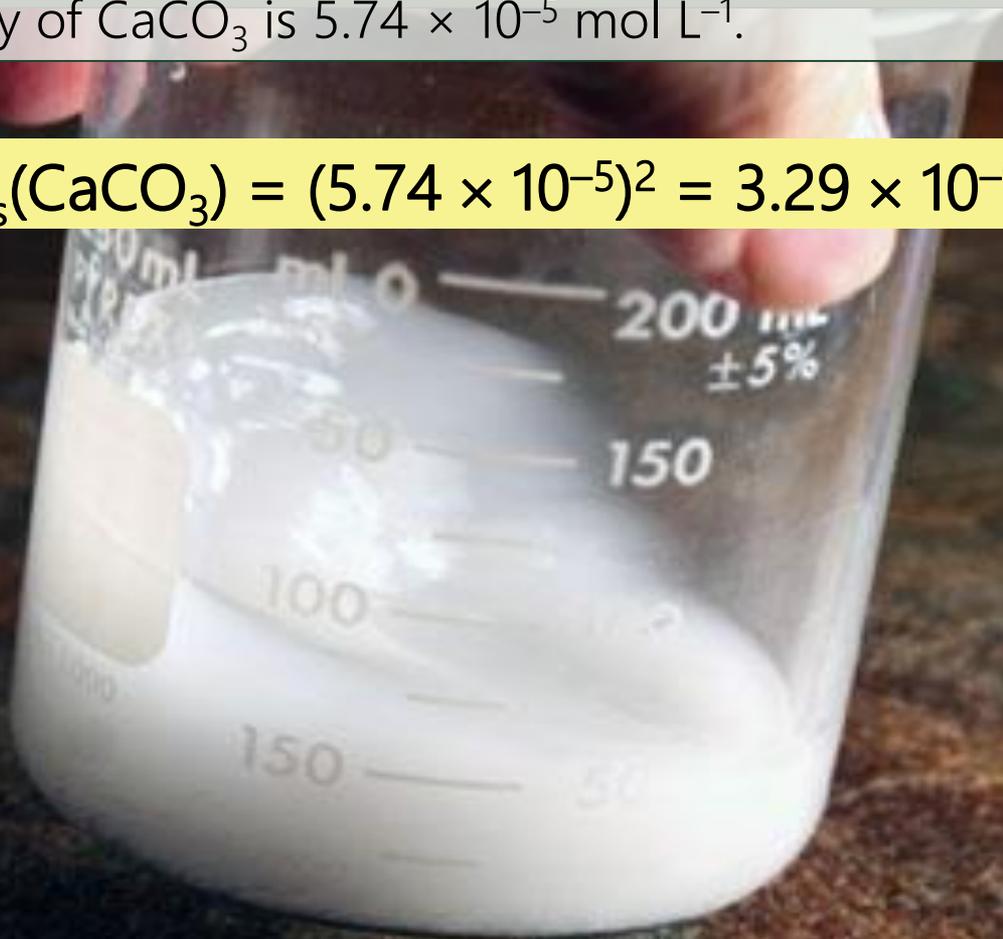
Question: 2a: (ii) Write the expression for $K_s(\text{CaCO}_3)$.

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

Question: 2a: (iii) Calculate the solubility product of CaCO_3 , $K_s(\text{CaCO}_3)$.

The solubility of CaCO_3 is $5.74 \times 10^{-5} \text{ mol L}^{-1}$.

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



NCEA 2016 Solubility

Achieved
Question

Question: 1a: Silver carbonate, Ag_2CO_3 , is a sparingly soluble salt.

$$K_s(\text{Ag}_2\text{CO}_3) = 8.10 \times 10^{-12} \text{ at } 25^\circ\text{C} \quad M(\text{Ag}_2\text{CO}_3) = 276 \text{ g mol}^{-1}$$

(a) Write the solubility product expression, K_s , for silver carbonate (Ag_2CO_3).

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



NCEA 2016 Solubility

Excellence
Question

Question: 1b: Silver carbonate, Ag_2CO_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 Ag_2CO_3 that will dissolve in 50 mL of water to make a saturated solution at 25°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°C .

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

Let s = solubility

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

$$[\text{OH}^-]^2 = (2s)^2$$

$$K_s = 4s^3$$

$$4s^3 = 4.80 \times 10^{-20}$$

$$\text{So; } s = 2.29 \times 10^{-7} \text{ mol L}^{-1}$$

NCEA 2018 Solubility

Merit
Question

Question: 1b (i). Write the equation for the equilibrium occurring in a saturated solution of calcium fluoride, Ca F_2 .

Question: 1b (ii). Calculate the solubility of Ca F_2 in water at 25°C .

$$K_s(\text{Ca F}_2) = 3.20 \times 10^{-11}$$



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

Let solubility be 's':

$$[\text{Ca}^{2+}] = s \quad [\text{F}^-] = 2s$$

$$K_s = 4s^3$$

$$s = \sqrt[3]{\left(\frac{3.20 \times 10^{-11}}{4} \right)}$$

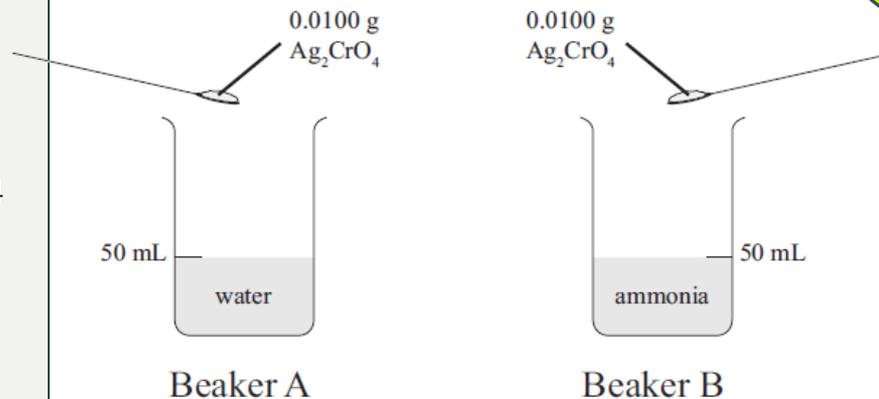
$$= 2.00 \times 10^{-4} \text{ mol L}^{-1}$$



NCEA 2013 solubility and Equilibrium

Excellence
Question

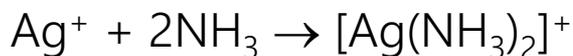
Question: 2c: In another experiment, 0.0100 g of Ag_2CrO_4 in beaker A was made up to a volume of 50.0 mL with water. In beaker B, 0.0100 g of Ag_2CrO_4 was made up to a volume of 50.0 mL with 0.100 mol L^{-1} ammonia solution. Compare and contrast the solubility of Ag_2CrO_4 in beaker A and beaker B.



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 1.44×10^{-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 Ag_2CrO_4 will dissociate completely and form an equilibrium.



The silver ion will then react further with NH_3 , removing it from the above equilibrium. Thus, more Ag_2CrO_4 will dissolve to re-establish equilibrium.

NCEA 2014 solubility and equilibrium

Excellence
Question

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 H_3O^{+} 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 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 $\text{Zn}^{2+} + 4\text{OH}^{-} \rightarrow [\text{Zn}(\text{OH})_4]^{2-}$

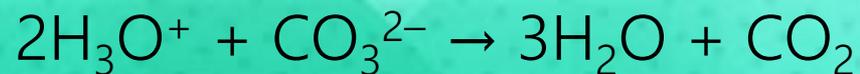
This decrease in $[\text{Zn}^{2+}]$ causes the position of equilibrium to shift further to the right, therefore more $\text{Zn}(\text{OH})_2$ dissolves.

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 CaCO_3 is higher in an acidic solution.

Use an equation to support your explanation.

The H_3O^+ from the acidic solution reacts with the CO_3^{2-} . This reduces $[\text{CO}_3^{2-}]$, causing the equilibrium to shift towards the products / RHS to replace some of the lost CO_3^{2-} . Therefore more solid CaCO_3 will dissolve.

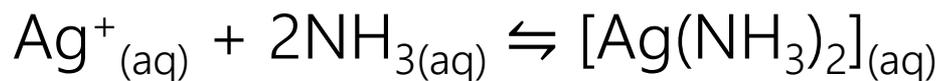


NCEA 2016 Solubility and equilibrium

Excellence
Question

Question: 1c: Explain how the solubility of Ag_2CO_3 will change if added to 50 mL of a 1.00 mol L^{-1} ammonia, NH_3 , solution.

Support your answer with balanced equations.



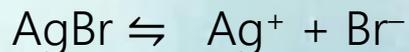
Then when a base is added to this system then it will react with the cation effectively reducing the concentration of this in the solution.

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

**Base "locks up" many cations
into complex ions**

Question 1b:

- (i) 40.0 mL of 0.150 mol L⁻¹ 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) (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⁻ is a common ion / added to solution

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

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

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 H_3O^+ ions neutralise

the 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 .

NCEA 2018 Solubility and Equilibrium

Excellence
Question

Question: 1c. Explain the effect of the following on the solubility of iron(III) hydroxide, $\text{Fe}(\text{OH})_3$, in water.

Include relevant equation(s) in your answer. No calculations are necessary.

(i) pH lowered below 4

In a saturated solution:



As the pH is lowered, $[\text{H}_3\text{O}^+]$ increases. The H_3O^+ will remove and neutralise OH^- /



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

This causes more solid $\text{Fe}(\text{OH})_3$ to dissolve, i.e. the solubility of $\text{Fe}(\text{OH})_3$ increases / so that $[\text{Fe}^{3+}][\text{OH}^-]^3$ will again equal K_s .

NCEA 2018 Solubility and Equilibrium

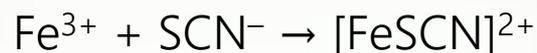
Excellence
Question

Question: 1c. Explain the effect of the following on the solubility of iron(III) hydroxide, $\text{Fe}(\text{OH})_3$, in water.

Include relevant equation(s) in your answer. No calculations are necessary.

(ii) Potassium thiocyanate, KSCN , solution added

The SCN^- ions can form a complex ion with Fe^{3+} ions:



Since the Fe^{3+} are removed from the equilibrium, more $\text{Fe}(\text{OH})_3$ dissolves to replace some of the Fe^{3+} , i.e. equilibrium will shift towards the products / speed up the forward reaction. As a result, the solubility of $\text{Fe}(\text{OH})_3$ increases.



NCEA 2018 Solubility and Equilibrium

Merit
Question

Question: (a) (i) Write the solubility product expression, K_s , for silver chloride, AgCl.
(ii) Why does the solubility of AgCl decrease when a small volume of silver nitrate, AgNO₃, solution is added to a saturated solution of AgCl?
Explain your answer.



The Ag⁺ is a common ion. By increasing [Ag⁺], the equilibrium will shift towards the reactants to use up some of the extra Ag⁺, so more solid AgCl will form, i.e. the solubility of AgCl will decrease.



<https://www.sciencesource.com/archive/Silver-chloride-precipitate-SS21845965.html>

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 $K_s = [Ag^+][Cl^-]$

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

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

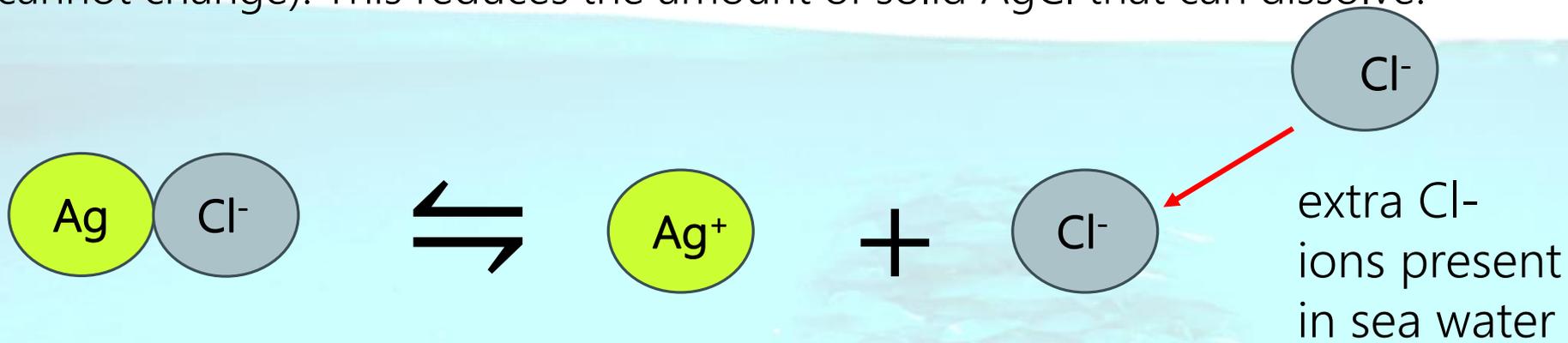
K_s is the maximum concentration of ions the solution can hold (at a given temperature)

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 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.



Favours reverse reaction therefore **solubility decreases**

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 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 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 6.4×10^{-8} is much less than 0.0025 .

Summary of Common ion calculations

Q = ratio of the concentrations of products and reactants.

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

1:1 salt

$$Q = (c) \times (c)$$

2:1 salt

$$Q = (c) \times (c)^2$$

Where can c come from?

S

(calculated from K_s)

$n = m/M$ and
then $c = n/v$

$c = \frac{\text{initial volume}}{\text{total volume}} \times \text{conc.}$

If $I.P. < K_s$ NO precipitate

If $I.P. > K_s$ precipitate forms

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

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

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

$$n(\text{Pb}(\text{NO}_3)_2) = \frac{2.00 \text{ g}}{331 \text{ g mol}^{-1}}$$

$$= 6.04 \times 10^{-3} \text{ mol}$$

$$\therefore [\text{Pb}^{2+}] = 6.04 \times 10^{-3} \text{ mol} / 0.500 \text{ L}$$
$$= 1.21 \times 10^{-2} \text{ mol L}^{-1}$$

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

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.

$$\text{pH} = 12.6$$

$$\text{pOH} = 1.4$$

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

NCEA 2016 Common Ion effect

Excellence
Question

Question: 1d: Show by calculation whether a precipitate of Ag_2CO_3 will form when 20.0 mL of 0.105 mol L^{-1} silver nitrate, AgNO_3 , solution is added to 35.0 mL of a 0.221 mol L^{-1} sodium carbonate, Na_2CO_3 , solution.

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

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

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

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

As $Q / \text{I.P.} > K_s$, a precipitate will form.

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



NCEA 2017 Common Ion effect

Excellence
Question

Question 1b (iii) : 40.0 mL of 0.150 mol L⁻¹ HBr solution was added to 25.0 mL of a saturated silver bromide, AgBr, solution.

Calculate the concentration of the silver ions, Ag⁺, after the HBr solution has been added.

$$K_s(\text{AgBr}) = 5.00 \times 10^{-13}$$

Assume the concentration of Br⁻ in the original saturated solution of AgBr is insignificant.

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

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

NCEA 2018 Common Ion Effect

Excellence
Question

Question: 3a (iii). Show by calculation whether a precipitate of AgCl will form when 70.0 mL of 0.0220 mol L⁻¹ AgNO₃ is added to 50.0 mL of 0.0550 mol L⁻¹ sodium chloride, NaCl.

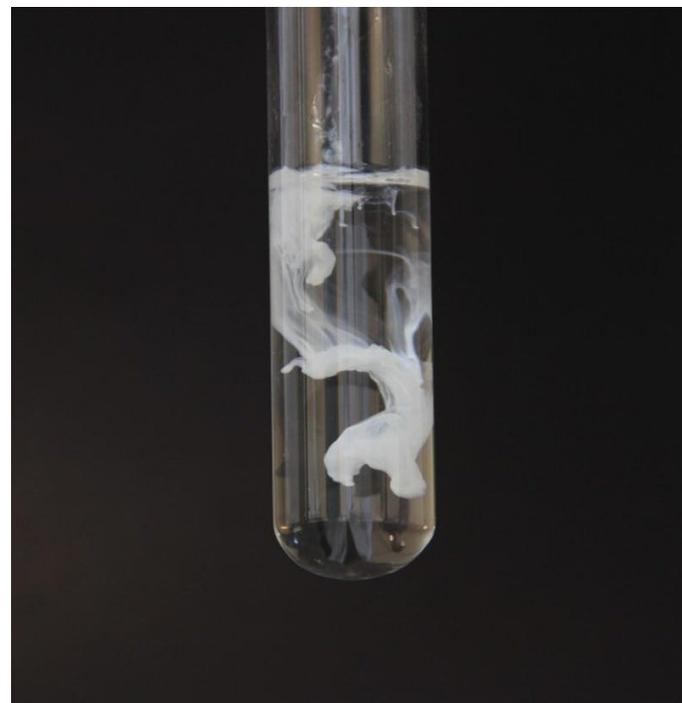
$$K_s(\text{AgCl}) = 1.80 \times 10^{-10}$$

$$\text{Final } [\text{Ag}^+] = 70 / 120 \times 0.0220 = 0.0128 \text{ mol L}^{-1}$$

$$\text{Final } [\text{Cl}^-] = 50 / 120 \times 0.0550 = 0.0229 \text{ mol L}^{-1}$$

$$Q = [\text{Ag}^+][\text{Cl}^-] = 0.0128 \times 0.0229 = 2.94 \times 10^{-4}$$

Since $Q > K_s$, AgCl will form a precipitate.



Solubility Key concepts

equations



Solubility expressions

$$K_s(CA) = [C] [A]$$

$$K_s(C_2A) = [C]^2 [A]$$

$$K_s(CA_2) = [C] [A]^2$$

Ks/s calculations

$$K_s(CA) = s^2 \quad s(CA) = \sqrt{k_s}$$

$$K_s(C_2A) = \quad s(C_2A) \stackrel{3}{=} \sqrt{k_s/4}$$

$$4s^3$$

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

K_s 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

K_s = 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**.



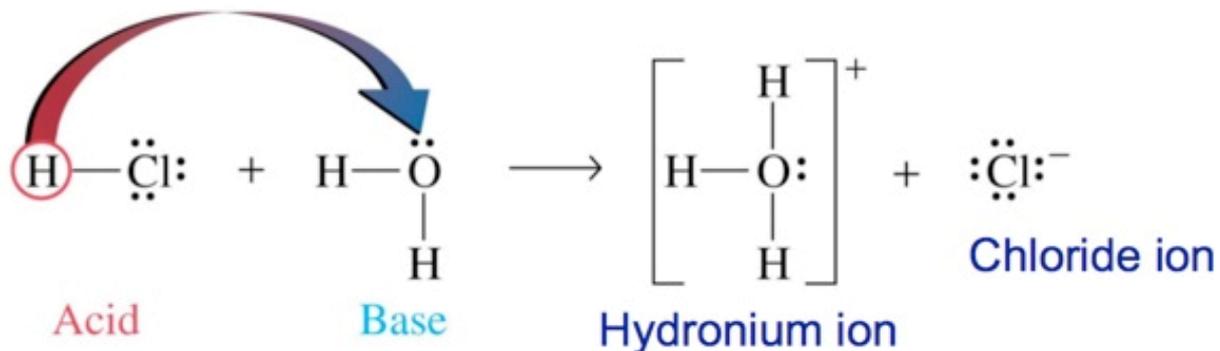
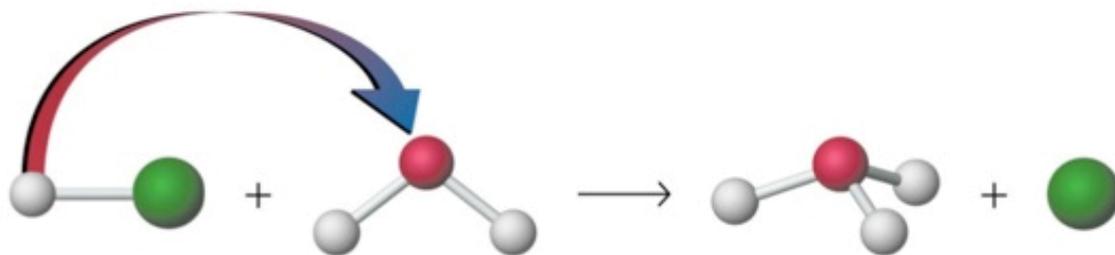
Acids – their characteristics

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

Common acids (that you need to know) include:

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

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



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

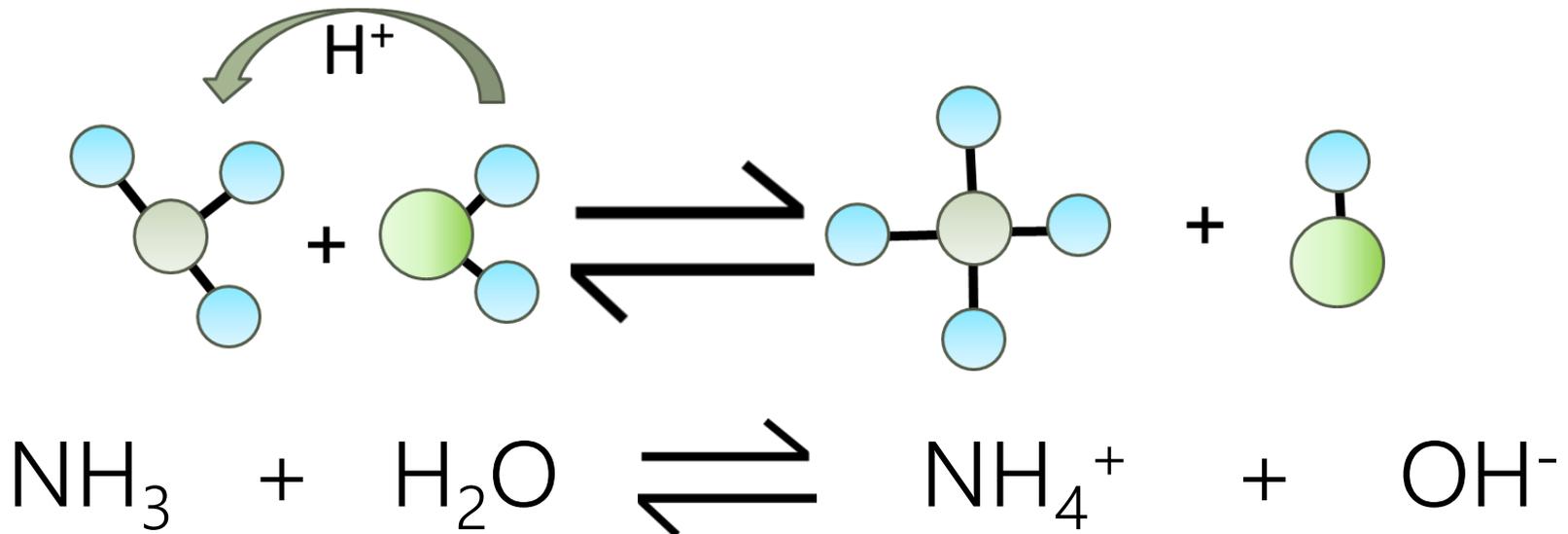
A **Base** accepts a **Hydrogen ion** that have been donated from an **Acid**.

Common bases (that you need to know) include:

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

Weak bases: **NH₃** – ammonia, **CH₃NH₂** - methylamine and **CH₃COO⁻** - 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⁺**

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

In water (or aqueous solutions) H⁺ ions exist as an H₃O⁺ ion, called **hydronium**.

Acids are substances that donate protons (H⁺) in solution



HCl gas dissolved in water

HCl has donated a **H⁺** so is acting as an acid

H₂O has accepted a **H⁺** so it is acting as a base

Solution becomes acidic since H₃O⁺ ions form

Bases are substances that accept protons (H⁺) in solution



NH₃ gas dissolved in water

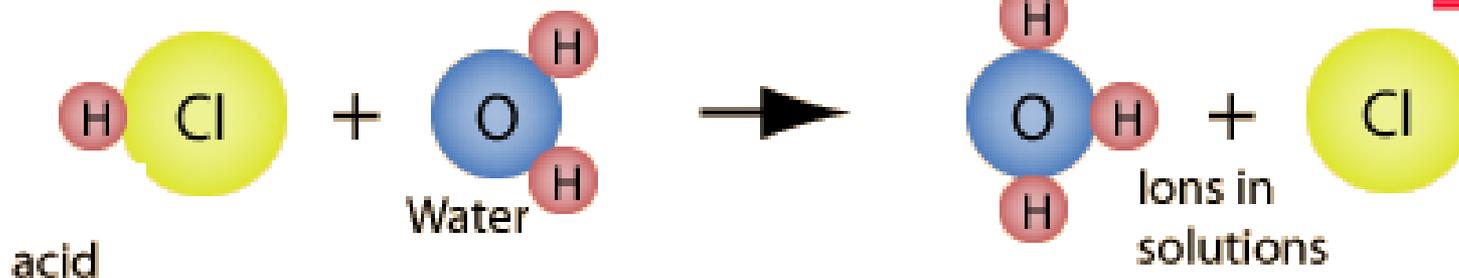
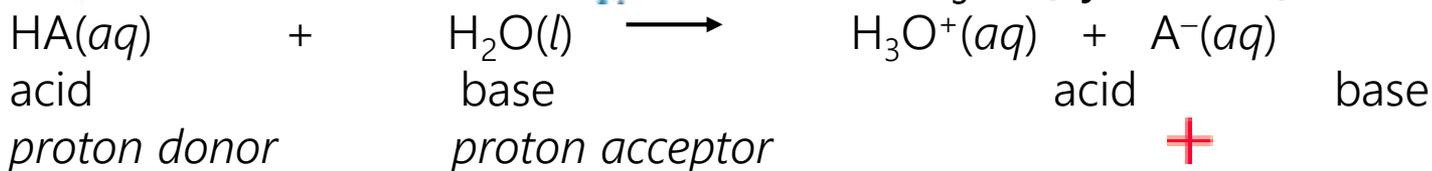
NH₃ has accepted a **H⁺** so it is acting as a base

H₂O has donated a **H⁺** so is acting as an acid

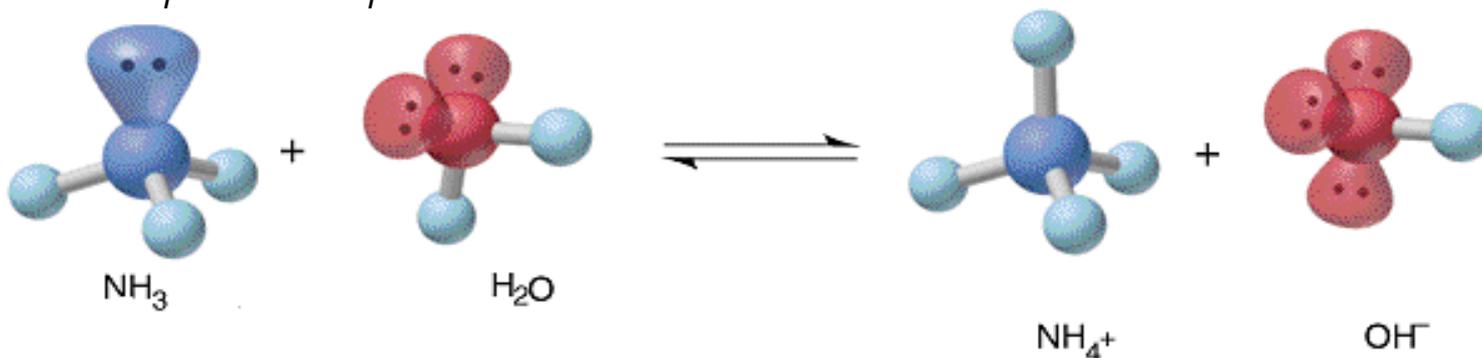
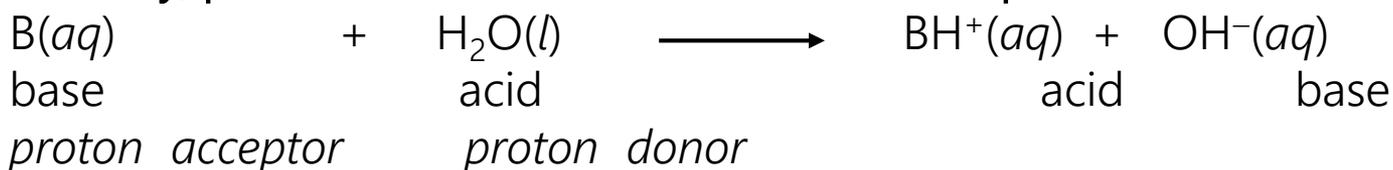
Solution becomes basic since OH⁻ ions form.

Brønsted–Lowry acids and bases summary

Proton donation to a water molecule forms H_3O^+ (hydronium) ions.



Similarly, proton donation from water to a base produces 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.

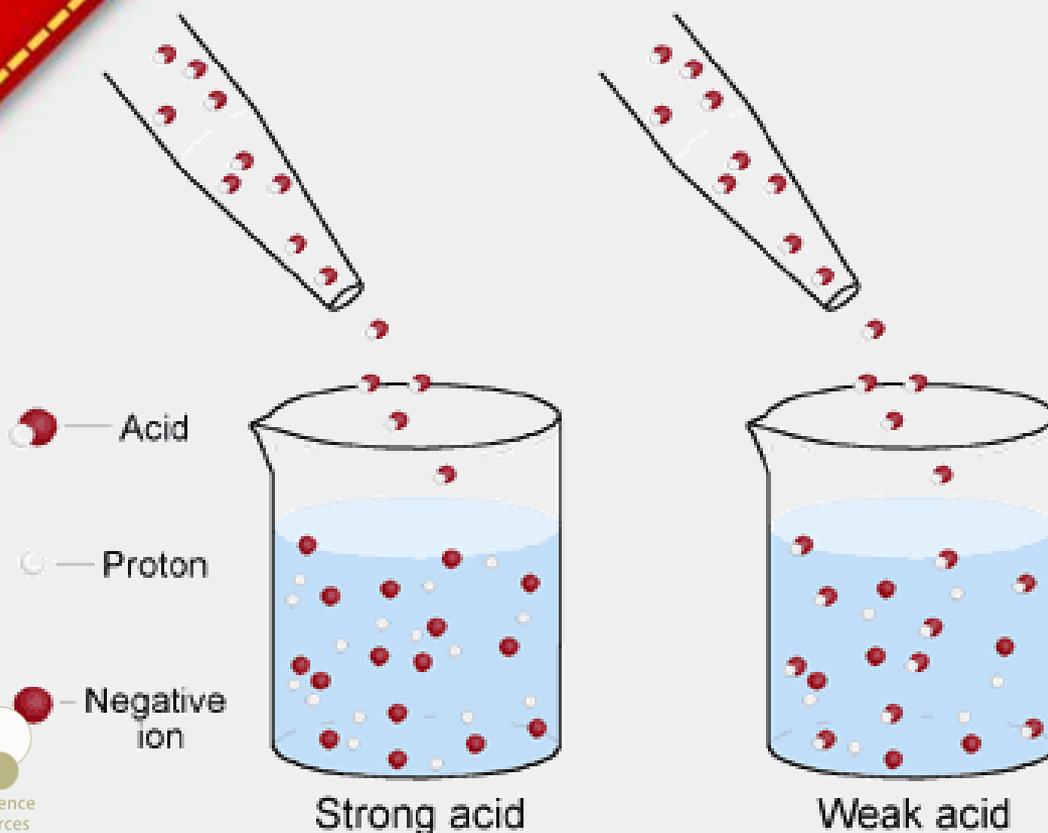
Examples of amphiprotic species include, H_2O , HCO_3^- , HSO_4^- , HPO_4^{2-} and H_2PO_4^-

Name of amphiprotic species	Chemical formula	Able to donate a proton, H^+	Able to accept a proton, H^+
Water	H_2O	$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$	$\text{H}_2\text{O}(\text{l}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_3\text{O}^+(\text{aq})$
Hydrogen carbonate ion	HCO_3^-	$\text{HCO}_3^-(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$	$\text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{CO}_3(\text{aq})$
Hydrogen sulfate ion	HSO_4^-	$\text{HSO}_4^-(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$	$\text{HSO}_4^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$
Dihydrogen phosphate ion	H_2PO_4^-	$\text{H}_2\text{PO}_4^-(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$	$\text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_3\text{PO}_4(\text{aq})$

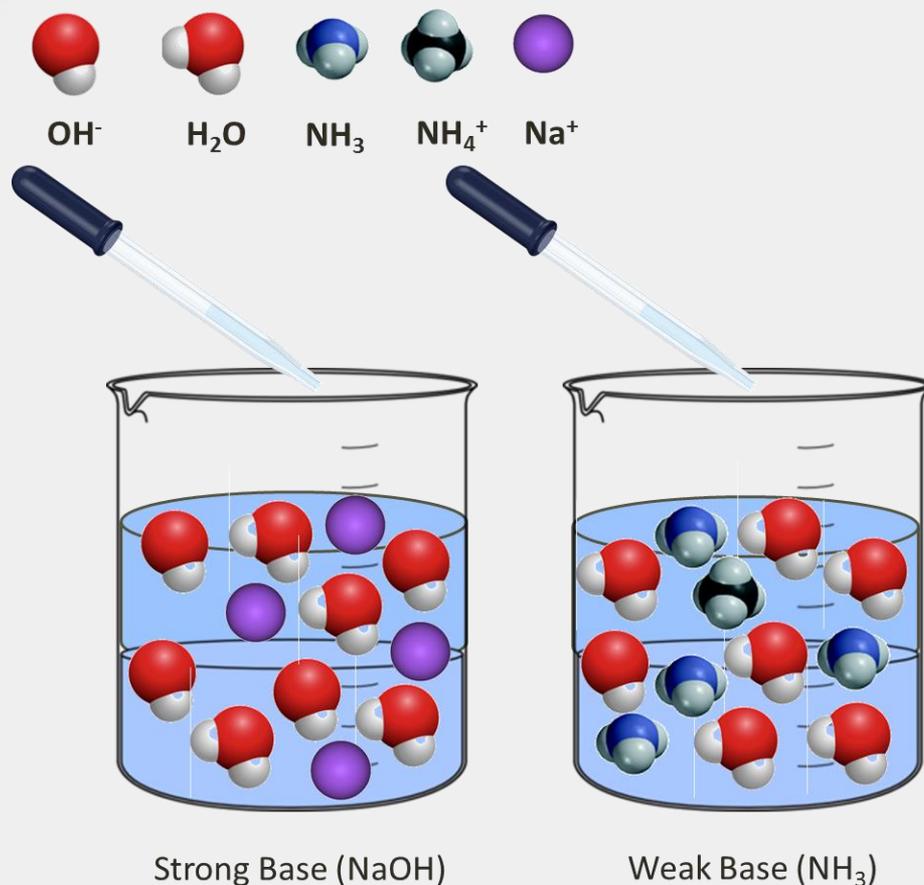
Strong and weak acids

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 H^+ ions (protons) break away from the original acid molecule in water. A **weak acid** only **partially dissociates** and loses just some of its H^+ ions (protons) in water.

For strong bases, all of the 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⁺ ion. A **weak base** is a compound where only some of the molecules will accept a H⁺ ion. Most weak base molecules remain unreacted.

Note: For strong alkalis, all of the OH⁻ ions break away from the molecule in water.

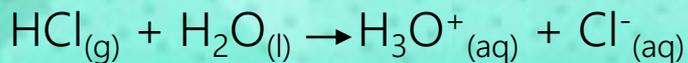
Strong and Weak Acids

The strength of an acid is determined by how readily it will donate its H^+ ions. Strong acids will have a low pH (0-3) and include HNO_3 , HCl , H_2SO_4 , and HBr

Weak acids will have a higher pH (4-6). They are mostly organic acids and include CH_3COOH , HF and NH_4^+

Strong acids

Donate protons (H^+) in aqueous solution to become **completely dissociated**.



HCl gas dissolved in water

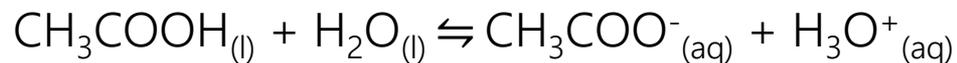
HCl has donated an H^+ so is acting as an acid

H_2O has accepted an H^+ so it is acting as a base

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

Weak acids

Donate protons (H^+) in aqueous solution to become **partially dissociated**.



CH_3COOH dissolved in water

Only some of the acetic acid molecules dissociate into acetate ions (CH_3COO^-)

Because the acetate ion is a strong base (conjugate pairs) it will readily accept H^+ (from H_3O^+) and become acetic acid.

Solution contains **mostly** intact CH_3COOH molecules.

Strong and Weak Bases

The strength of a base is determined by how readily it will accept H^+ ions. Strong bases will have a high pH (12-14) and include NaOH and KOH. Weak acids will have a lower pH (8-11). They include NH_3 , CH_3NH_2 and CH_3COO^-

Strong Bases

Completely accept protons (H^+) in aqueous solution



NaOH completely dissociates

The OH^- ions will readily accept H^+ ions.

Solution contains very few intact NaOH molecules after reaction.

Weak Bases

Partially accept protons (H^+) in aqueous solution



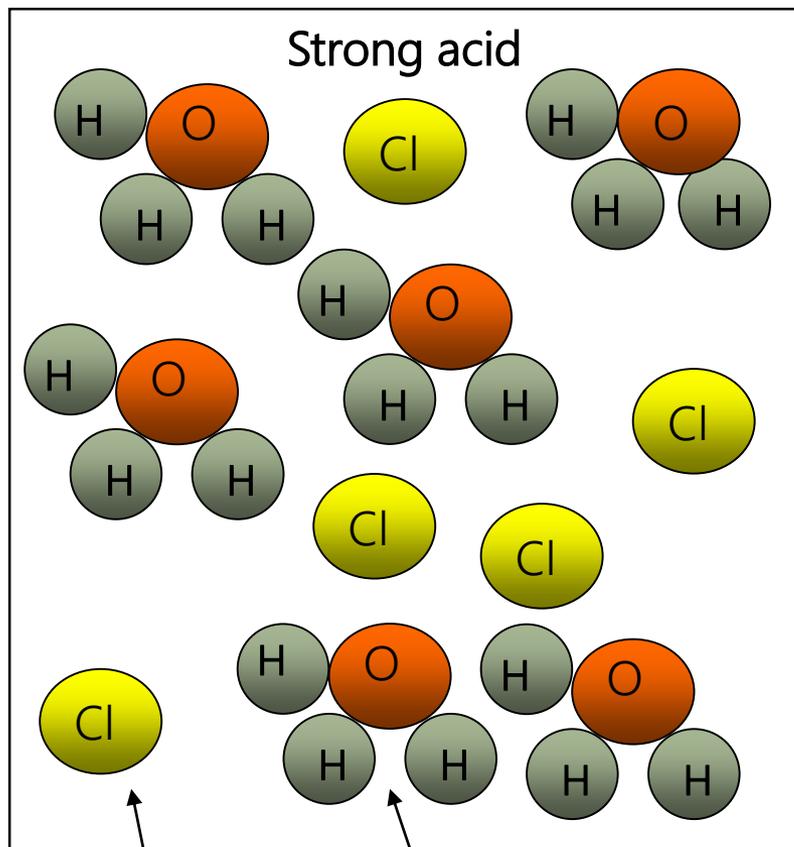
Only some of the ammonia molecules dissociate into ammonium ions (NH_4^+)

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

Solution contains mostly intact NH_3 molecules.

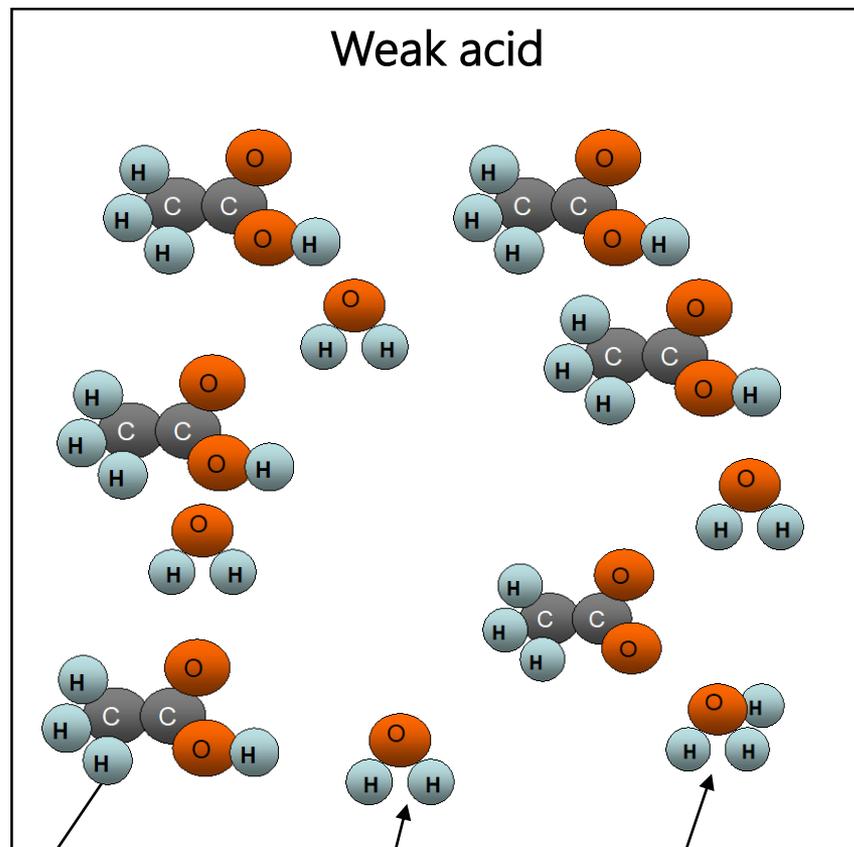
Strong and Weak Acids

In reality the strong acid molecules would be almost completely dissociated in an aqueous solution. The Cl^- would remain in solution and free 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

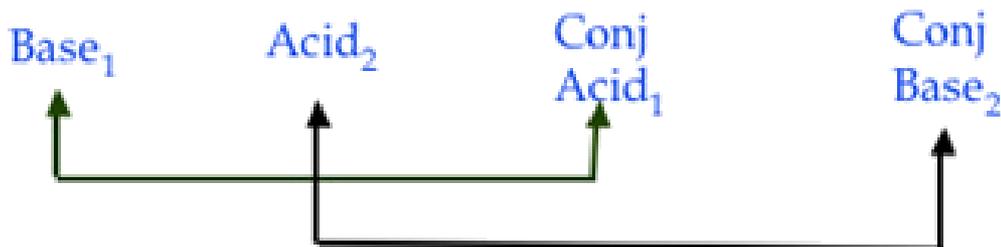
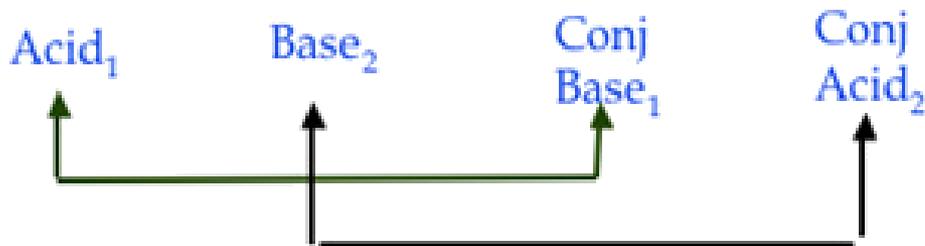
Conjugate pairs

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

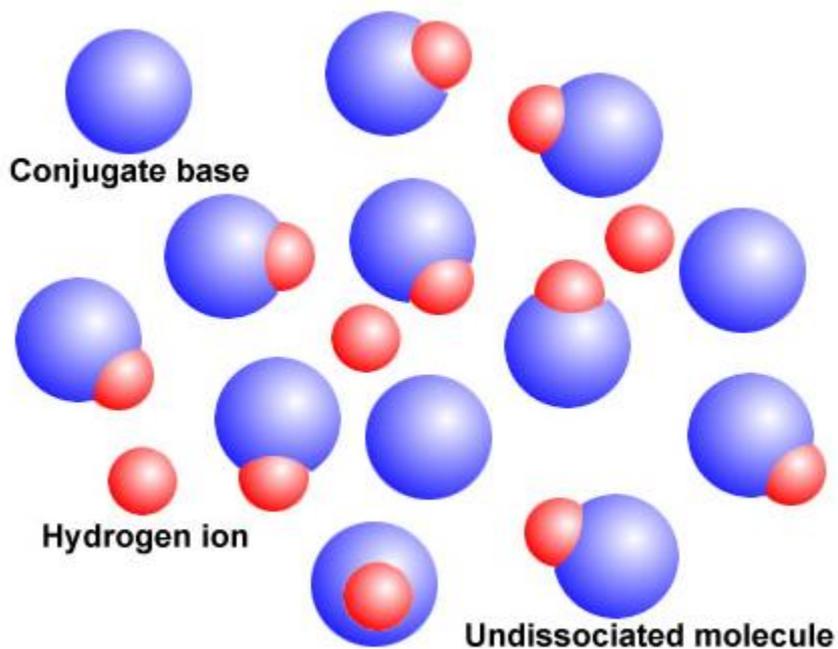
Examples of acid-base pairs are $\text{H}_2\text{SO}_4/\text{HSO}_4^-$ and $\text{NH}_4^+/\text{NH}_3$.

The acid is always the species with the additional proton.

It can also be said that NH_3 is the conjugate base of NH_4^+ .



Transfer of hydrogen ions in conjugate pairs



When a base accepts a proton, it becomes a conjugate acid because it now has a proton that it can donate. In addition, when an acid donates a proton it becomes a conjugate base, because it now can accept a proton.

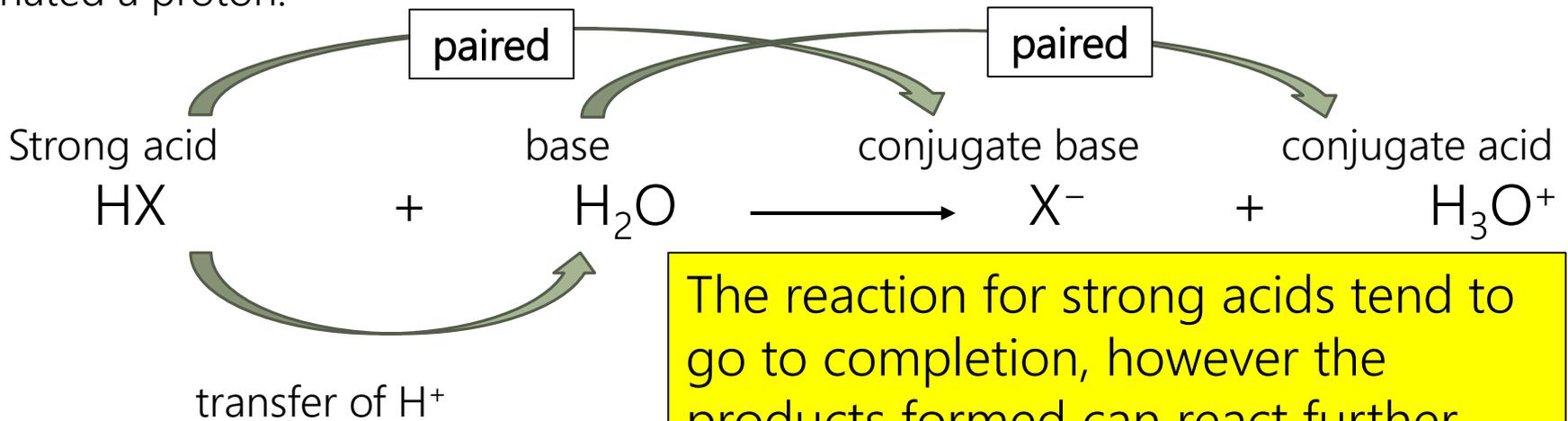
These are what we call **conjugate pairs** of acids and bases.

In other words: 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 substance is called the **conjugate acid** of that original base.

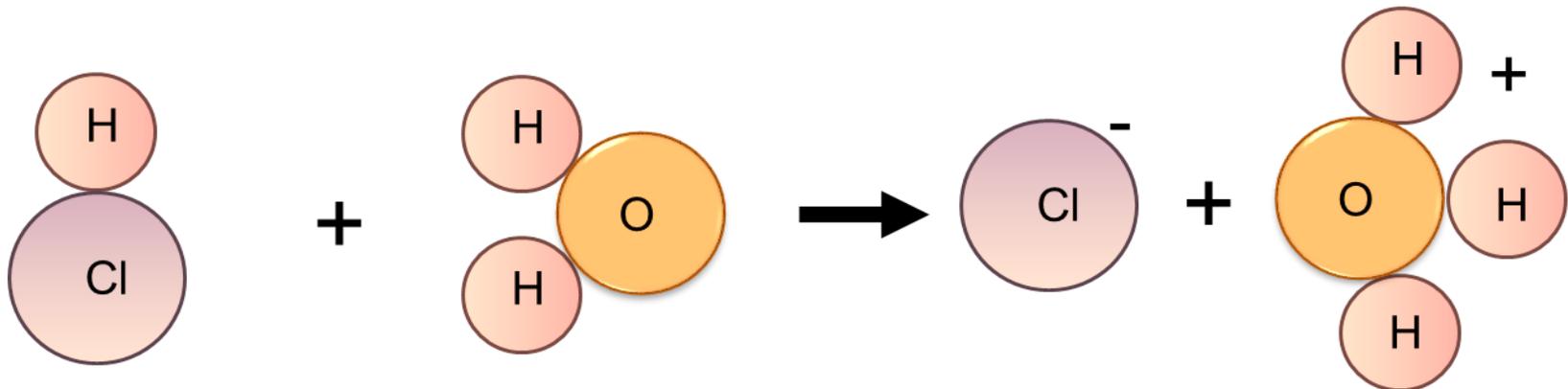
Conjugate Acid and Base pairs (Strong Acid)

HX is a symbol used for a strong acid. A conjugate acid can be seen as the substance formed from the base after accepting a proton (H^+)

The conjugate base produced, X^- , is formed from the remainder of the acid after it has donated a proton.

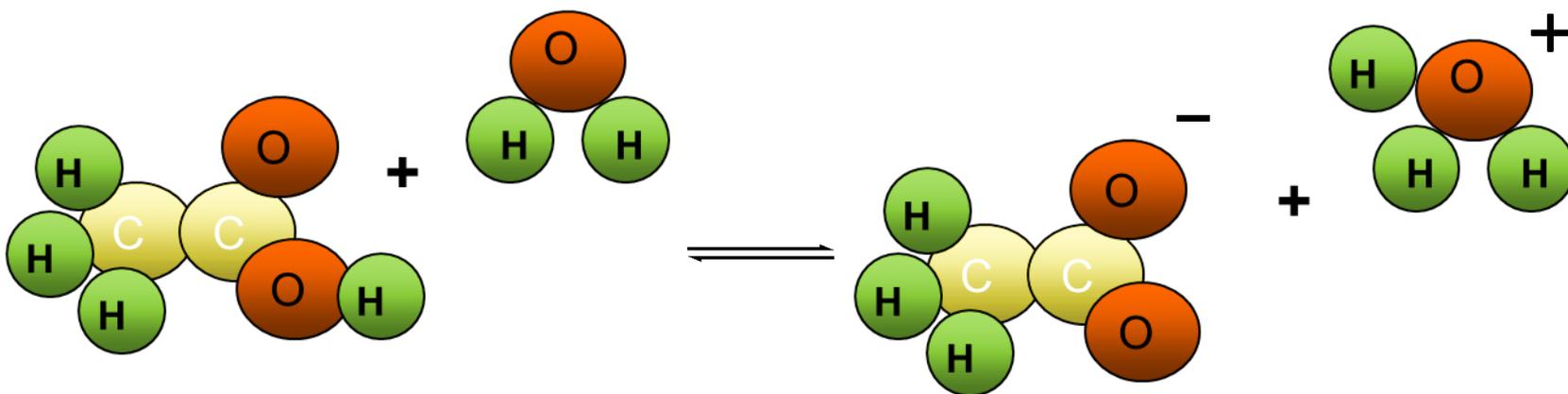
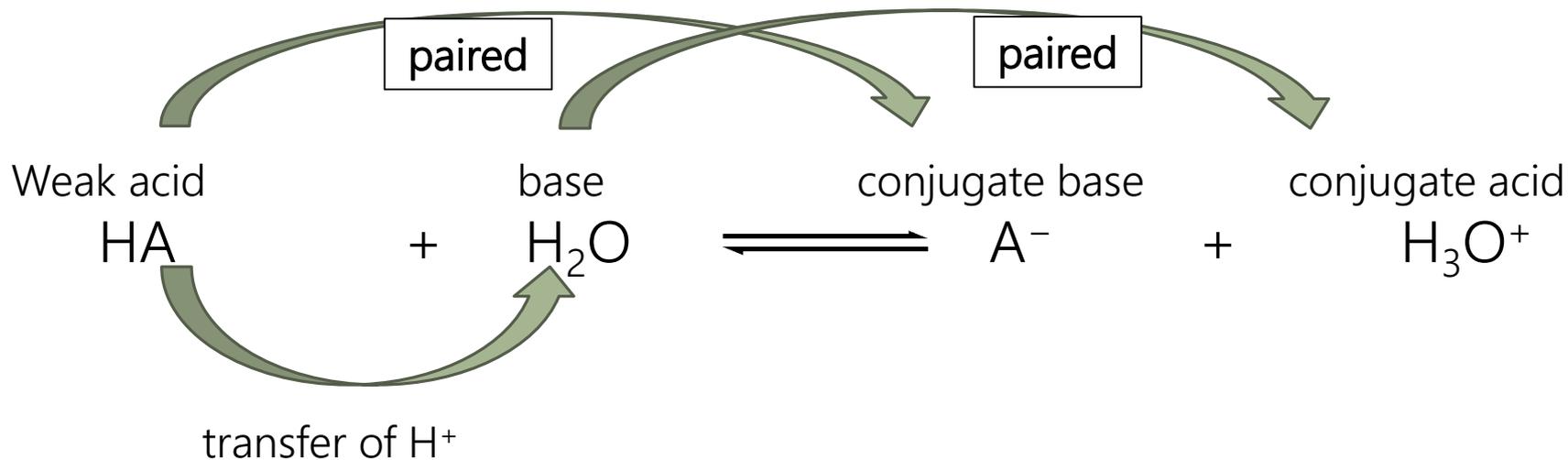


The reaction for strong acids tend to go to completion, however the products formed can react further



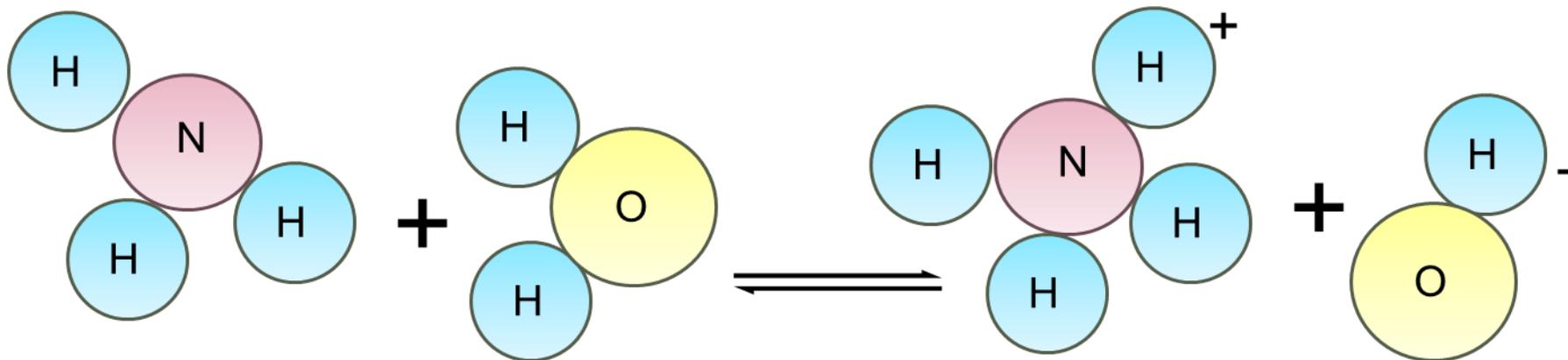
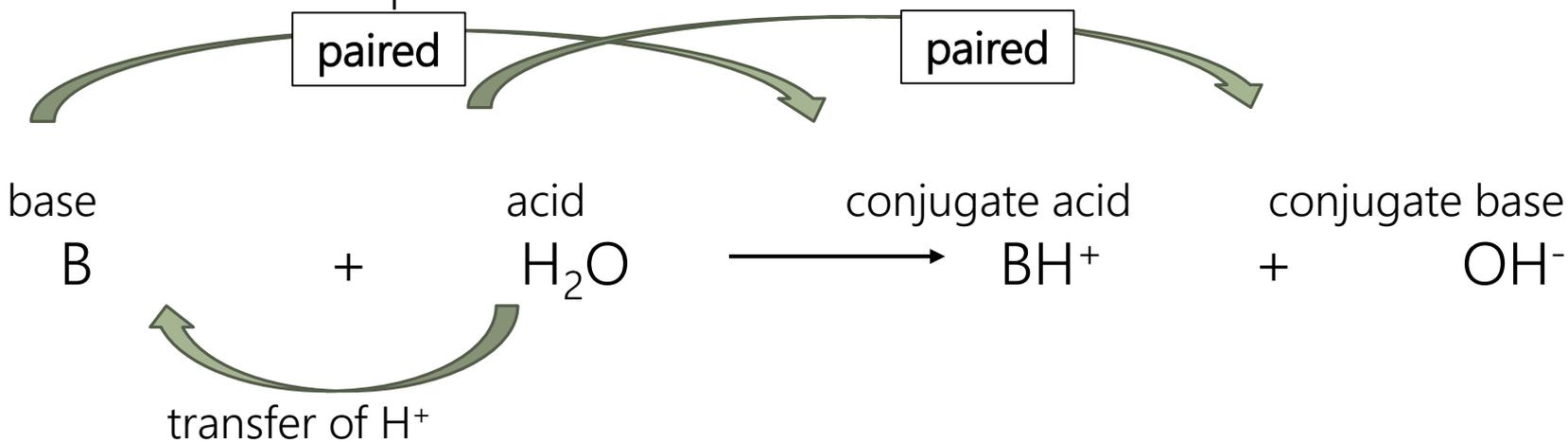
Conjugate Acid and Base pairs (weak acid)

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



Conjugate Acid and Base pairs (Base)

B is a symbol used for a base. The base now accepts the hydrogen ion from the water. The hydroxide ion, OH^- , is the paired conjugate of the water once the H^+ has been removed. Strong bases use a single direction arrow and weak bases use a double arrow to show equilibrium.



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 NH_3 is the conjugate base of NH_4^+ .

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

Conjugate Acid and Base pairs

	ACID	BASE		
← Relative acid strength increasing	negligible	OH^-	O^{2-}	strong
		HS^-	S^{2-}	
		H_2O	OH^-	
		HPO_4^{2-}	PO_4^{3-}	
		HCO_3^-	CO_3^{2-}	
		NH_4^+	NH_3	
		HCN	CN^-	
		H_2PO_4^-	HPO_4^{2-}	
	weak	HSO_3^-	SO_3^{2-}	weak
		H_2S	HS^-	
		H_2CO_3	HCO_3^-	
		$\text{C}_5\text{H}_5\text{NH}^+$	$\text{C}_5\text{H}_5\text{N}$	
		$\text{CH}_3\text{CO}_2\text{H}$	CH_3CO_2^-	
		HF	F^-	
		H_3PO_4	H_2PO_4^-	
		H_2SO_3	HSO_3^-	
		HSO_4^-	SO_4^{2-}	
		H_2O	H_2O	
		H_3O^+	NO_3^-	negligible
strong	HNO_3	HSO_4^-		
	H_2SO_4	Cl^-		
	HCl	Br^-		
	HBr			

Relative base strength increasing →

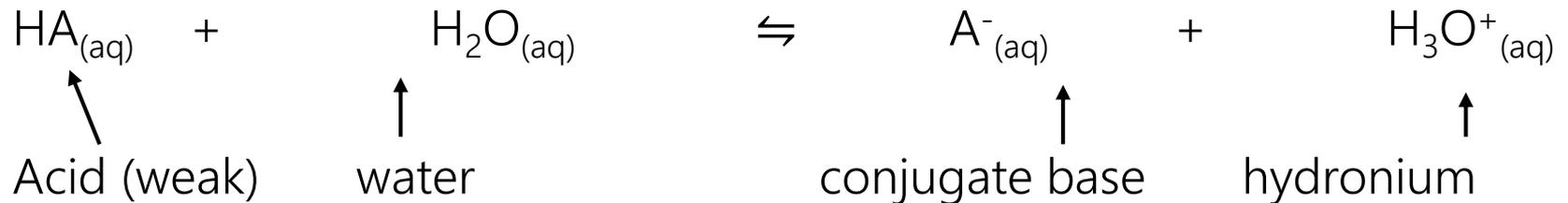
The stronger an acid, normally the weaker its conjugate base, and, conversely, the stronger a base, the weaker its conjugate acid.

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

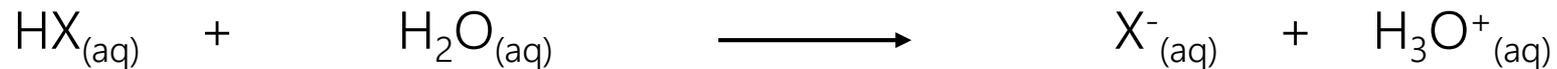
Weak and strong acids

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

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 H_3O^+

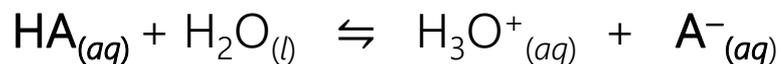
so $\text{pH} = -\log c(\text{HX})$

Summary of Dissociation equations and Equilibrium expressions

Weak Acids

HF, CH₃COOH, and NH₄⁺

Write an equation using:



Assume H₂O has no change in concentration

Write an expression using:

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

strong acids HCl, HBr, HNO₃, H₂SO₄

Weak Bases

NH₃, CH₃NH₂, and CH₃COO⁻

Write an equation using:



Write an expression using:

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

strong bases KOH, NaOH

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.



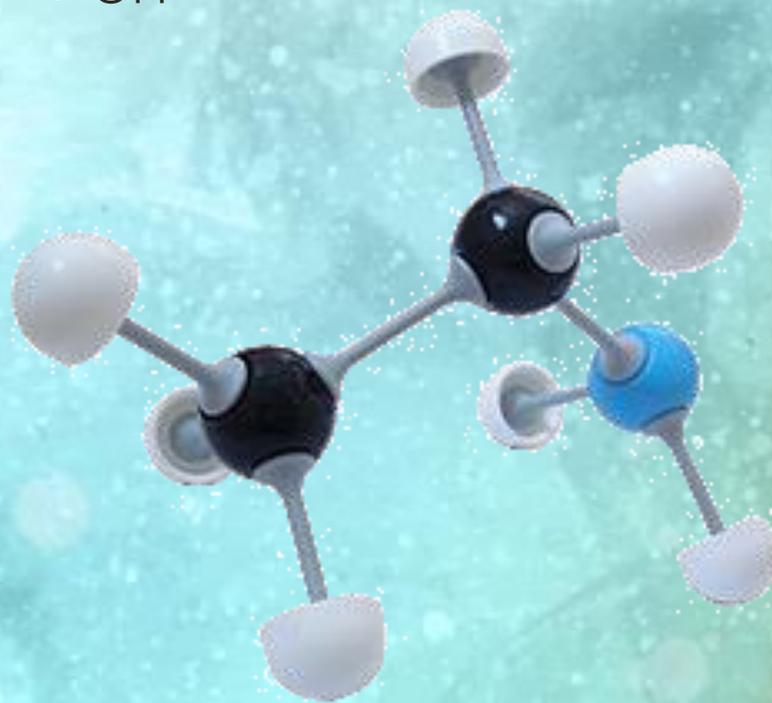
NCEA 2016 dissociation equations

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

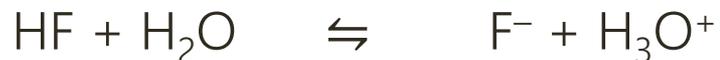
Achieved
Question

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

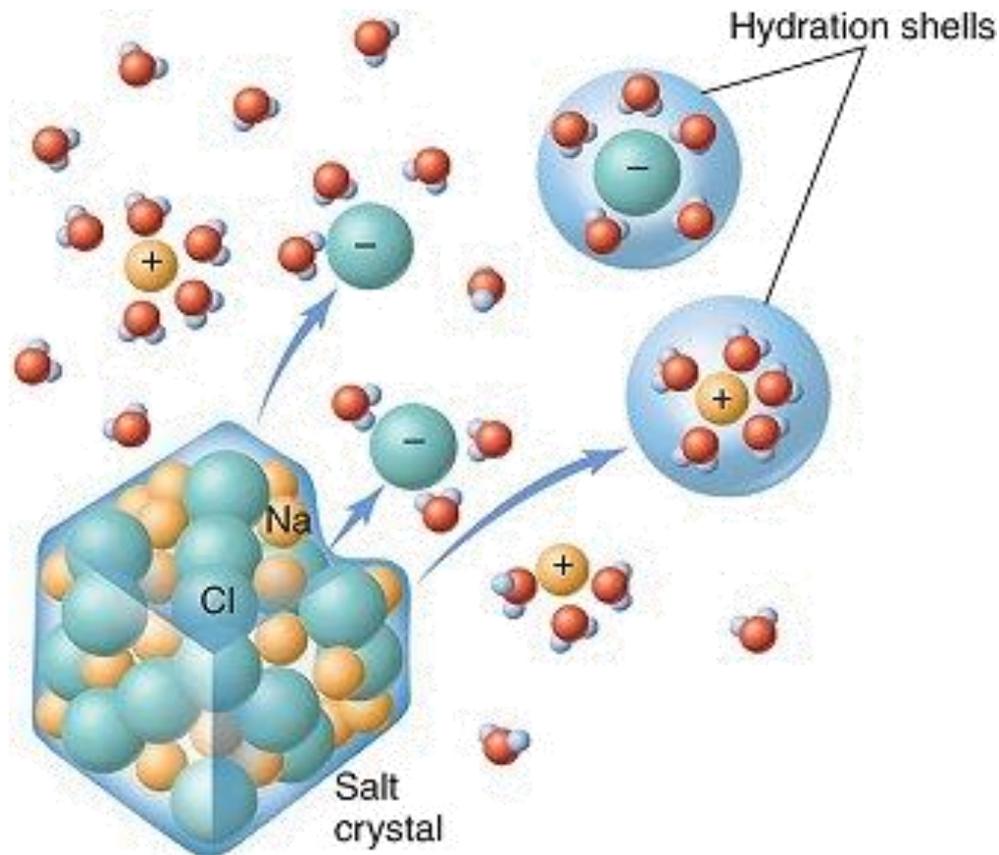
A solution is formed by mixing a **solute** (a dissolved substance) into a **solvent** (the solution that dissolves the solute).

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

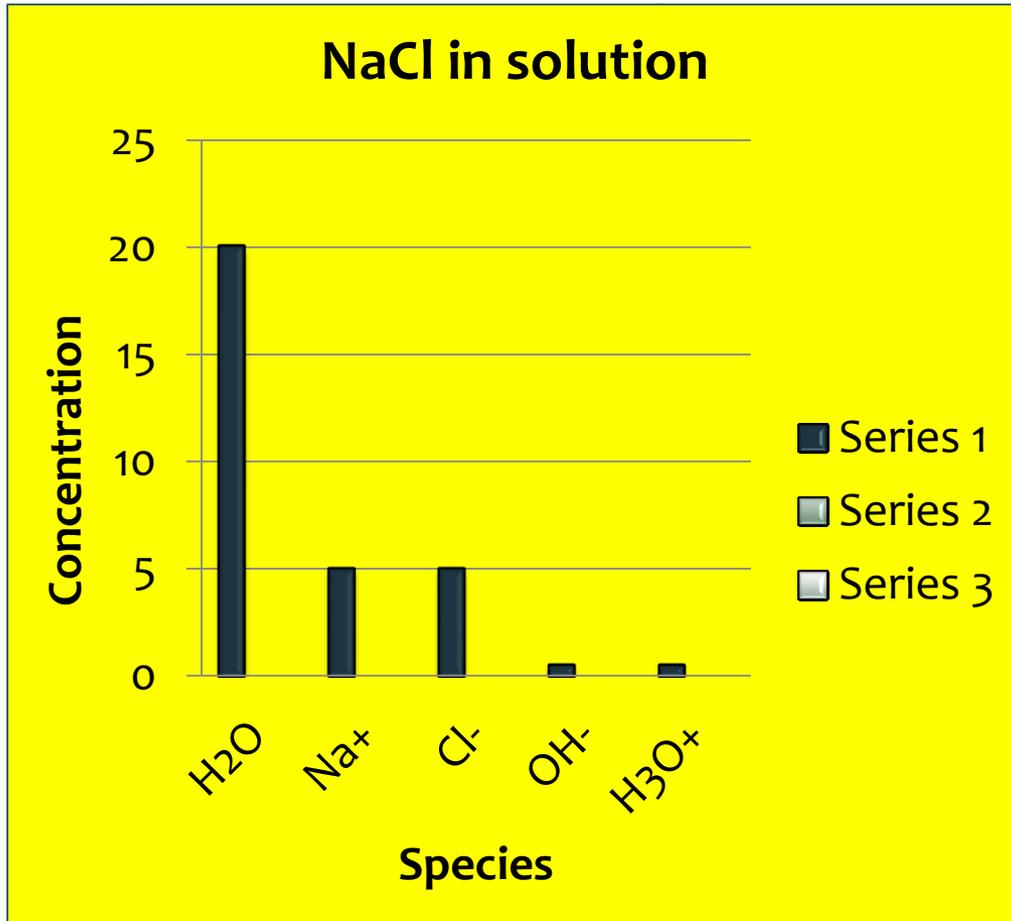
A solute dissolves by bonds being broken between solute particles (endothermic) and new bonds being formed between solute and solvent (exothermic).

A small amount of H_3O^+ and 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.



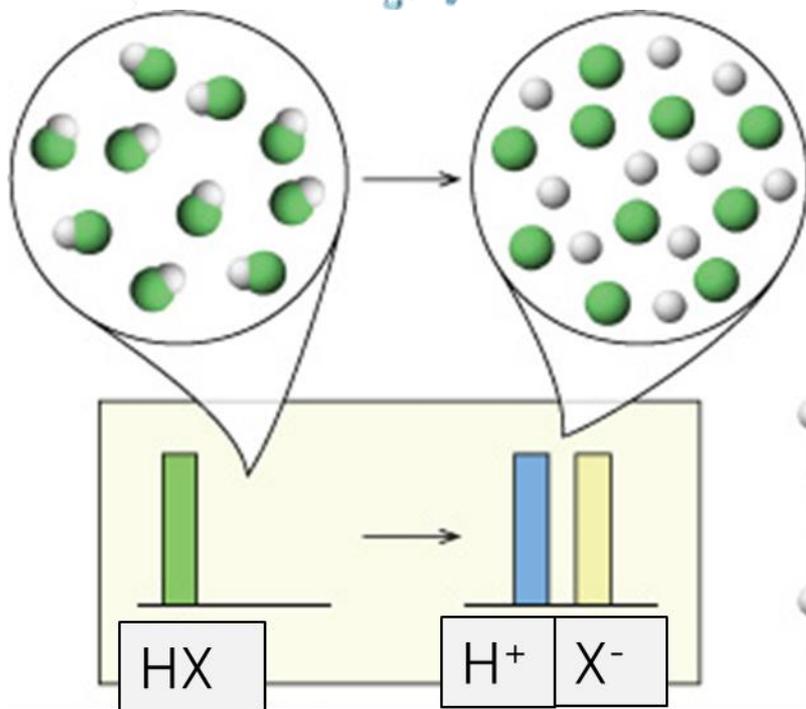
Concentration of species in solution



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

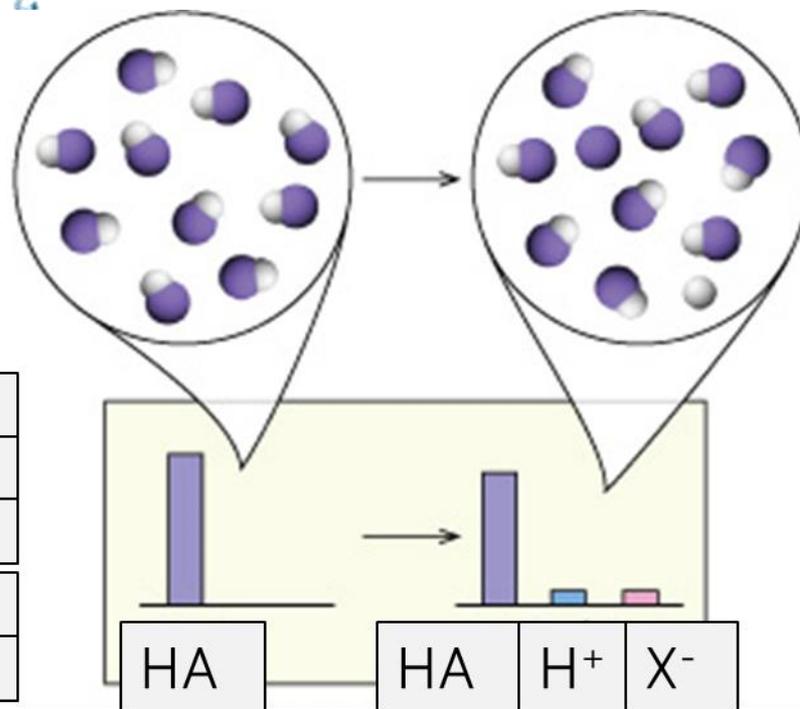
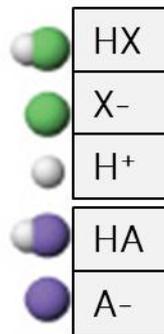
- In aqueous solutions water will almost always be present in the highest concentration.
- Small quantities of H₃O⁺ and OH⁻ will also be present, according to the $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}$
- Information on relative concentration can often be presented in a bar graph.

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.

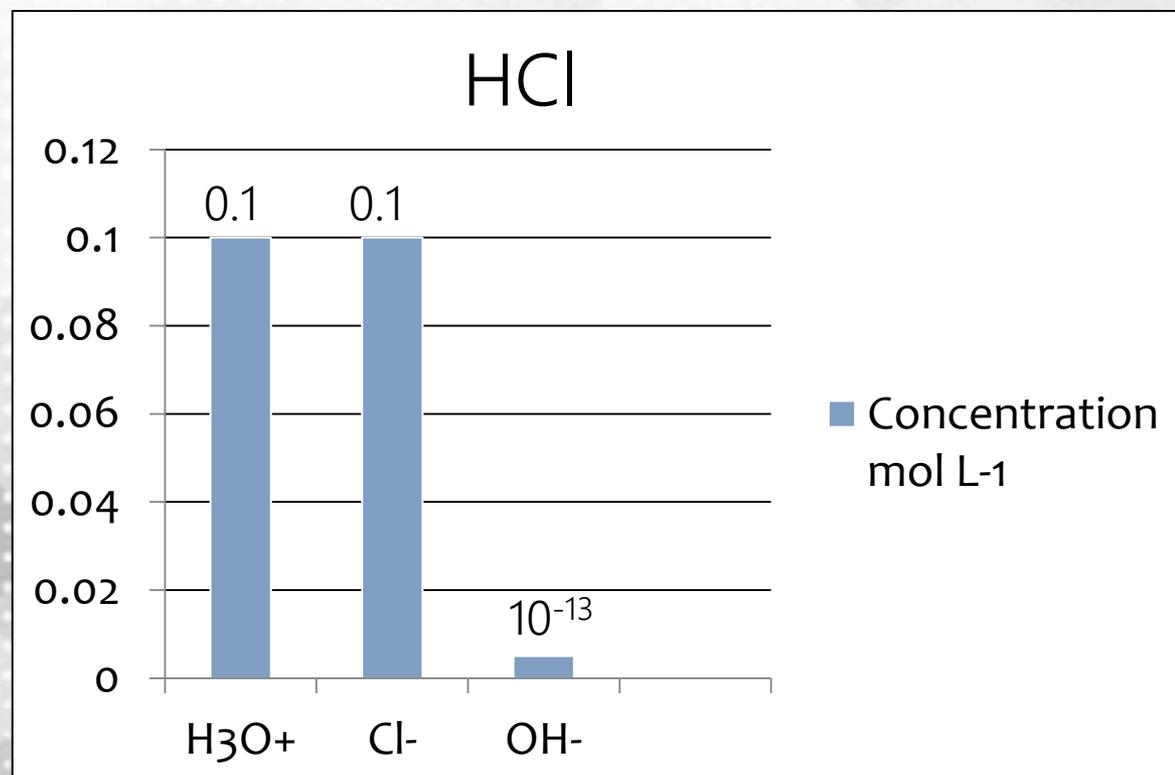
Equal quantities of conjugate base and hydronium are formed, but in small amounts

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 H_3O^+ ions



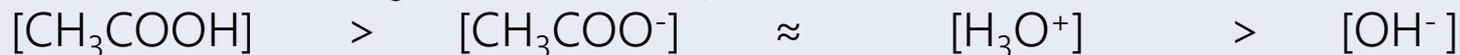
No strong acid will be left in the final mixture.

H_3O^+ and Cl^- are produced in equal concentrations – in the same concentration as the original strong acid.

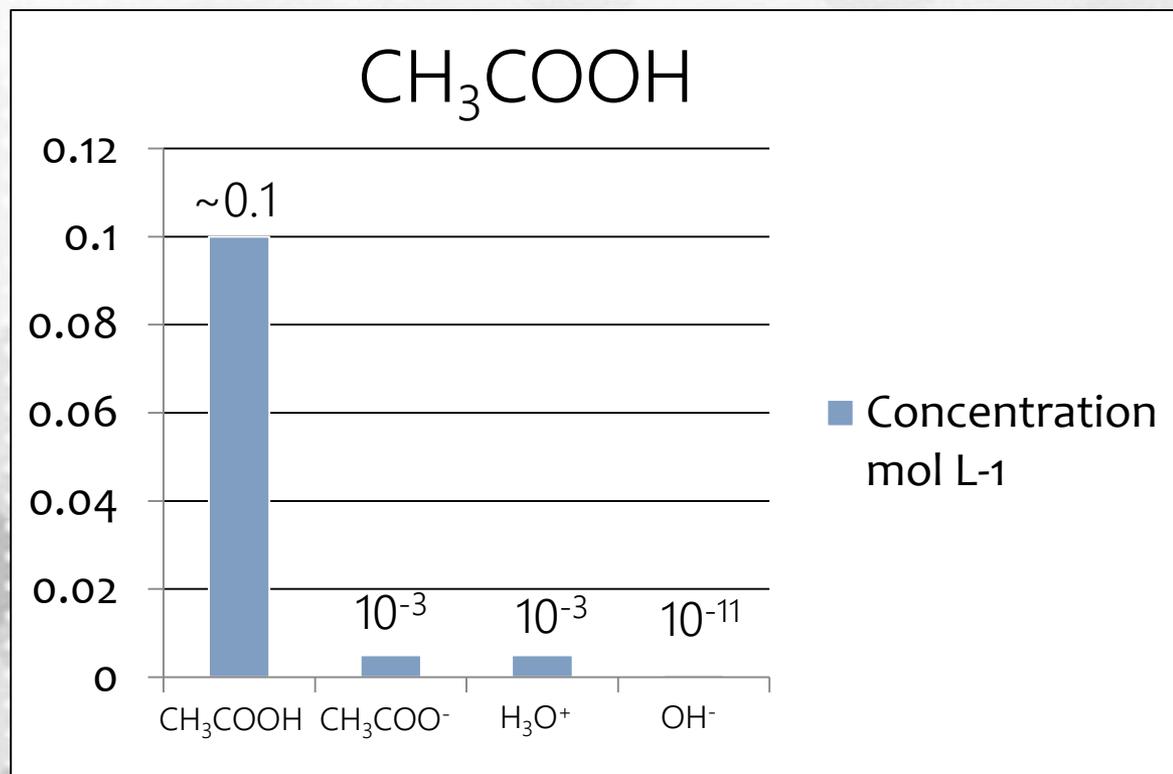
A small amount of OH^- is present as water dissociates into H_3O^+ and OH^-

Concentration of ions in solution – Weak Acid

Weak Acid i.e. CH_3COOH reacting with water



weak acids will provide **poor conductivity** and **pH 3-6** due to the low presence of H_3O^+ ions (but still higher than OH^- ions)



Most weak acid will be left in the final mixture.

H_3O^+ and CH_3COO^- are produced in equal concentrations – a small amount of the weak acid had dissociated.

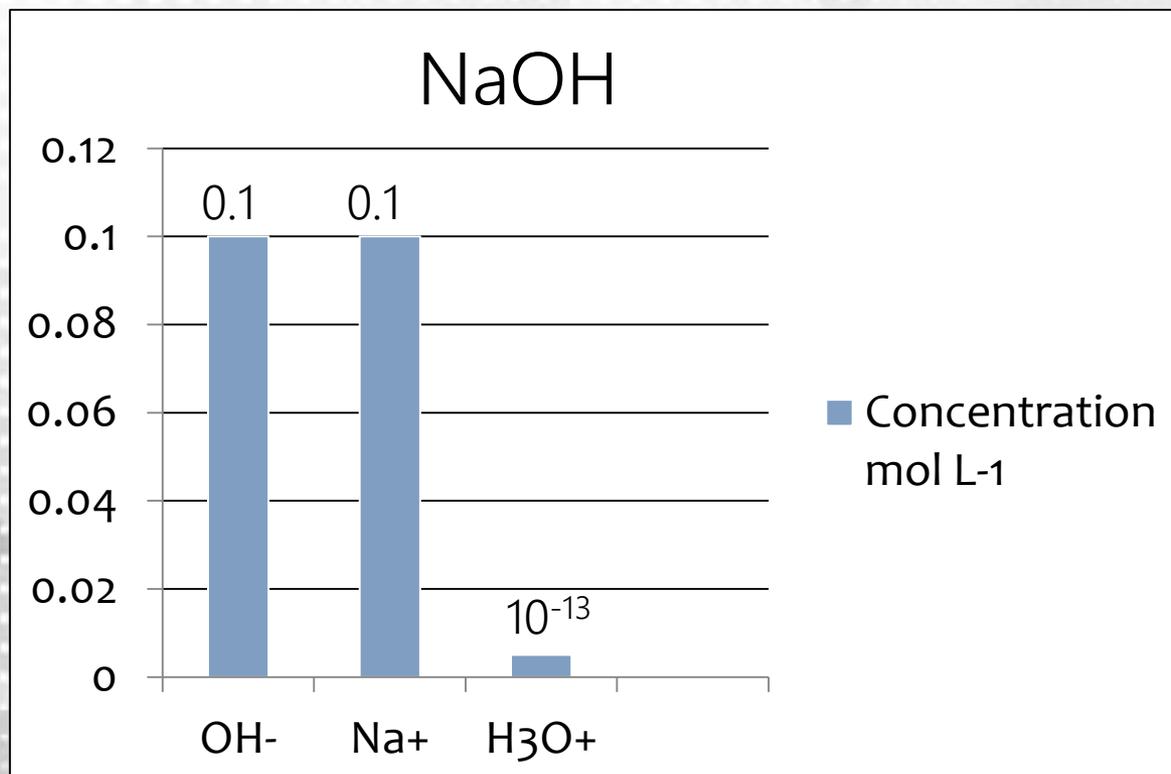
A small amount of OH^- is present as water dissociates into H_3O^+ and OH^-

Concentration of ions in solution – Strong Base

Strong Base i.e. NaOH reacting with water



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



No strong base will be left in the final mixture.

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

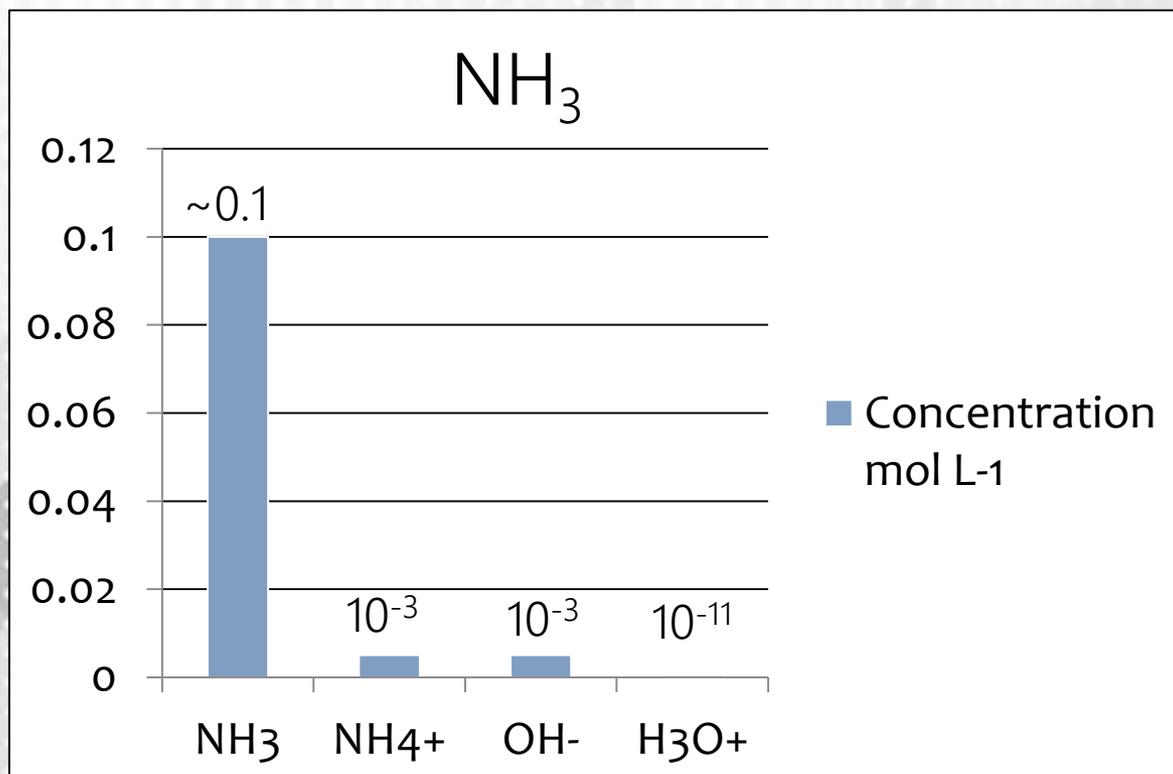
A small amount of H_3O^+ is present as water dissociates into H_3O^+ and OH^-

Concentration of ions in solution – Weak Base

Weak Base i.e. NH_3



weak bases will provide **poor conductivity** and **pH 8 – 11** due to the low presence of OH^- ions (but still higher than H_3O^+ ions)



Most weak base will be left in the final mixture.

OH^- and NH_4^+ are produced in equal concentrations – a small amount of the weak base had dissociated.

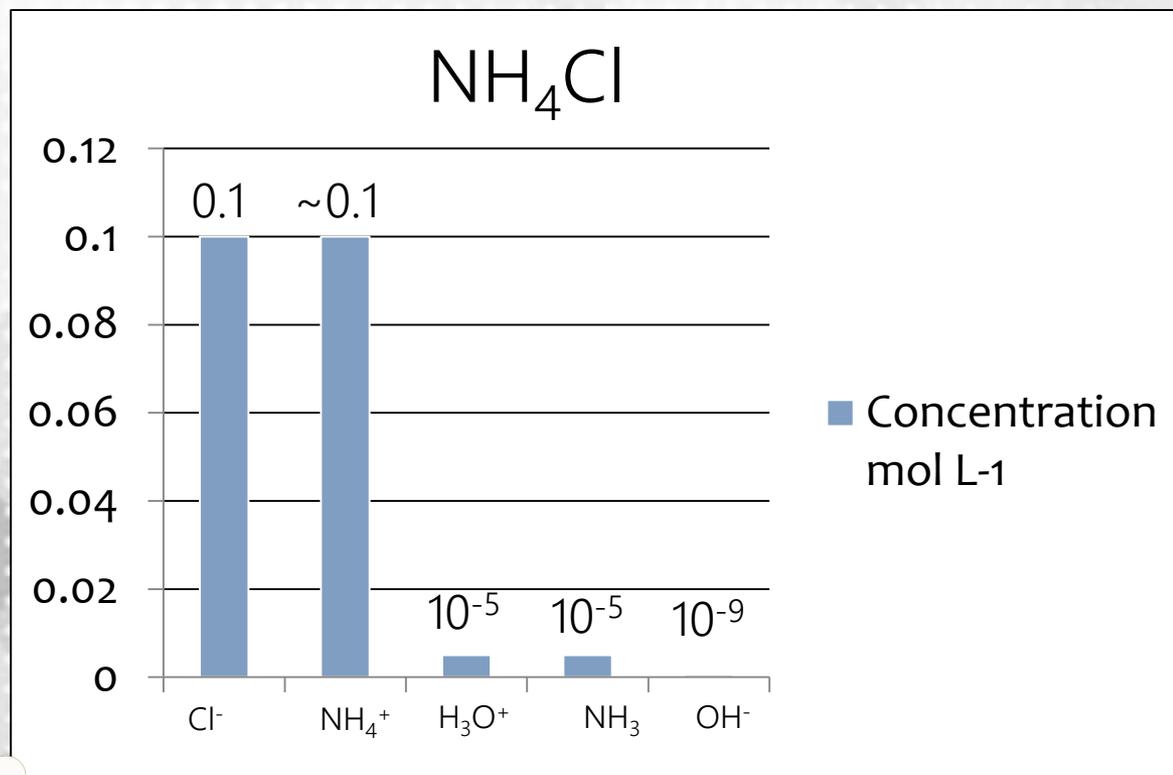
A small amount of H_3O^+ is present as water dissociates into H_3O^+ and OH^-

Concentration of ions in solution – acid salt

Acid Salt i.e. NH_4Cl



Acid salts will provide **good conductivity** and **pH < 7** due to the high presence of ions from dissolving and to a lesser extent H_3O^+ ions



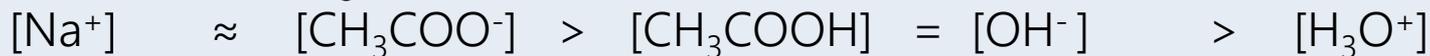
The spectator ion will be left in the highest concentration followed by the weak acid.

H_3O^+ and NH_3 are produced in equal concentrations – a small amount of the weak acid had dissociated.

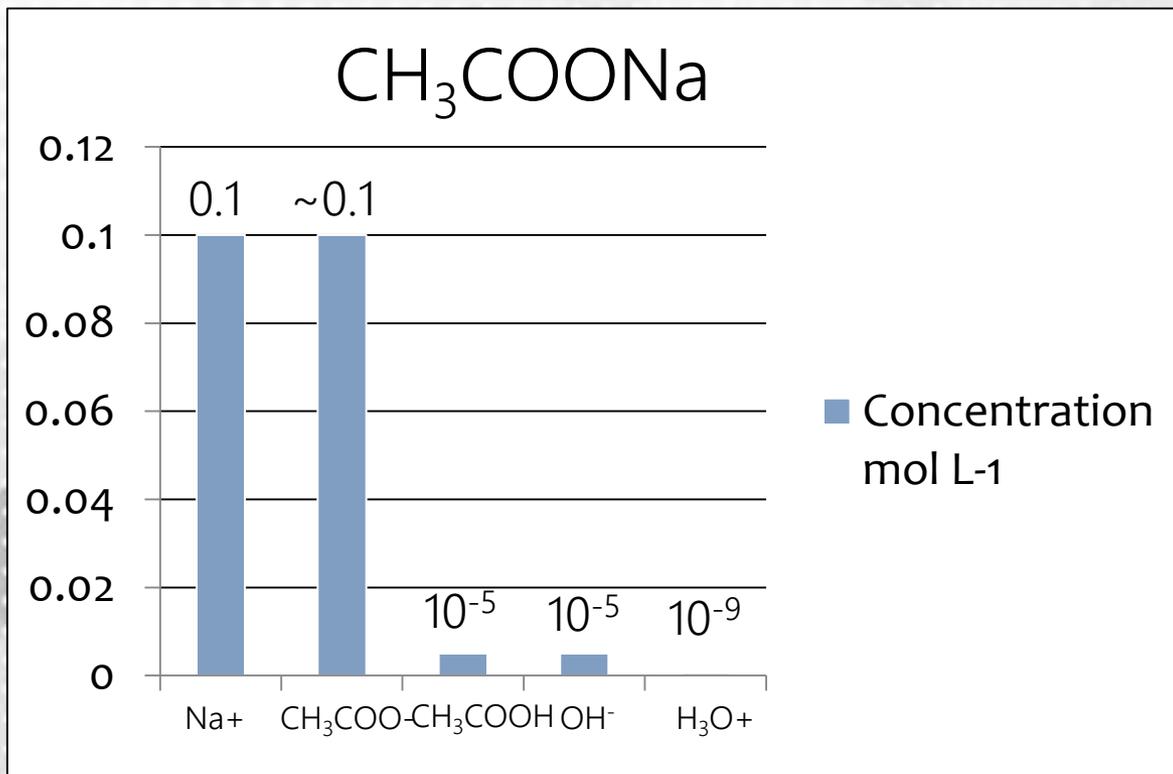
A small amount of OH^- is present as water dissociates into H_3O^+ and OH^-

Concentration of ions in solution – base salt

Base Salt i.e. CH_3COONa



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



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

OH^- and CH_3COOH are produced in equal concentrations – a small amount of the weak base had dissociated.

A small amount of H_3O^+ is present as water dissociates into H_3O^+ and OH^-

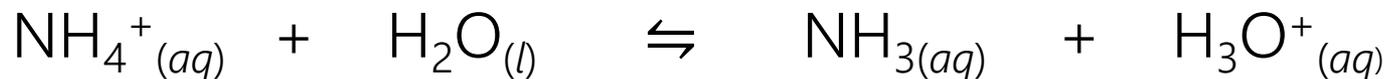
pH of salt solutions

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

The ionic salt will first dissolve into its two ions. This equation needs to be shown.

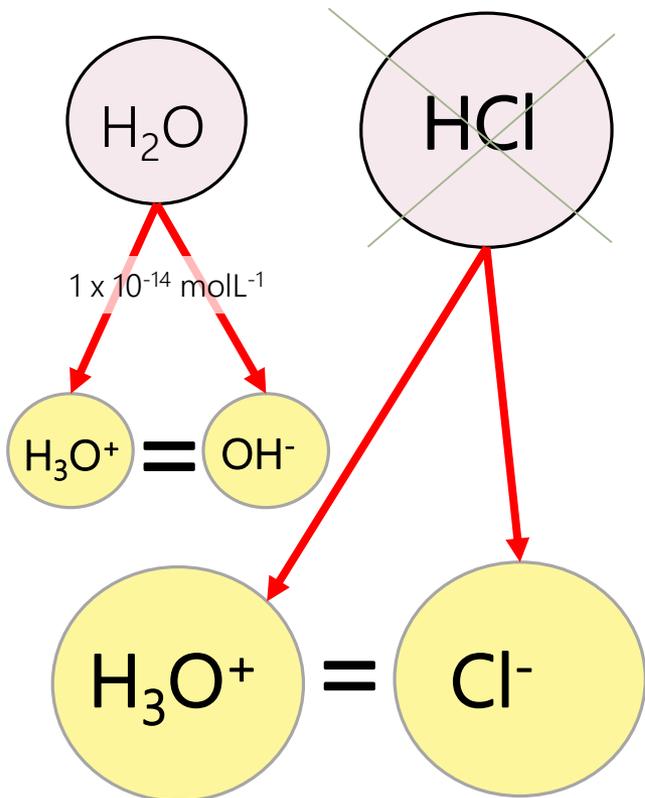
There will then be a further equation as the ion acting as a weak acid or base undergoes an acid/base reaction with water.

The non-reacting ion is left off as the spectator.



Summary of Species/conductivity in Solution - Acid

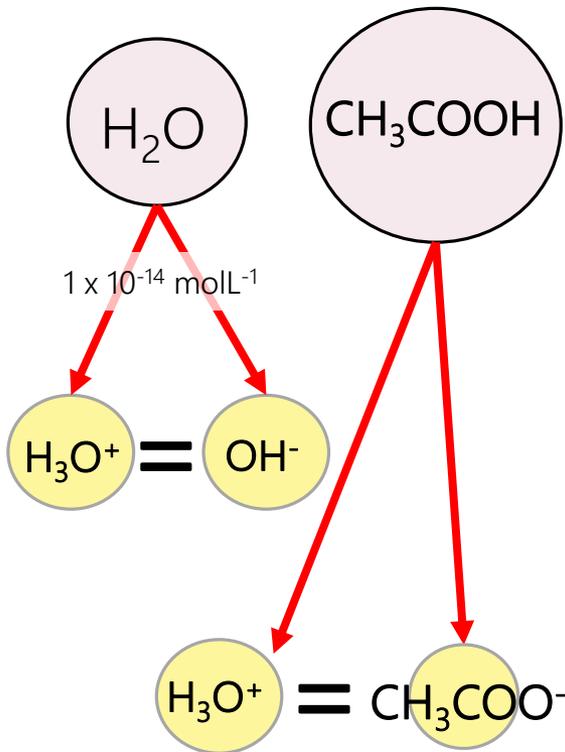
Strong Acids



Complete dissociation
 No strong acid remains

High conductivity

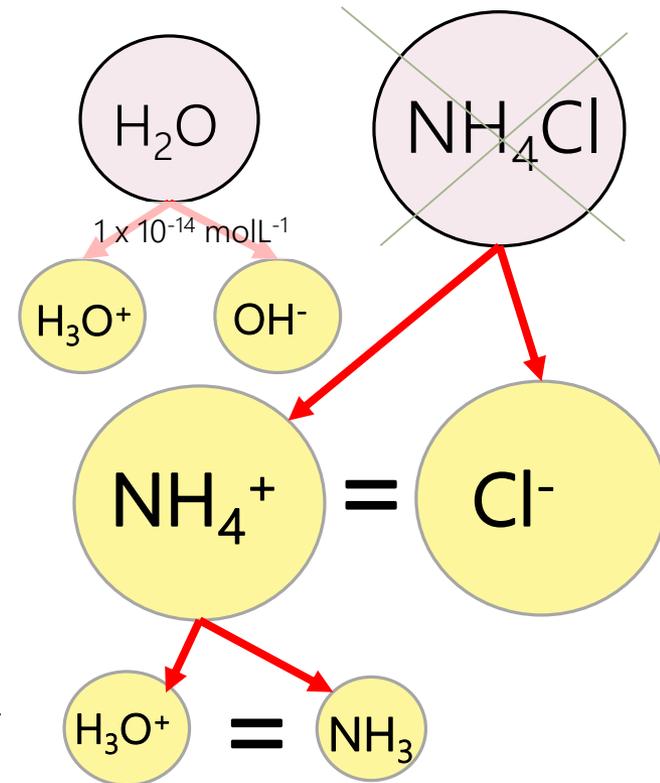
Weak Acids



Partial dissociation
 Most weak acid remains

Low conductivity

Acid salts



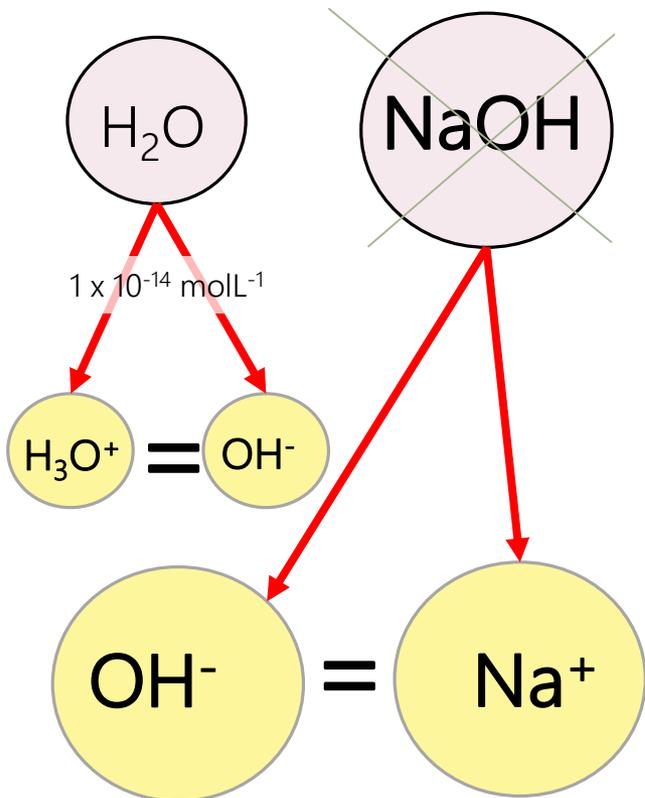
Weak acid reacts further
 No salt remains

High conductivity

Water concentration is assumed to remain constant so is left out

Summary of Species / conductivity in Solution - Base

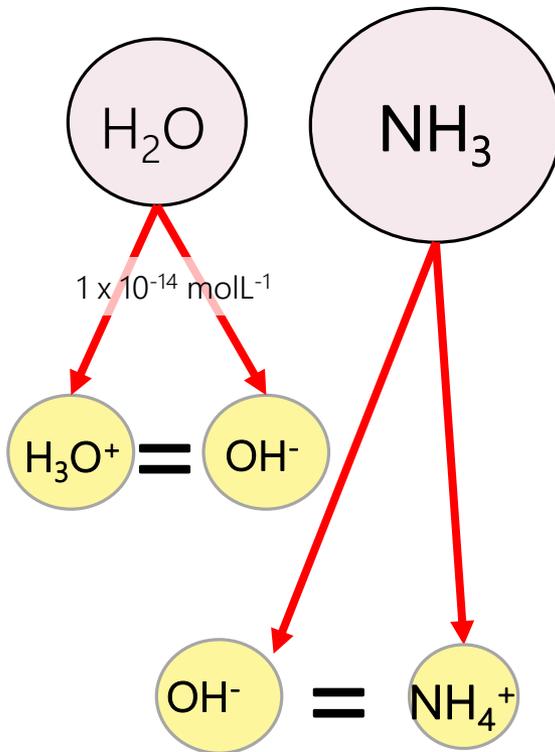
Strong Bases



Complete dissociation
 No strong base remains

High conductivity

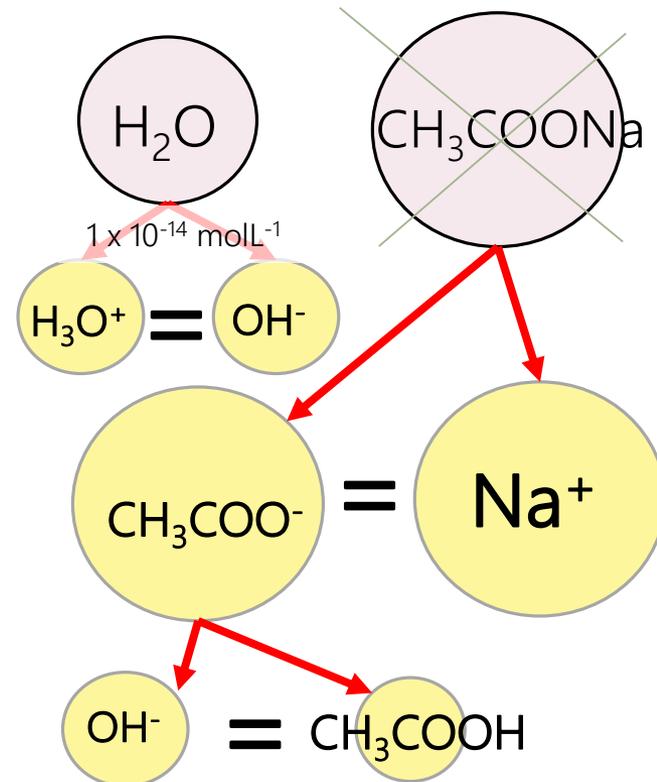
Weak Bases



Partial dissociation
 Most weak base remains

Low conductivity

Base salts



Weak base reacts further
 No salt remains

High conductivity

water concentration is assumed to remain constant so is left out

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⁻¹ H₃O⁺ and hence a low pH.
$$\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$$
- CH₃NH₃Cl dissociates completely in water to form CH₃NH₃⁺ and Cl⁻. CH₃NH₃⁺, a weak acid, partially reacts with water to form less than 1 mol L⁻¹ H₃O⁺ and hence a higher pH than HCl.
$$\text{CH}_3\text{NH}_3\text{Cl} \rightarrow \text{CH}_3\text{NH}_3^+ + \text{Cl}^-$$
$$\text{CH}_3\text{NH}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_2 + \text{H}_3\text{O}^+$$
- CH₃NH₂, a weak base, partially reacts with water to form OH⁻ ions. So there are more OH⁻ ions than H₃O⁺ ions and the pH is thus high.
$$\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-$$

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.

H_3O^+ and OCl^- are produced in equal amounts / there is a small contribution to H_3O^+ 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).

NCEA 2016 Species in Solution

Excellence
Question

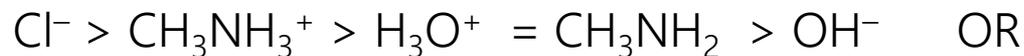
Question: 2c: Ethyl ammonium chloride, $\text{CH}_3\text{CH}_2\text{NH}_3\text{Cl}$, is a weak acid that will also react with water.

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.

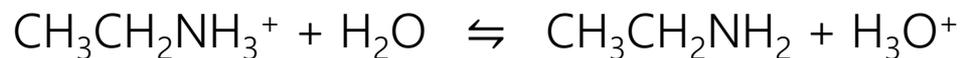
Include equations, where necessary.



$\text{CH}_3\text{CH}_2\text{NH}_3\text{Cl}$ 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 H_3O^+ are formed.

(However, H_3O^+ is slightly more concentrated than $\text{CH}_3\text{CH}_2\text{NH}_2$, as there is a small contribution from water).

OH^- is present in the lowest concentration as this comes from the dissociation of water only.

Conductivity of solutions

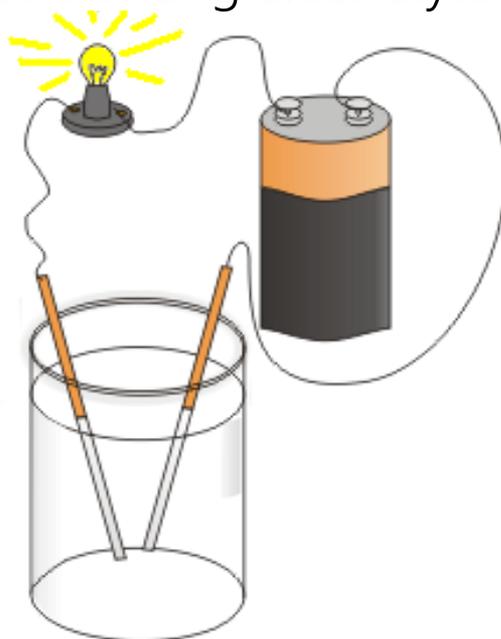
Conductivity is related to the availability of free moving charged particles.

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

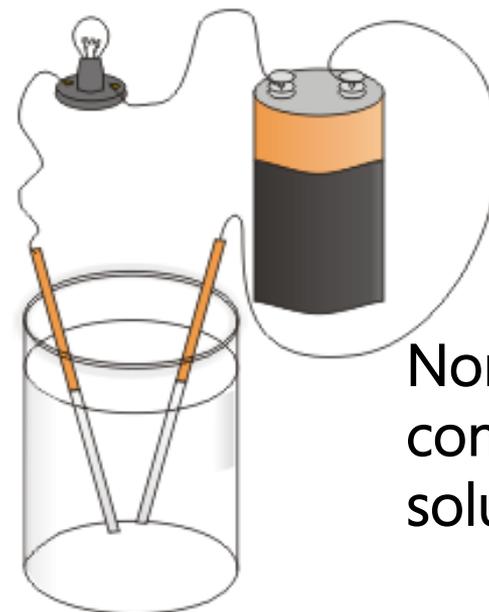
High conductivity

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



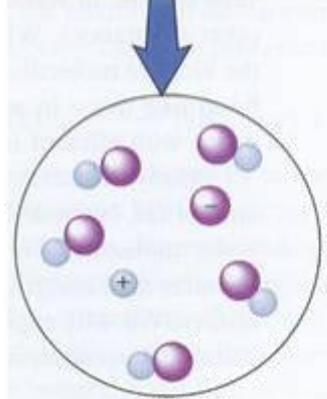
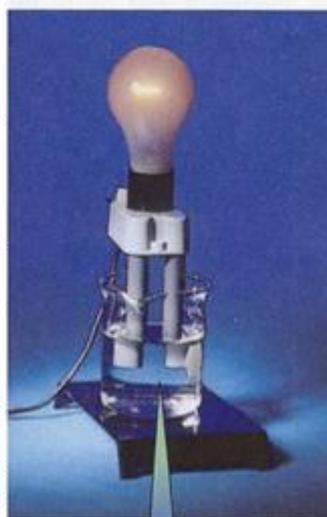
Conductivity of solutions

Low Conductivity

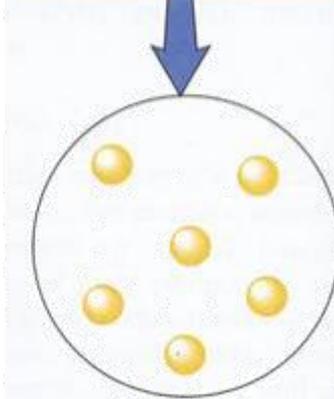
A weak electrolyte is formed from a weak acid or base that only partially dissociates. Only a small concentration of ions are created to carry charge. (such as acetic acid)

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



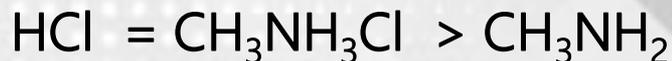
glucose

NCEA 2013 Conductivity

Excellence
Question

Question: 1b: The conductivity of the 1 mol L⁻¹ solutions formed in (a) can be measured. CH₃NH₃Cl CH₃NH₂ HCl

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



CH₃NH₃Cl and HCl will dissociate completely in water to produce 2 mol L⁻¹ ions.

CH₃NH₂ will only partially react with water to produce less than 1 mol L⁻¹ of ions.

NCEA 2015 Conductivity

Excellence
Question

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	CH₃NH₂	CH₃COONa
pH	13.2	11.9	8.98
Electrical conductivity	good	poor	good

The pH of a solution is calculated from its $[\text{H}_3\text{O}^+]$.

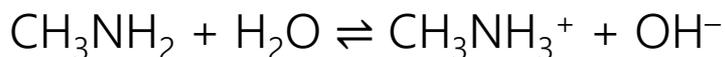
- **NaOH** is an ionic solid that is a strong base and dissociates completely to produce a high OH^- concentration (low $[\text{H}_3\text{O}^+]$). Since $[\text{OH}^-]$ is high / $[\text{H}_3\text{O}^+]$ is low, the pH is high.



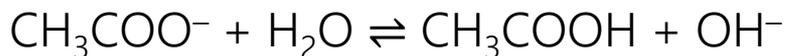
Question: 1b: The table shows the pH and electrical conductivity of three solutions. The concentrations of the solutions are the same. Compare and contrast the pH and electrical conductivity of these three solutions. Include appropriate equations in your answer.

Solution	NaOH	CH ₃ NH ₂	CH ₃ COONa
pH	13.2	11.9	8.98
Electrical conductivity	good	poor	good

- ❑ CH₃NH₂ is a weak base that partially reacts / dissociates / ionises with H₂O producing a lower concentration of OH⁻, Therefore it has a lower pH than NaOH:



- ❑ The CH₃COONa is an ionic solid that dissociates completely in H₂O. The CH₃COO⁻ ion is a weak base that partially reacts / dissociates / ionises with H₂O producing a lower concentration of OH⁻.



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	CH₃NH₂	CH₃COONa
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⁺ and OH⁻ ions in solution.

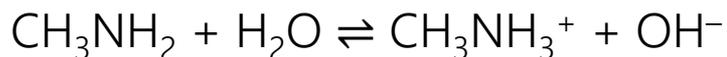
NaOH → Na⁺ + OH⁻ Therefore it is a good conductor.

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 ₃ NH ₂	CH ₃ COONa
pH	13.2	11.9	8.98
Electrical conductivity	good	poor	good

Electrical conductivity:

- ❑ Since CH₃NH₂ 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.



- ❑ CH₃COONa is also an ionic solid. It dissolves completely to produce a high concentration of Na⁺ and CH₃COO⁻ ions:



Therefore it is a good conductor.

Question: 1a (ii) : Compare and contrast the electrical conductivity of 0.150 mol L^{-1} 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 $[\text{Br}^-]$ and $[\text{H}_3\text{O}^+]$. In contrast, HF is a weak acid and therefore only partially dissociates to produce a lower [ions], i.e. F^- and H_3O^+ .

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

NCEA 2018 Conductivity

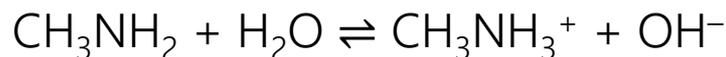
Question: 2. A titration was carried out by adding 0.210 mol L^{-1} hydrochloric acid, HCl, to 25.0 mL of 0.168 mol L^{-1} methanamine, CH_3NH_2 .

The equation for the reaction is: $\text{HCl} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{NH}_3^+ + \text{Cl}^-$

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

(c) Why is the solution at the equivalence point a better electrical conductor than the initial solution of methanamine? Your answer should include relevant equation(s) and elaborate on the relative concentrations of the different species in each solution. No calculations are necessary.

Electrical conductivity in solution requires ions. The initial solution is the weak base, methanamine. It only partially dissociates to produce a **lower [ions]**, i.e. CH_3NH_3^+ and OH^- ions. This means there is mainly CH_3NH_2 present, which has no charge. The solution is therefore a poor conductor of electricity compared to the solution at the equivalence point.



The solution at the equivalence point is made up of the products from the titration / CH_3NH_3^+ and Cl^- . As there are more ions in solution / higher [ions] the solution at the equivalence point is a better conductor.

K_w – the ionic product for water

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



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

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

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

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

Temperature increase causes an increase in K_w as the reaction is endothermic this favours the forward reaction (Le Chateliers Principle)

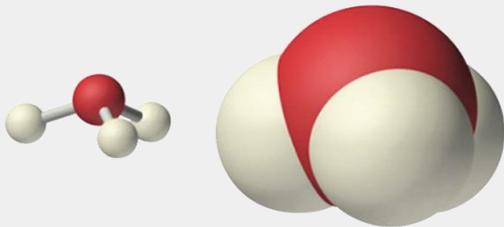
Using K_w to Calculate $[\text{OH}^-]$ or $[\text{H}_3\text{O}^+]$

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

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

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

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



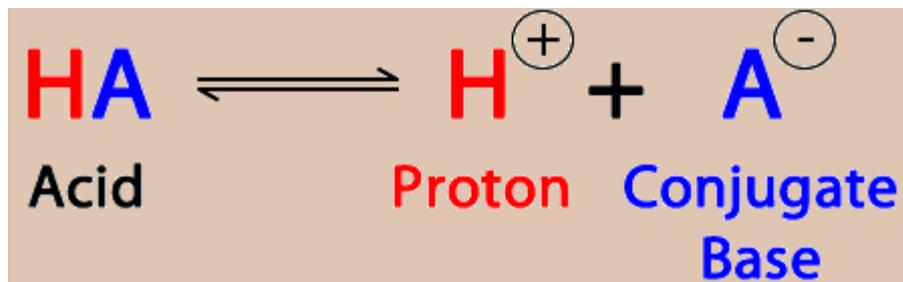
Hydronium ion,
 H_3O^+

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^- and H^+ are said to be **in equilibrium** when their concentrations do not change with the passing of time.

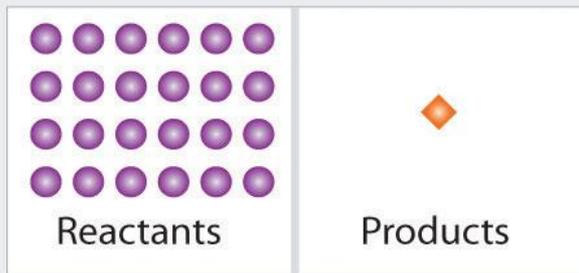
Acidity constant

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

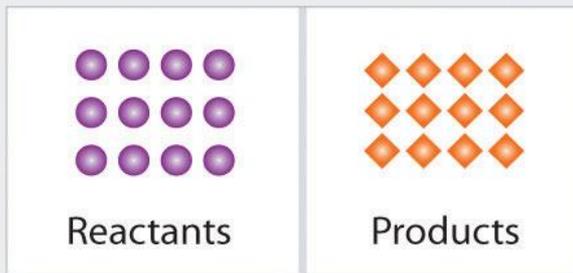
Magnitude of K increasing →

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



Mostly reactants

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



Significant amounts
of reactants and products

Large
($K > 10^3$)

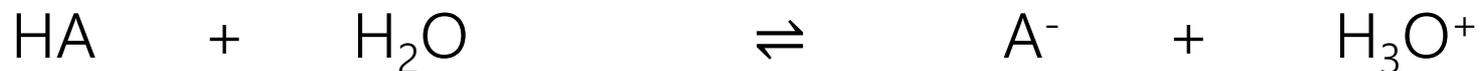


Mostly products

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_2O 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_3O^+ and A^- are the same, as one mole of H_3O^+ forms every time one mole of A^- is created

In a weak acid we can assume that the $[\text{HA}]$ concentration at equilibrium is no different from the starting concentration $c(\text{HA})$ 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 $c(HA)$

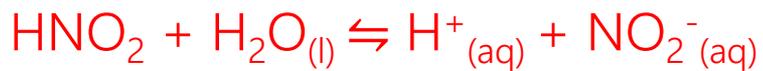
$$[H_3O^+] = \sqrt{K_a \times c(HA)}$$

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 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 $(0.01 - x) = 0.01$

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

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

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

$$\text{pH} = 2.7$$

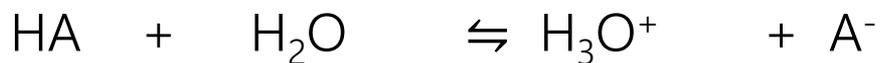
$$pK_a = -\log K_a$$

→ negative for strong acids (HX)

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

→ larger pKa more reactants

Weaker acid = stronger conjugate base



reactants

products

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

pH calculations – Weak acid

1. Convert pK_a to K_a
(if required)

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

2. Calculate $[H_3O^+]$

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

3. Calculate pH
(start here if strong acid)

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

pH calculations – Weak acid

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

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

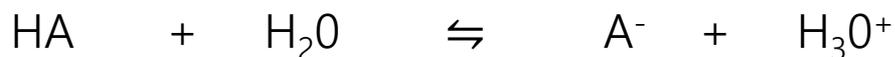


$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

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

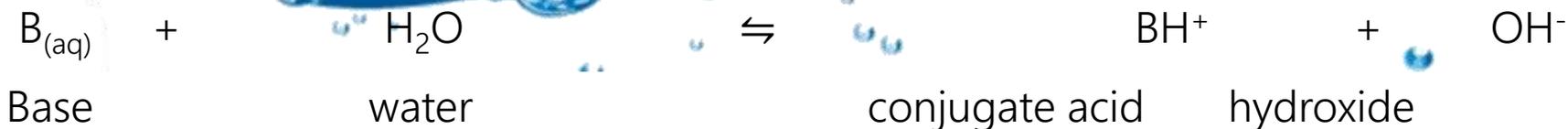


Use this equation to compare number of mols.

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.



Bases



Strong base – completely dissociates (accepts all H⁺ ions)

$$pH = -\log[H_3O^+] \quad [H_3O^+] = 1 \times 10^{-14} / [OH^-]$$

Strong bases will have a conjugate weak acid

Weak base – partly dissociates (accepts few H⁺ ions)

[B] assumed to be same as c(B) – initial concentration

K_b – base dissociation constant

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

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

K_b is small if K_a is large – weak base and strong acid

K_b is large if K_a is small – strong base and weak acid



pH calculations – Weak base

1. Convert pK_a to K_a
(if required)

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

Note the K_a is for the conjugate acid

2. Rearrange equation

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

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

$$K_b = K_w / K_a$$

3. Calculate $[H_3O^+]$

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

4. Calculate pH

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

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 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⁻¹ CH₃NH₃Cl 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 mol L^{-1} solution of ethanamine.

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

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

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

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

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

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

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

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

NCEA 2017 pH calculations

Excellence
Question

Question: 2a: Ammonia, 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.

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

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

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

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

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

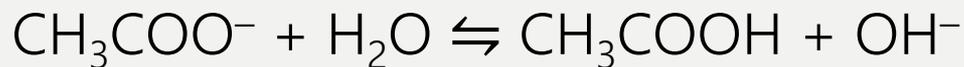
$$[\text{H}_3\text{O}^+] = \sqrt{K_a \times K_w \div [\text{B}]}$$

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

NCEA 2018 pH calculations

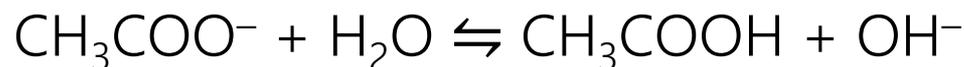
Merit
Question

Question: 1a: (a) When sodium ethanoate, CH_3COONa , is dissolved in water, the resulting solution has a pH greater than 7 due to the production of hydroxide ions, OH^- , as shown in the equation below.



$$p_{K_a}(\text{CH}_3\text{COOH}) = 4.76 \quad K_a(\text{CH}_3\text{COOH}) = 1.74 \times 10^{-5}$$

Calculate the pH of a 0.420 mol L^{-1} CH_3COONa solution.



$$\begin{aligned} [\text{H}_3\text{O}^+] &= \sqrt{\frac{K_a \times K_w}{[\text{CH}_3\text{COO}^-]}} \\ &= \sqrt{\left(\frac{1.74 \times 10^{-5} \times 1 \times 10^{-14}}{0.420} \right)} \\ &= 6.44 \times 10^{-10} \end{aligned}$$

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

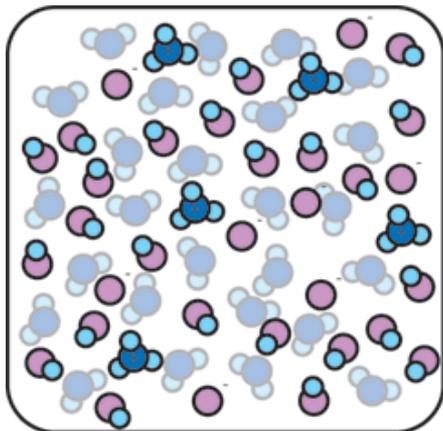
$$[\text{H}_3\text{O}^+] = \sqrt{K_a \times K_w \div [B]}$$

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

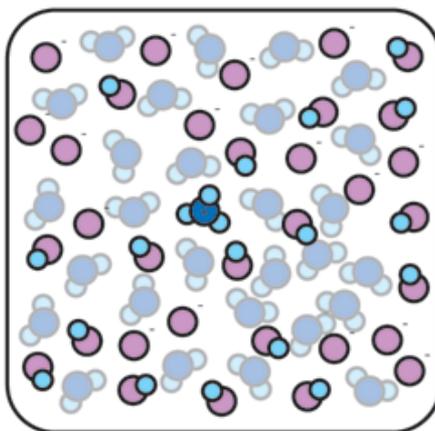
Buffer solutions

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.

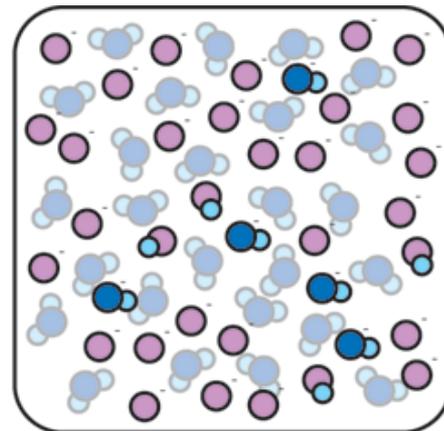
A buffer solution consists of a **weak acid** (to supply protons to any added strong base) and its **conjugate weak base** (to receive protons from any added strong acid). A buffer solution is a solution that resists changes in pH when small amounts of acid or base are added.



8 A⁻
24 HA
pH < pK_a



16 A⁻
16 HA
pH = pK_a

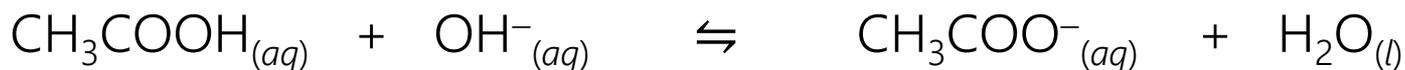


28 A⁻
4 HA
pH > pK_a

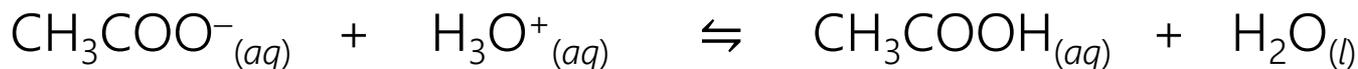
Buffer solutions

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 (OH^-) ions are added they will react with the ethanoic acid.



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



These reactions show that any added acid (H_3O^+) or base (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



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

$[A^-]$ and $[HA]$
swapped

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

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

Reminder that $pH = -\log[H_3O^+]$
So applied to both sides

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.

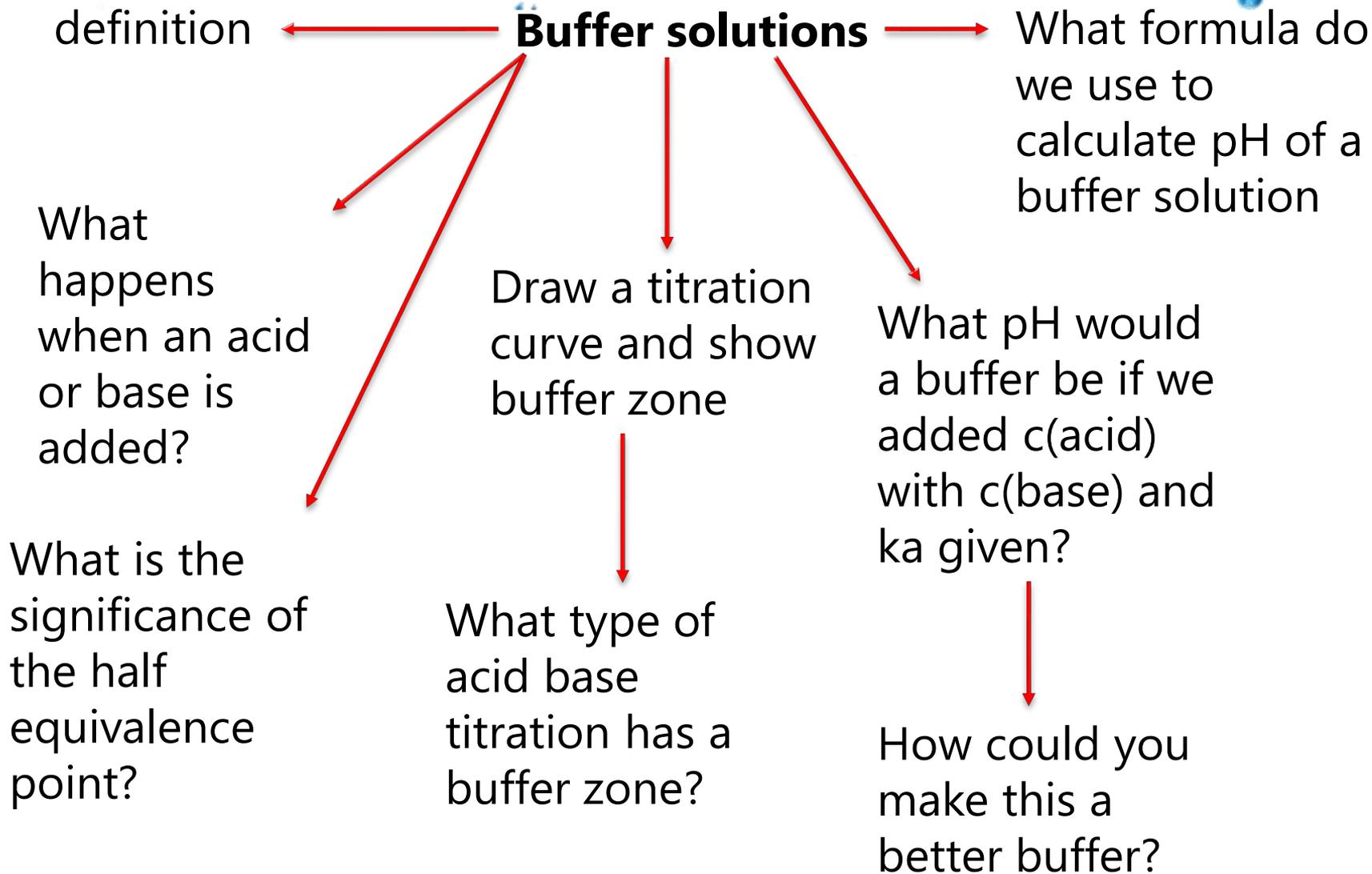
If [weak base] = [weak acid] in a buffer solution, then $\text{pH} = \text{pK}_a$.

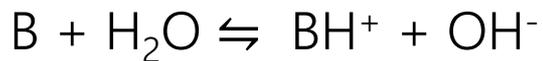
Example

If a buffer solution is made up of 0.050 mol L^{-1} benzoic acid and 0.050 mol L^{-1} sodium benzoate, show that the pH of the solution = 4.19, given that $\text{pK}_a(\text{benzoic acid}) = 4.19$.

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

Buffer Key Questions





pH of Base

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

$$K_b = K_w / K_a$$

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

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

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

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



pH of Acid

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

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

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

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

$$[H_3O^+] = 10^{-pH}$$

pH of buffer

$$A^- = H_3O^+$$

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

$$n = c \times v$$

$$m = n \times M$$

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

$$[H_3O^+]$$

pH

mass

mass

[H₃O⁺]

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⁻¹ CH₃NH₃Cl and 30.0 mL of 1 mol L⁻¹ CH₃NH₂
Calculate the pH of the resultant buffer solution. pK_a (CH₃NH₃⁺) = 10.64

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

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

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

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

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

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

$$\text{pH} = 10.8$$

$$[\text{CH}_3\text{NH}_2] = \frac{\text{original volume} \times \text{conc.}}{\text{total volume}}$$

NCEA 2013 Buffers

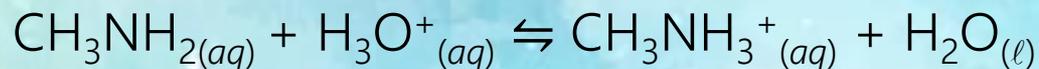
Excellence
Question

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

20.0 mL of 1 mol L⁻¹ CH₃NH₃Cl and 30.0 mL of 1 mol L⁻¹ CH₃NH₂

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

When a small amount of acid (H₃O⁺) ions are added, they will react with the CH₃NH_{2(aq)} molecules to form CH₃NH_{3⁺(aq)} ions.



The added acid (H₃O⁺), is mostly consumed, and the pH of the solution changes very little.

NCEA 2014 Buffers

Excellence
Question

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⁻¹ HF to give a buffer solution with a pH of 4.02.

Assume there is no change in volume.

$$M(\text{NaF}) = 42.0 \text{ g mol}^{-1} \quad pK_a(\text{HF}) = 3.17$$

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

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

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

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

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

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

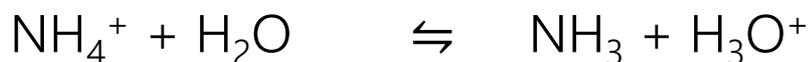
$$n(\text{F}^-) = n(\text{NaF})$$
$$n = c \times v$$

As question is asking for mass, use:

$$n = c \times V$$
$$m = n \times M$$

Question 2a (ii) : Dilute hydrochloric acid, HCl, is added to the NH₃ solution until the ratio of NH₃ to NH₄⁺ 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.



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

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

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

$$\text{pH} = 9.94$$

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

5:1 ratio

pH is +1
to -1
from pKa
to form
buffer
zone

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 [NH₃] > [NH₄⁺] / pH > pKa, the buffer will be more effective at neutralising added strong acid.

NCEA 2018 Buffers

Achieved
Question

Question: 2. A titration was carried out by adding 0.210 mol L^{-1} hydrochloric acid, HCl, to 25.0 mL of 0.168 mol L^{-1} methanamine, CH_3NH_2 .

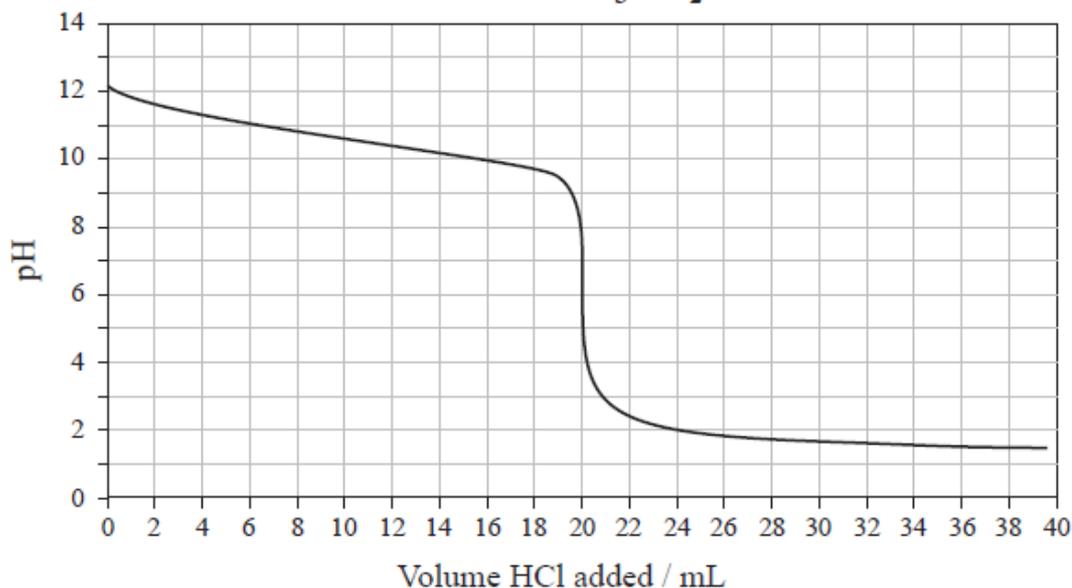
The equation for the reaction is: $\text{HCl} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{NH}_3^+ + \text{Cl}^-$

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

(a) Between pH 9.60 – 11.6, the solution is a buffer.

(i) From the titration curve, estimate the volume of the HCl solution that must be added to the CH_3NH_2 solution above to make a buffer solution of pH 10.0.

Titration Curve for CH_3NH_2 versus HCl



Volume from curve
at pH 10.0 = 15 –
16.0 mL

NCEA 2018 Buffers

Merit
Question

Question: 2. A titration was carried out by adding 0.210 mol L^{-1} hydrochloric acid, HCl, to 25.0 mL of 0.168 mol L^{-1} methanamine, CH_3NH_2 .

The equation for the reaction is: $\text{HCl} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{NH}_3^+ + \text{Cl}^-$

$$p_{K_a}(\text{CH}_3\text{NH}_3^+) = 10.6 \quad K_a(\text{CH}_3\text{NH}_3^+) = 2.51 \times 10^{-11}$$

(ii) Explain how the buffer solution resists large changes in pH as the HCl solution is added between a pH of 9.60 – 11.6.

Include an appropriate equation in your answer.

As the HCl is added, the H_3O^+ ions are neutralised by the basic component of the buffer, CH_3NH_2 , according to the equation below:



OR



Since the H_3O^+ are removed from the solution, the pH of the solution does not significantly change.

NCEA 2018 Buffers

Excellence
Question

Question: 3b. 5.11 g of sodium methanoate, HCOONa, was added to 125 mL of 0.105 mol L⁻¹ methanoic acid, HCOOH, to make a buffer solution. Assume there is no change in the total volume.

$$pK_a(\text{HCOOH}) = 3.74 \quad K_a(\text{HCOOH}) = 1.82 \times 10^{-4}$$

(i) Give the pH range over which the resulting solution will function as a buffer.

(ii) Show, by calculation, that the pH of this buffer solution is 4.50.

$$M(\text{HCOONa}) = 68.0 \text{ g mol}^{-1}$$

The solution will function as a buffer over a pH range 2.74 – 4.74 ($pK_a \pm 1$).

$$n(\text{HCOONa}) = \frac{m}{M} = \frac{5.11}{68} = 0.0751 \text{ mol}$$

$$c(\text{HCOO}^-) = \frac{n}{V} = \frac{0.0751}{0.125} = 0.601 \text{ mol L}^{-1}$$

$$K_a = 1.82 \times 10^{-4} = \frac{[\text{HCOO}^-][\text{H}_3\text{O}^+]}{[\text{HCOOH}]}$$

$$= \frac{0.601 \times [\text{H}_3\text{O}^+]}{0.105}$$

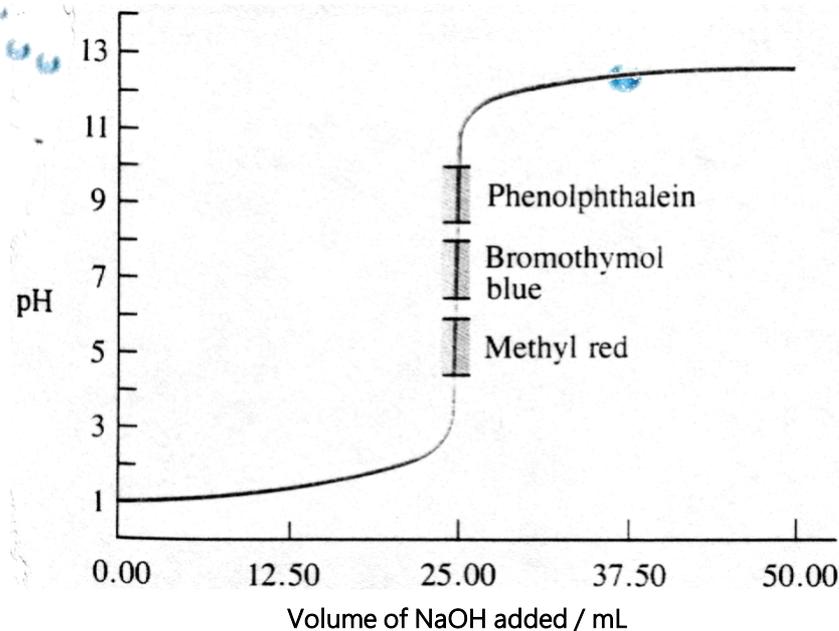
$$[\text{H}_3\text{O}^+] = 3.18 \times 10^{-5} \text{ mol L}^{-1}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = 4.50$$

Since the pH of the solution falls within the buffer zone (2.74 – 4.74), it will function as a buffer. However, as the pH > pK_a, / this means [HCOO⁻] > [HCOOH], so the buffer will be more effective against added strong acid.

Acid – base titration curves

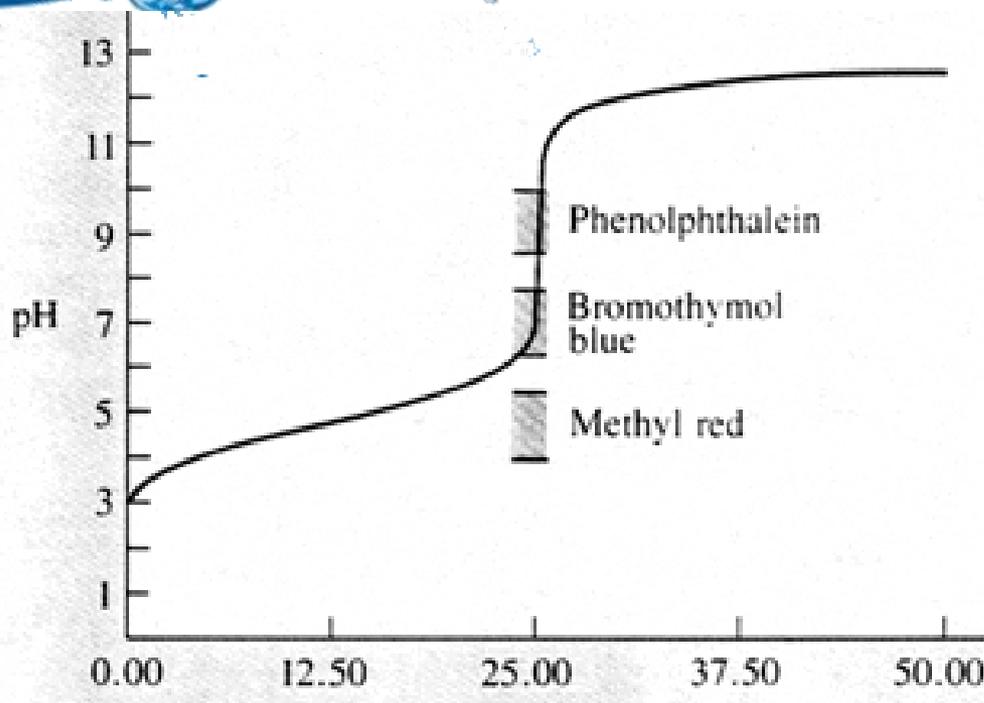
A plot of the pH of an acid solution against the volume of added base (or vice-versa) produces what is called a **pH titration curve**. The example below shows how the pH (measured using a pH meter) changes when a strong acid is added to a strong base. There are characteristic points on the curve that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

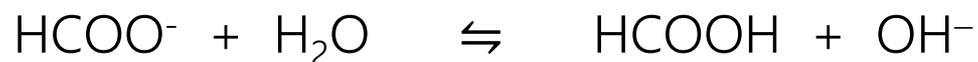
Acid – base titration curves

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.



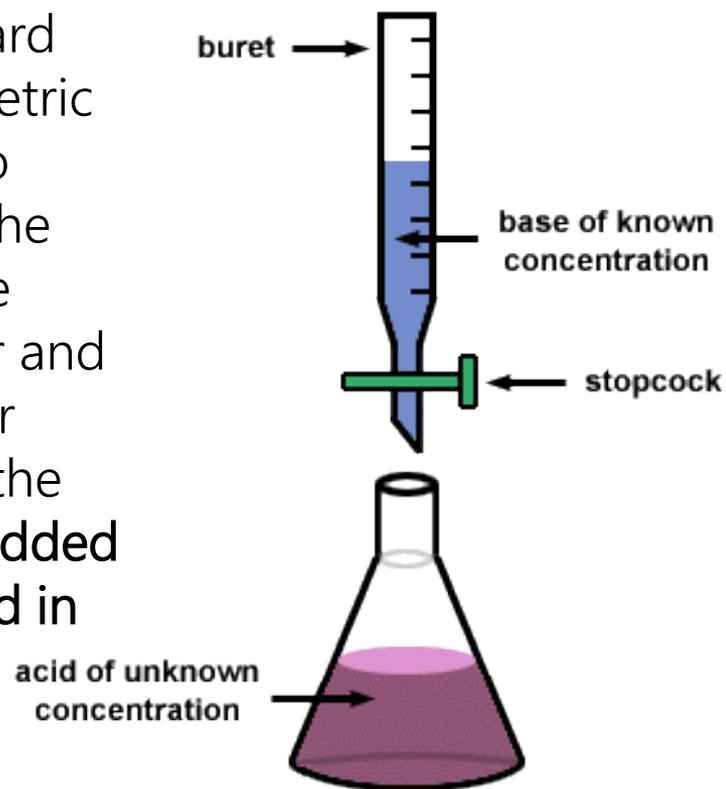
The equivalence point is at a pH greater than 7 so only indicators with a pK_a about 8-9 will change colour at the correct pH and be useful

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.**

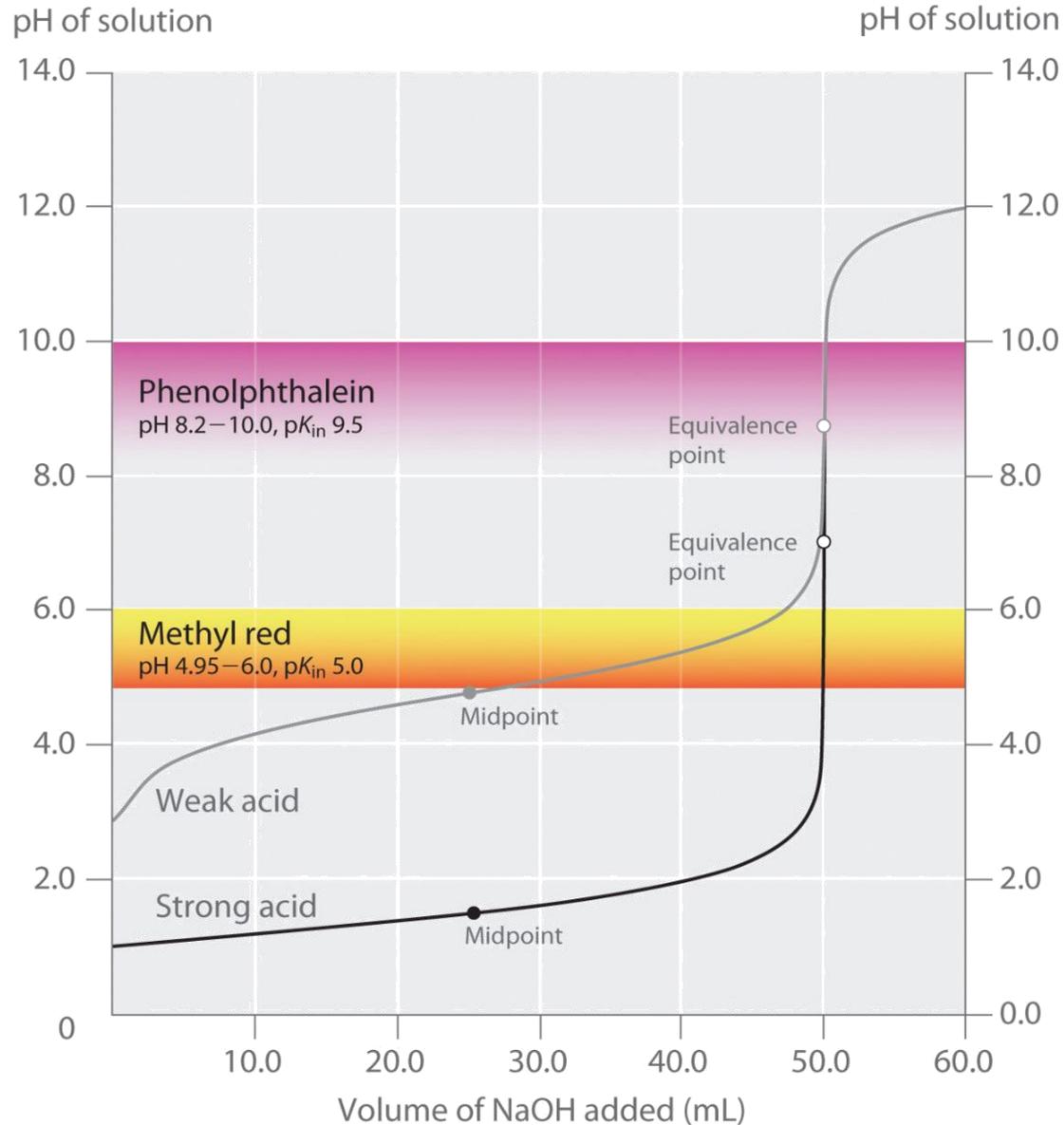


Neutralisation of acids

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

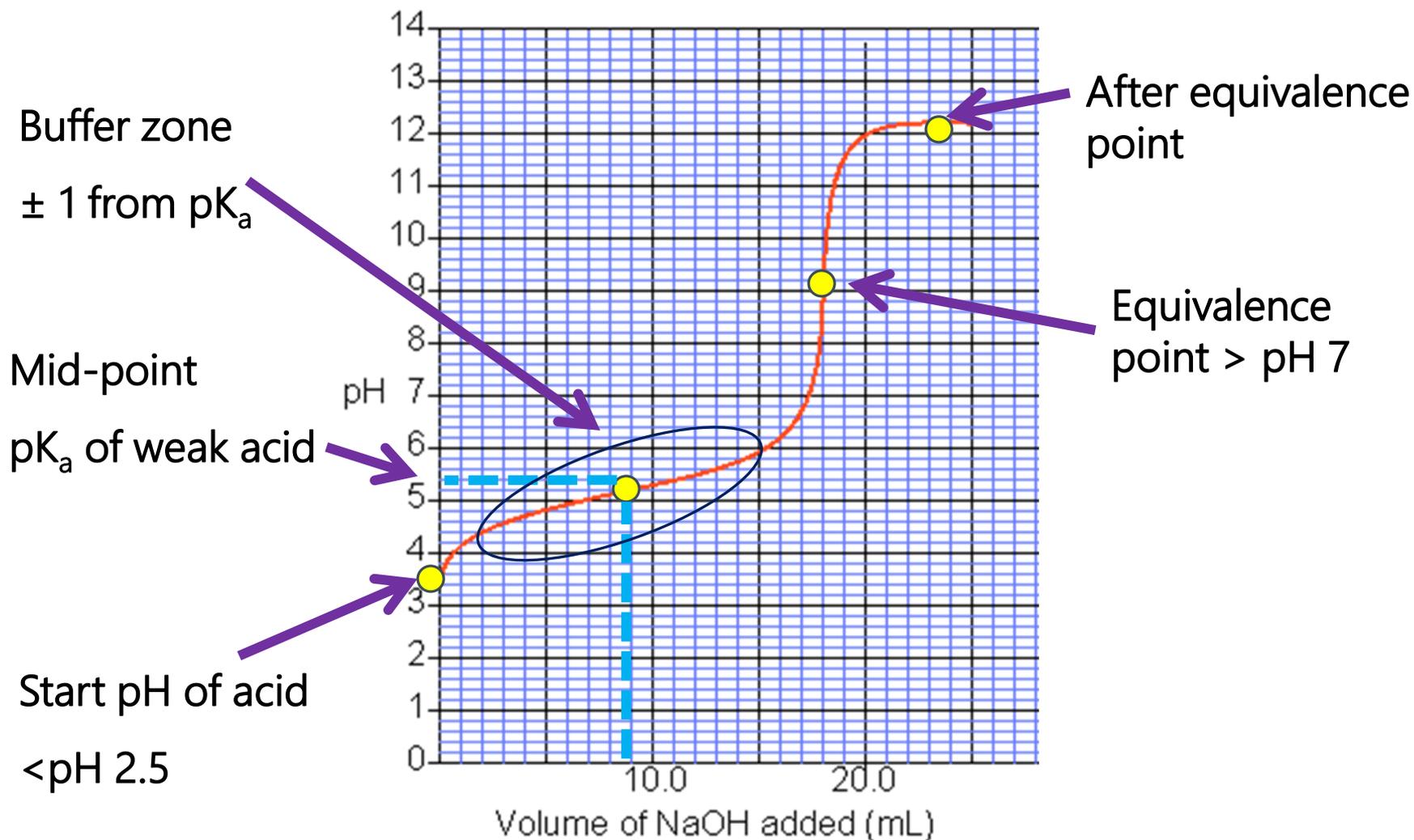


methyl red



phenolphthalein

Features of a titration curve – strong base/weak acid

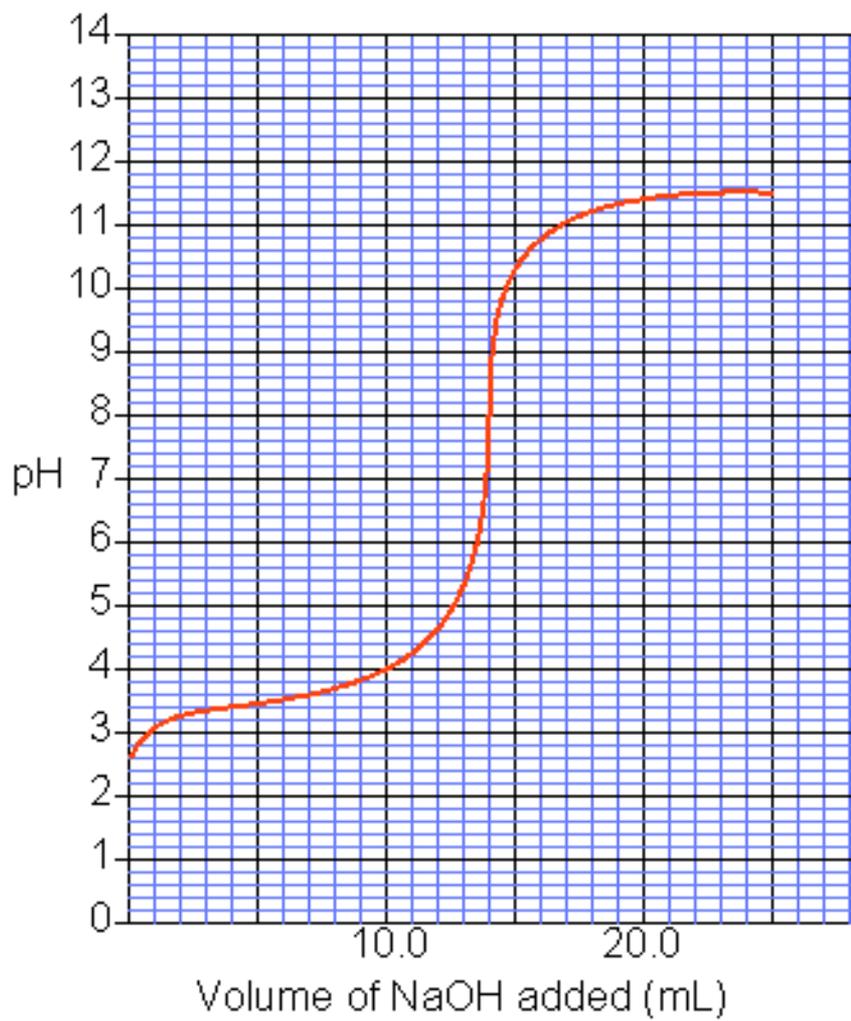


Features of a titration curve – strong base/weak acid

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 pK_a will be the pH of the midpoint.
4. **Buffer Zone** – This will be an area 1 pH either side of the mid - point. It can be plotted on the graph as a circled area
5. **After the equivalence point** – The pH depends on the concentration of the solution being added from the burette.

Acid – base titration curves

Strong Base added to Strong Acid

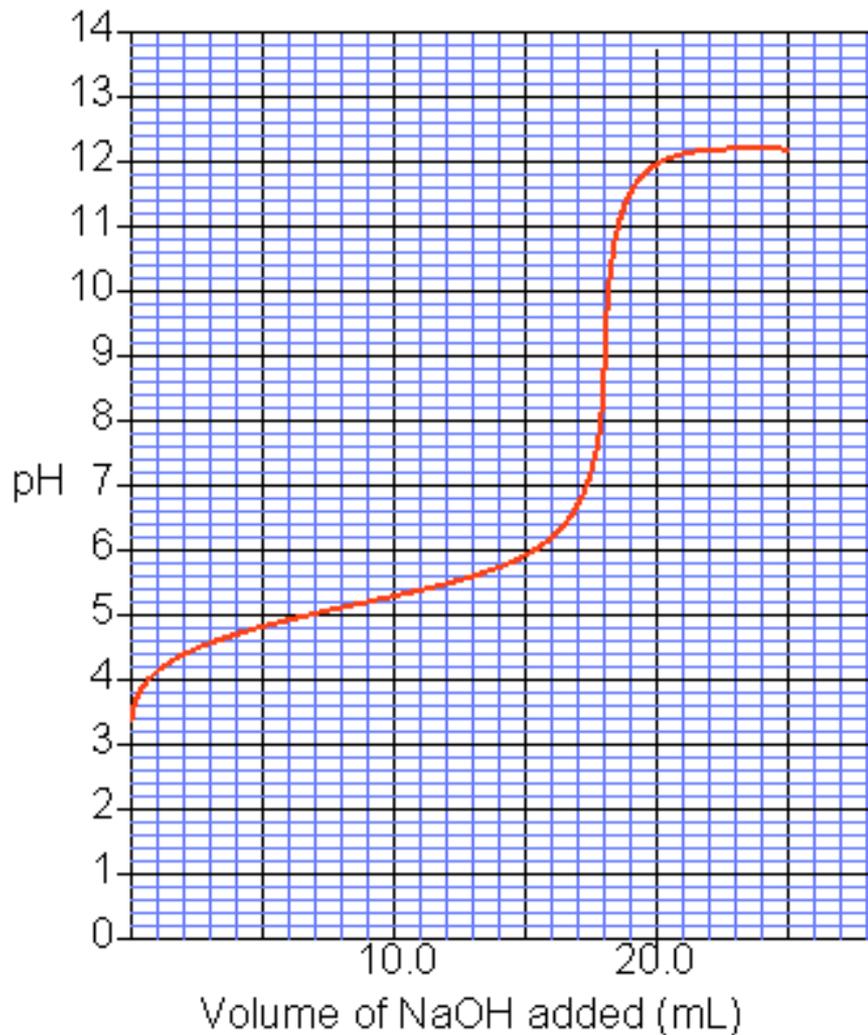


Characteristics

- 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

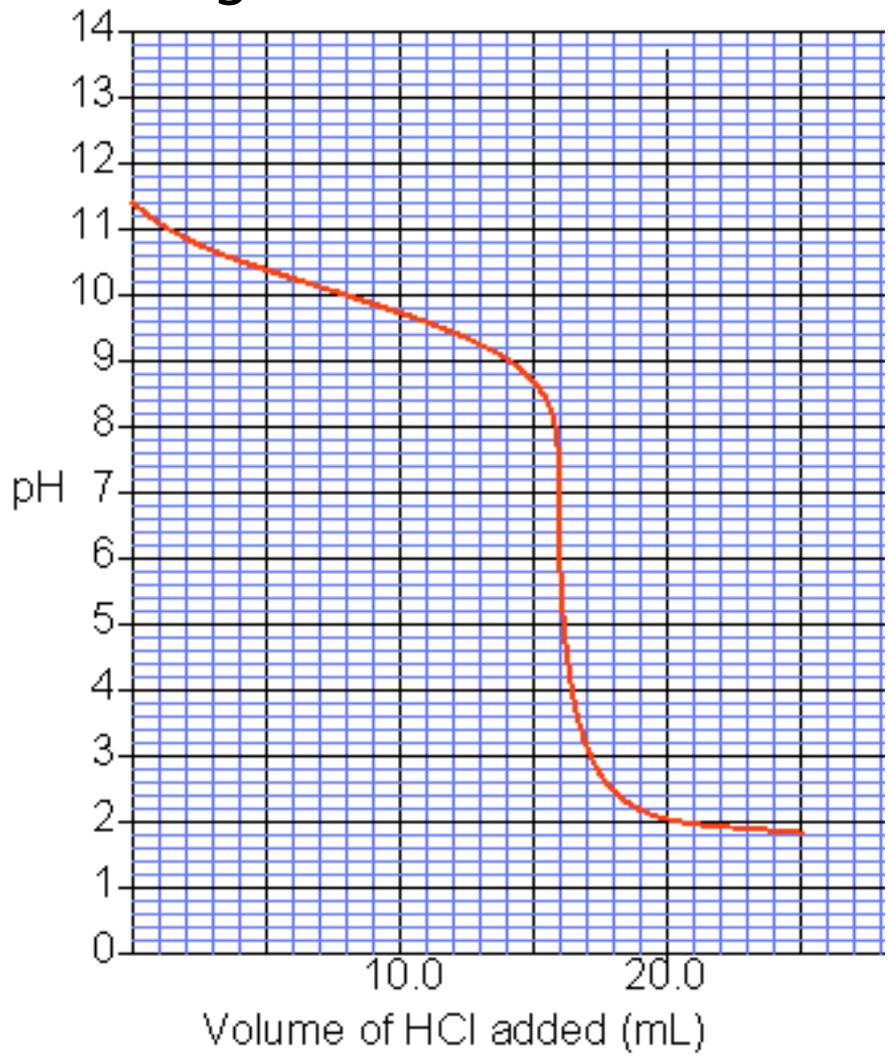
Equivalence point above 7

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⁻¹ ethanoic acid is titrated with 0.100 mol L⁻¹ sodium hydroxide up to a total of 30mL
pKa (CH₃COOH) = 4.76

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

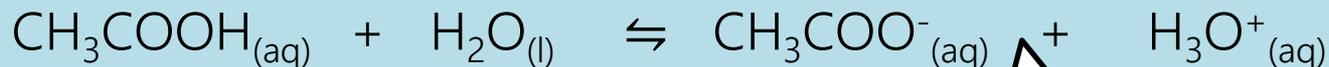
1. The pH before any base is added
2. The volume of the base at equivalence point
3. The volume of base when pH = pKa
4. The pH at equivalence point
5. The pH after all of the base 30mL has been added

Step One:
Start pH

Find the pH of:

Information given

0.0896 molL⁻¹ of CH₃COOH_(aq) pK_a = 4.76



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

Dissociation equation
of weak acid

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

$$= 10^{-4.76}$$

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

K_a expression

Calculate K_a from pK_a
given

Assume

1. [CH₃COO⁻] = [H₃O⁺]

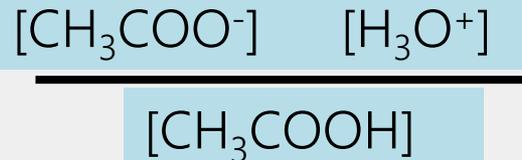
2. [CH₃COOH] = 0.0896 molL⁻¹

Assumptions for pH
calculation

Step One:
Start pH

Equilibrium expression of acid dissociation in water

$K_a =$



1.74×10^{-5}

$$= \frac{[\text{H}_3\text{O}^+]^2}{0.0896 \text{ mol L}^{-1}}$$

Rearrange:

$$1.74 \times 10^{-5} \times 0.0896 \text{ mol L}^{-1} = [\text{H}_3\text{O}^+]^2$$

$$1.25 \times 10^{-3} \text{ mol L}^{-1} = [\text{H}_3\text{O}^+]$$

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

Calculate

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

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

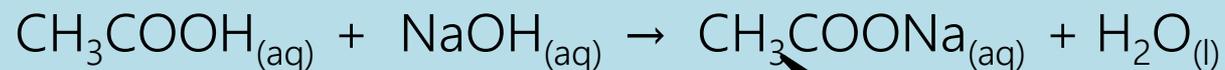
$$\text{pH} = 2.90$$

Double check your answer by making sure the pH fits within the range of your starting acid or base (weak or strong)

Step Two:
Volume of equivalence

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

Titration reaction is:



$$\begin{aligned} n(\text{CH}_3\text{COOH}) &= cV \\ &= 0.0896 \text{ mol L}^{-1} \times 0.0200\text{L} \\ &= 1.79 \times 10^{-3} \text{ mol} \end{aligned}$$

Neutralisation equation at end point

From the equation 1:1. Every mole of $\text{CH}_3\text{COOH} = \text{NaOH}$

$$\begin{aligned} n(\text{NaOH}) &= n(\text{CH}_3\text{COOH}) \\ &= 1.79 \times 10^{-3} \text{ mol} \end{aligned}$$

Volume of acid in flask at start

$$\begin{aligned} V(\text{NaOH}) &= n / c \\ V(\text{NaOH}) &= \frac{1.79 \times 10^{-3} \text{ mol}}{0.100 \text{ molL}^{-1}} \end{aligned}$$

Rearrange $n=c/v$ to calculate v of NaOH needed to neutralise CH_3COOH present

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

Convert to mL for titration curve

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

When exactly $\frac{1}{2}$ way to end point then $\frac{1}{2}$ acid has dissociated into conjugate
 $(\text{CH}_3\text{COOH}) = (\text{CH}_3\text{COO}^-)$

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

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

These points intercept 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 pH 4.76
Once the curve is drawn this can be sketched as a circle around the area from 3.76 – 5.76 on the line.

The buffer zone is where pH will change slowly (flatter line) due to equilibrium principles

Step Four:
pH of equivalence

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

1.79×10^{-3} mol of CH_3COONa in
($20\text{mL} + 17.9\text{mL} = 37.9\text{mL}$) of solution

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

Total volume from starting flask + added from burette

$$c = n/v$$

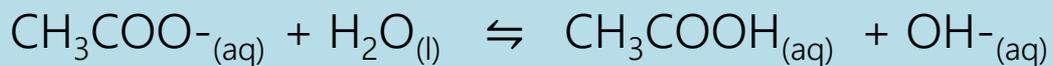
At neutralisation (from equation), for every mole of original acid there is now an equal amount of conjugate (CH_3COO^-) formed

We need to calculate the pH of a solution of CH_3COONa with this concentration: 0.0472 molL^{-1}

As the pH of the equivalence point is determined by a conjugate that is base (paired with starting weak acid) then it will be above pH 7

The amount of conjugate of the weak acid present will determine the pH at end point. All acid at start has been now been neutralised

Step Four:
pH of equivalence



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

$$[\text{H}_3\text{O}^+] = \sqrt{(10^{-4.76} \times 10^{-14} \div [0.0472 \text{ molL}^{-1}])}$$

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

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

Intercept this this pH point with v calculated for the endpoint

pH = 8.72

Each mol of conjugate formed will produce 1 mol of OH⁻ ions, which determines the pH

Assume

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

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

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

Step Five:
Final pH

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

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

Volume of after equivalence point

Calculate concentration of added base or acid. Although the conjugate does react we assume all $[\text{OH}^-]$ or $[\text{H}_3\text{O}^+]$ comes from excess added

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

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

Original concentration

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

New concentration after dilution

Dilution calculation

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

Step Five:
Final pH

NaOH is a strong base

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

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

Strong bases or acids fully dissociate

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

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

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

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

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

Plot this point on your graph

$$\text{pH} = 12.4$$

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

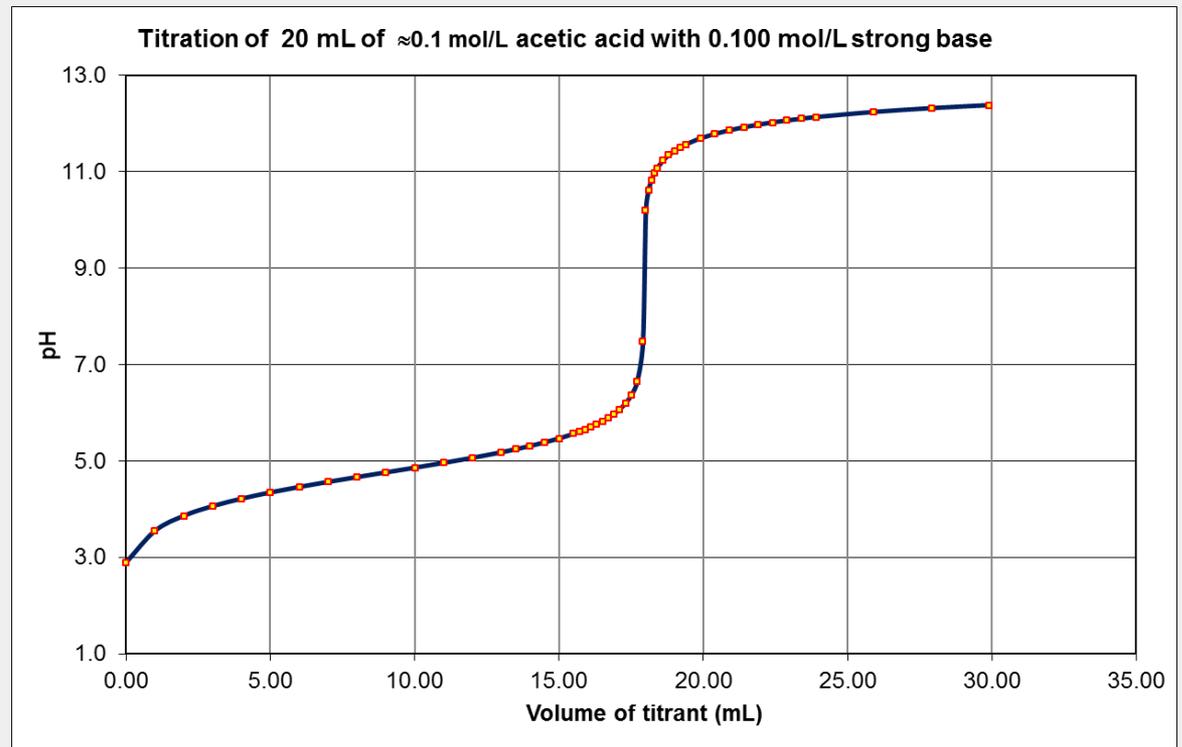
volume pH

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



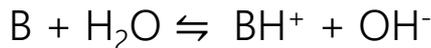
$$K_a = 10^{-pK_a}$$

Titration calculations

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

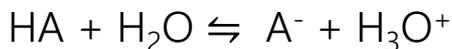
1. Start pH

W BASE (add acid)



5. Final pH

W ACID (add base)



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

$$C(\text{from burette}) = \frac{V(\text{after eq.})}{V(\text{total})} \times C(\text{original})$$

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

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

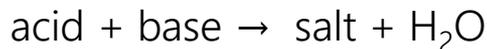
Strong acid

Strong base

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

2. Volume of endpoint

pH

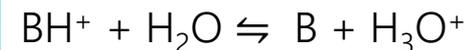


pH below 7

pH above 7

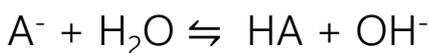
$$n(\text{in flask}) = C \times V$$

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



$$n(\text{acid}) = n(\text{base})$$

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



$$V(\text{from burette}) = n \div C$$

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

3. Midpoint buffer zone

$$x = \text{Endpoint } v \div 2$$

$$y = pK_a$$

4. pH of equivalence point

Drawing titration curves (additional Notes)

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_2O concentration is the same before and after

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

Drawing titration curves (additional notes)

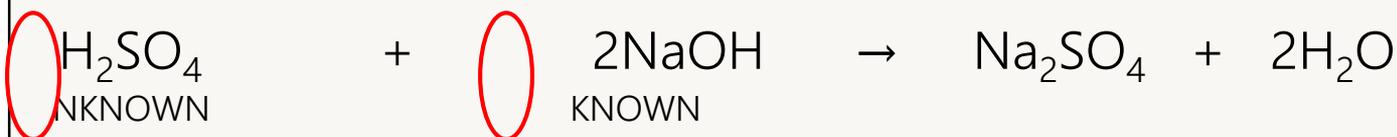
Step Two: Calculate the volume at equivalence point

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 H₂SO₄



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

c) Rearrange equation to calculate volume

v = volume (L) c = concentration (molL⁻¹)

$$v = n / c$$

Drawing titration curves (additional notes)

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. $\text{Acid} + \text{water} \rightleftharpoons \text{conjugate base} + \text{H}_3\text{O}^+$

$$\text{So } K_a = \frac{[\text{conjugate base}][\text{H}_3\text{O}^+]}{[\text{acid}]}$$

If they are equal concentration they are cancelled and $K_a = [\text{H}_3\text{O}^+]$

Therefore $pK_a = pH$ as $pK_a = -\log K_a$ and $pH = -\log [\text{H}_3\text{O}^+]$

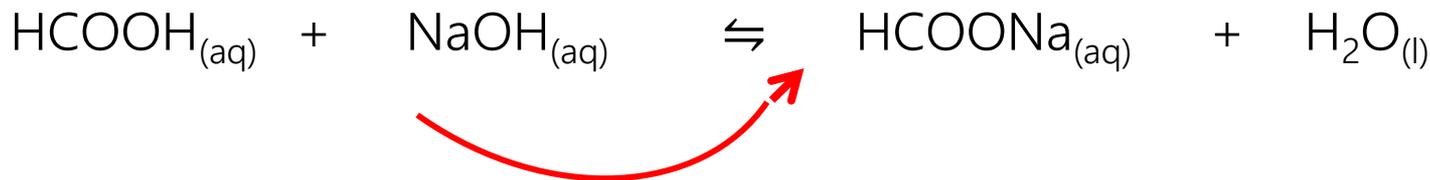
Drawing titration curves (additional notes)

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

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

Drawing titration curves (additional notes)

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.

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⁻¹ CH₃COOH + 15 mL 0.20 mol L⁻¹ NaOH



n	[CH ₃ COOH]	[NaOH]	[CH ₃ COO ⁻]
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⁻] = 0.001 mol / 0.035 L

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

Calculating the start concentration

Sample question: A titration was carried out by adding hydrobromic acid, HBr, to 20.0 mL of aqueous methylamine, CH₃NH₂, solution.

The equation for the reaction is: CH₃NH₂ + HBr → CH₃NH₃⁺ + Br⁻

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

The aqueous methylamine, CH₃NH₂, 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⁻¹.

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

calculate [H₃O⁺]

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

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

write out K_a expression

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

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

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

Add in values [H₃O⁺] = 10^{-pH}
substitute [OH⁻] = k_w/[H₃O⁺]

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

$$[\text{weak base}] = K_a \times K_w \div [\text{H}_3\text{O}^+]^2$$

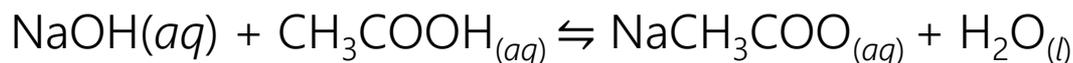
$$= 0.0912 \text{ mol L}^{-1}$$

calculate

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

Sample question: 20.0 mL of 0.0896 mol L⁻¹ ethanoic acid is titrated with 0.100 mol L⁻¹ sodium hydroxide. pK_a (CH₃COOH) = 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
($n(\text{CH}_3\text{COOH}) - n(\text{NaOH})$ after 5mL)

$c = n/v$
Volume is 25ml total

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

Equivalence point pH

Sample question: 20.00 mL of 0.320 mol L⁻¹ ammonia, NH₃, is titrated with 0.640 mol L⁻¹ hydrochloric acid, HCl. $pK_a(\text{NH}_4^+) = 9.24$ $\text{NH}_3 + \text{HCl} \rightleftharpoons \text{NH}_4^+ + \text{Cl}^-$

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

$$n(\text{NH}_3) = cv$$

$$n(\text{NH}_3) = 0.320 \text{ mol L}^{-1} \times 0.0200\text{L}$$

$$n(\text{NH}_3) = 6.40 \times 10^{-3} \text{ mol}$$

calculate n(Base) to neutralise (and reach equivalence point and therefore n(Acid) from 1:1 equation) $n = cv$
also assume $n(\text{NH}_3) = n(\text{NH}_4^+)$

$$v = n/c$$

$$v = 6.40 \times 10^{-3} \text{ mol} / 0.640 \text{ mol L}^{-1}$$

$$v = 0.0100\text{L} (10.0\text{mL})$$

calculate v(Acid) to neutralise ($n(\text{NH}_3) = n(\text{HCl})$ from 1:1 equation)

$$c = n/\text{total } v$$

$$c = 6.40 \times 10^{-3} \text{ mol} / 0.0300\text{L}$$

$$c = 0.213 \text{ mol L}^{-1}$$

calculate [B⁺] $c = n/\text{total } v$
also assume $n(\text{B}) = n(\text{B}^+)$ see step 1.
 $\text{B} = \text{NH}_3$ $\text{B}^+ = \text{NH}_4^+$
total $v = \text{start volume base} + v \text{ acid added}$

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

$$[\text{H}_3\text{O}^+] = \sqrt{10^{-9.24} \times 0.213 \text{ mol L}^{-1}}$$

$$[\text{H}_3\text{O}^+] = 1.11 \times 10^{-5} \text{ mol L}^{-1}$$

calculate $[\text{H}_3\text{O}^+]$ $K_a = 10^{-pK_a}$
 $[\text{H}_3\text{O}^+] = \sqrt{K_a \times c(\text{B}^+)}$

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

$$\text{pH} = -\log [1.11 \times 10^{-5} \text{ mol L}^{-1}]$$

$$\text{pH} = 4.96$$

Calculate pH $\text{pH} = -\log [\text{H}_3\text{O}^+]$ 3sgf

Check pH against estimate on curve

Question: 3a: 20.0 mL of 0.0896 mol L⁻¹ ethanoic acid is titrated with 0.100 mol L⁻¹ sodium hydroxide. pK_a (CH₃COOH) = 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 Titrations - (PART TWO)

Excellence
Question

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

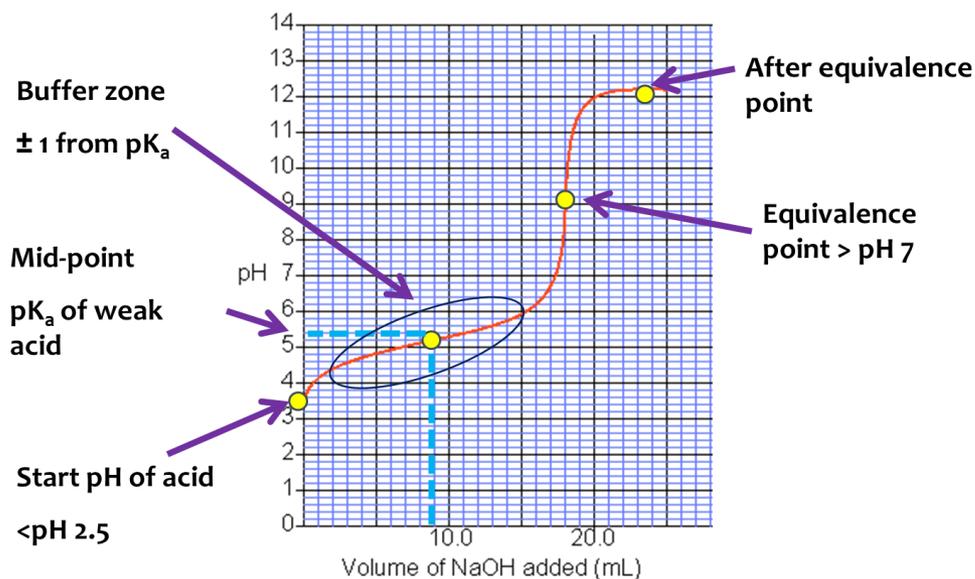
Discuss the reason for this.

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



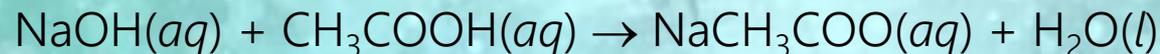
NCEA 2013 Titrations - (PART THREE)

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.



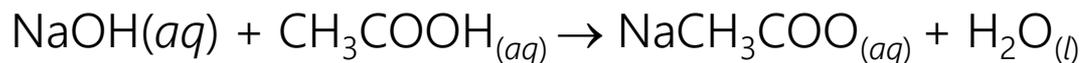
- $[\text{CH}_3\text{COO}^-]$ increases as it is formed in reaction
- $[\text{Na}^+]$ increases as NaOH is added
- $[\text{CH}_3\text{COOH}]$ decreases as it reacts with NaOH
- $[\text{H}_3\text{O}^+]$ decreases because $[\text{CH}_3\text{COO}^-] / [\text{CH}_3\text{COOH}]$ increases and K_a is a constant.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

NCEA 2013 Titrations - (PART FOUR)

Excellence
Question

Question: 3c: 20.0 mL of 0.0896 mol L⁻¹ ethanoic acid is titrated with 0.100 mol L⁻¹ sodium hydroxide. pK_a (CH₃COOH) = 4.76

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



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

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

After 5 mL NaOH added: (total 25mL)

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

(n(CH₃COOH – n(NaOH) after 5mL)

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

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

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

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

$$\text{pH} = 4.35$$

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

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

NCEA 2014 Titrations - (PART ONE)

Excellence
Question

Question: 3a: A titration was carried out by adding hydrobromic acid, HBr, to 20.0 mL of aqueous methylamine, CH₃NH₂, solution.

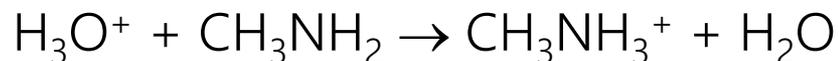
The equation for the reaction is:



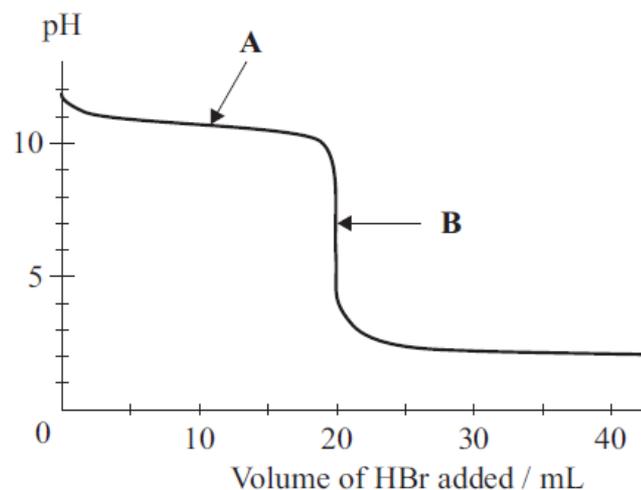
$$K_a(\text{CH}_3\text{NH}_3^+) = 2.29 \times 10^{-11}$$

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, [CH₃NH₂] ≈ [CH₃NH₃⁺]. So the solution has buffering properties in the proximity of point A. When HBr is added, the H₃O⁺ is consumed:



Since the H₃O⁺ is removed from the solution (neutralised), the pH does not change significantly.



NCEA 2014 Titrations - (PART TWO)

Excellence
Question

Question: 3b: A titration was carried out by adding hydrobromic acid, HBr, to 20.0 mL of aqueous methylamine, CH₃NH₂, solution.

The equation for the reaction is: CH₃NH₂ + HBr → CH₃NH₃⁺ + Br⁻

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

The aqueous methylamine, CH₃NH₂, 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⁻¹.

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

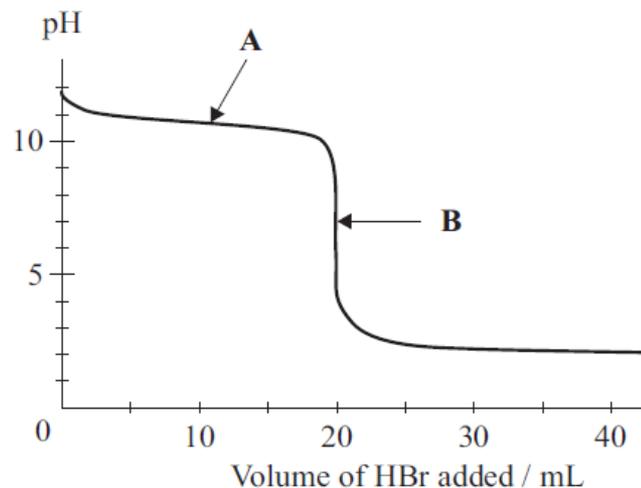
$$K_a = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+]}$$

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

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

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

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

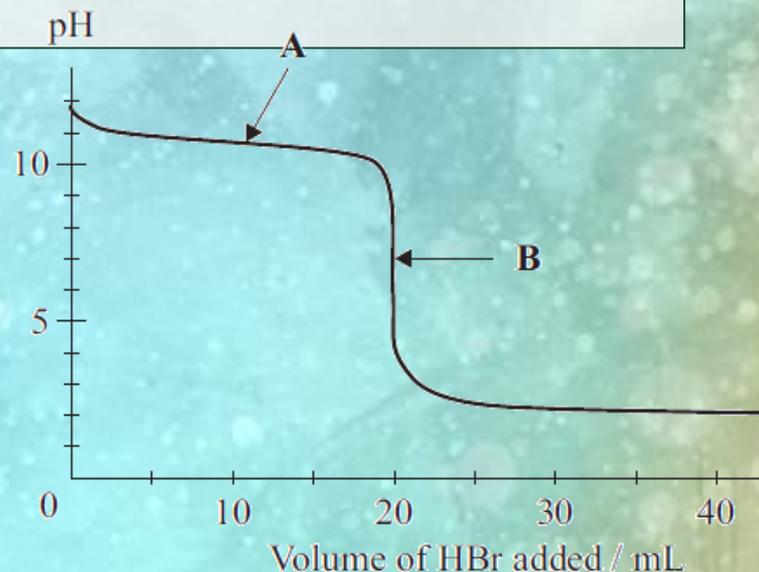


Question: 3c: Write the formulae of the four chemical species, apart from water and OH^- , that are present at the point marked **B** on the curve.

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

In your answer you should include:

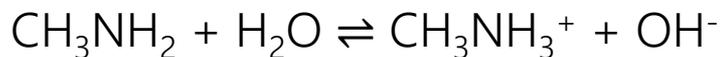
- a comparison of species present AND their relative concentrations
- a comparison of electrical conductivity linked to the relevant species present in each solution
- equations to support your answer.



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 (CH_3NH_2) which only partially reacts with water to produce a relatively low concentration of ions.

As a result, the initial CH_3NH_2 solution will be a poor electrical conductor.

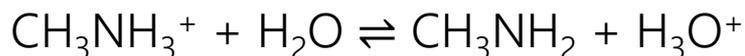


Therefore species present are $\text{CH}_3\text{NH}_2 > \text{OH}^- \geq \text{CH}_3\text{NH}_3^+ > \text{H}_3\text{O}^+$

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 (CH_3NH_3^+ and Br^-) present in the solution, so it will be a good electrical conductor / electrolyte.



CH_3NH_3^+ reacts with water according to the equation



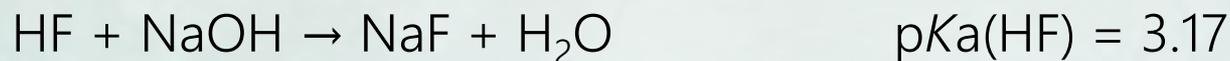
Species present are $\text{Br}^- > \text{CH}_3\text{NH}_3^+ > \text{H}_3\text{O}^+ \geq \text{CH}_3\text{NH}_2 > (\text{OH}^-)$

NCEA 2015 Titrations - (PART ONE)

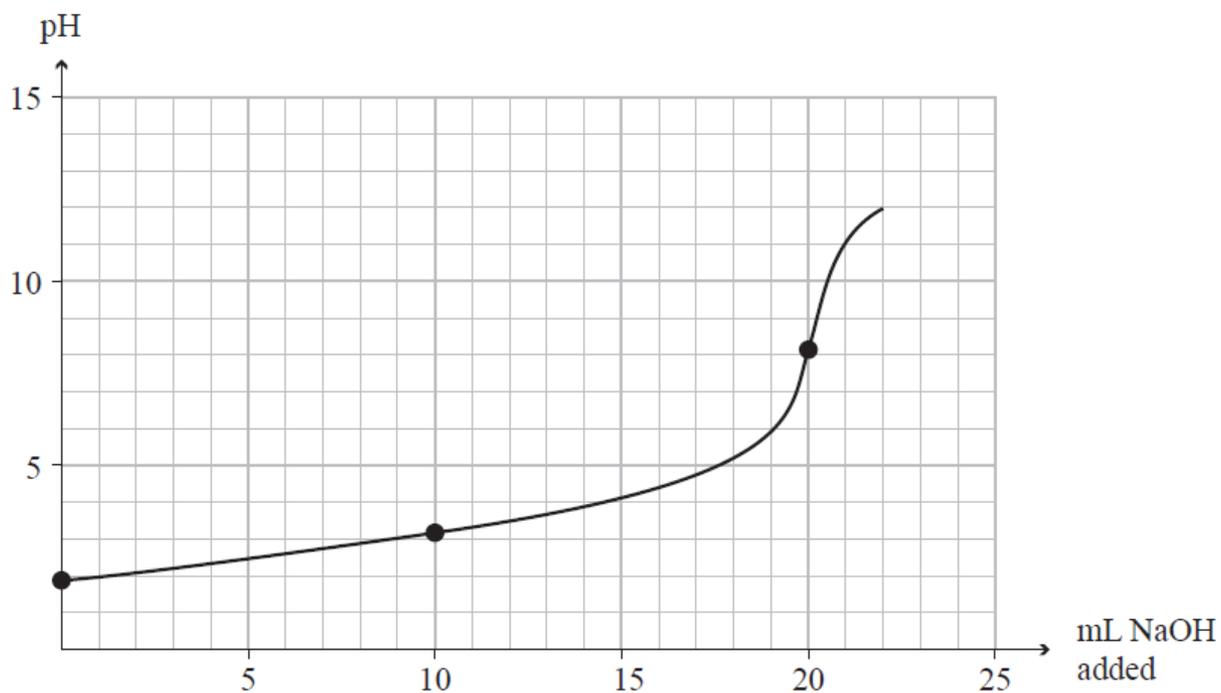
Achieved
Question

Question: 3a: 20.0 mL of 0.258 mol L⁻¹ 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.

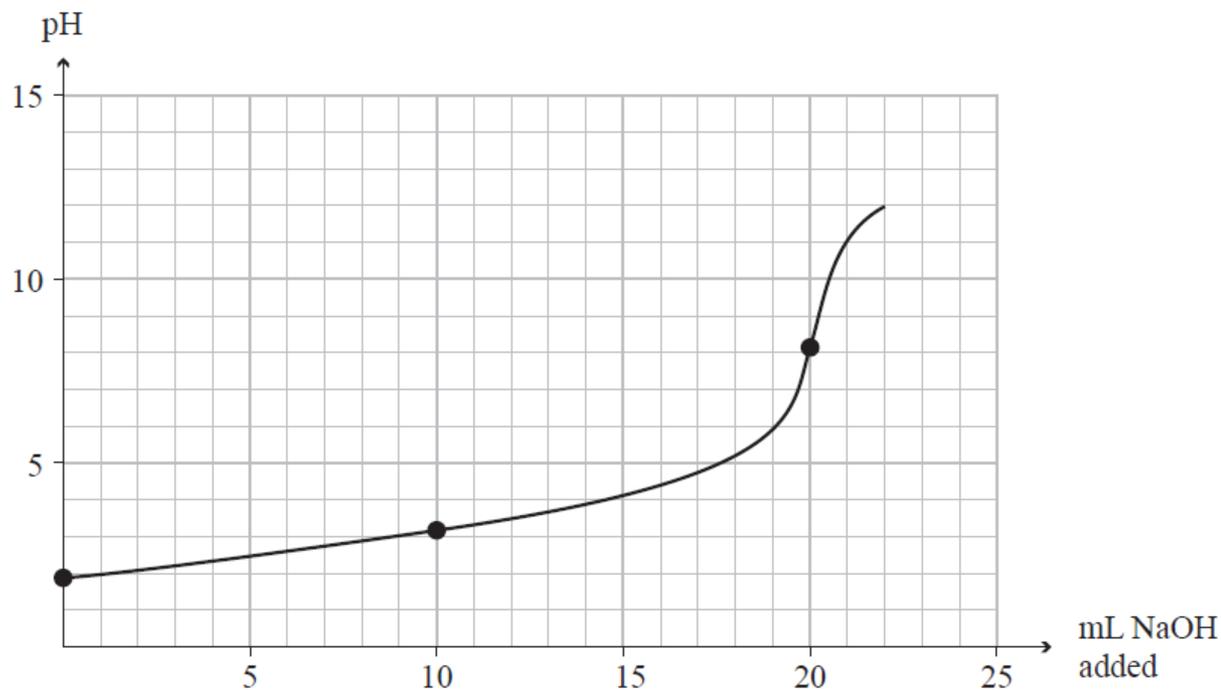


Na^+ , F^- ,
 H_2O , HF ,
 OH^- , H_3O^+ .

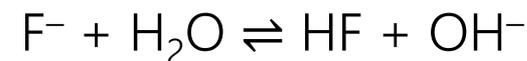
NCEA 2015 Titrations - (PART TWO)

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⁻¹ 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⁻.

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

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

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

$$\text{pH} = pK_a + \log \frac{[\text{F}^-]}{[\text{HF}]}$$

$$= 3.17 + \log 0.5$$

$$= 2.87$$

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_a, / [HF] > [F⁻], it is more effective against added base than acid.

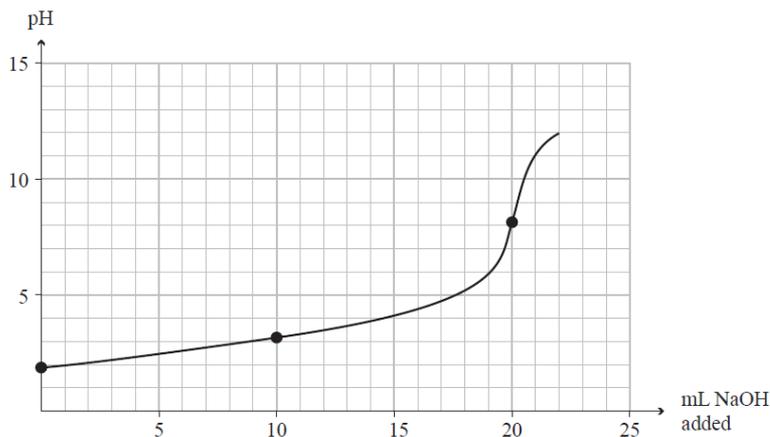
NCEA 2015 Titrations - (PART FOUR)

Excellence
Question

Question: 3a: 20.0 mL of 0.258 mol L⁻¹ 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⁻¹ 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 mol L^{-1} ethanoic acid, CH_3COOH , 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 pK_a more reactants

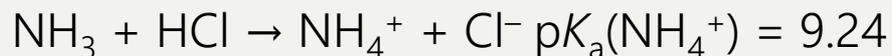
Since CH_3COOH has a higher pK_a , it is a weaker acid than HF . Therefore its conjugate base, CH_3COO^- , will be a stronger base than F^- . This means $[\text{OH}^-]$ will be higher at the equivalence point for the CH_3COOH vs NaOH titration, so the equivalence point pH will be higher.

NCEA 2016 Titrations - (PART ONE)

Merit
Question

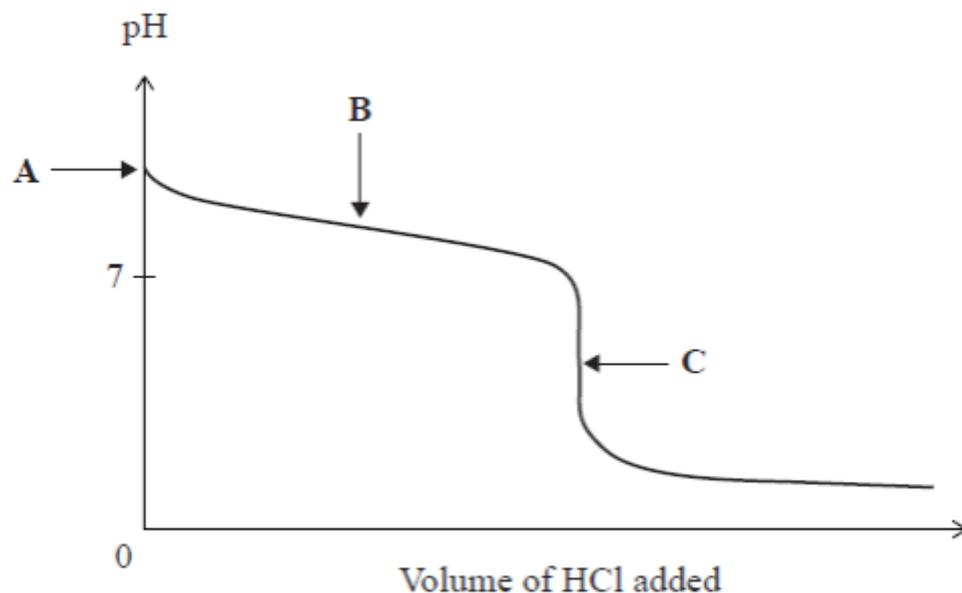
Question: 3a: 20.00 mL of 0.320 mol L⁻¹ ammonia, NH₃, is titrated with 0.640 mol L⁻¹ hydrochloric acid, HCl.

The equation for this reaction is:

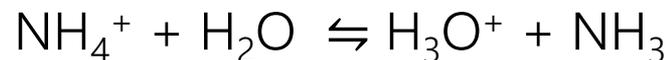


The curve for this titration is given below.

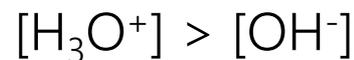
Explain why the pH at the equivalence point (point C) is not 7.



(Ammonium chloride) is acidic



So therefore



When considering pH think about which ion, H₃O⁺ or OH⁻, will be at the higher concentration

NCEA 2016 Titrations - (PART TWO)

Excellence
Question

Question 3b: 20.00 mL of 0.320 mol L⁻¹ ammonia, NH₃, is titrated with 0.640 mol L⁻¹ hydrochloric acid, HCl. pK_a(NH₄⁺) = 9.24

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

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

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

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

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

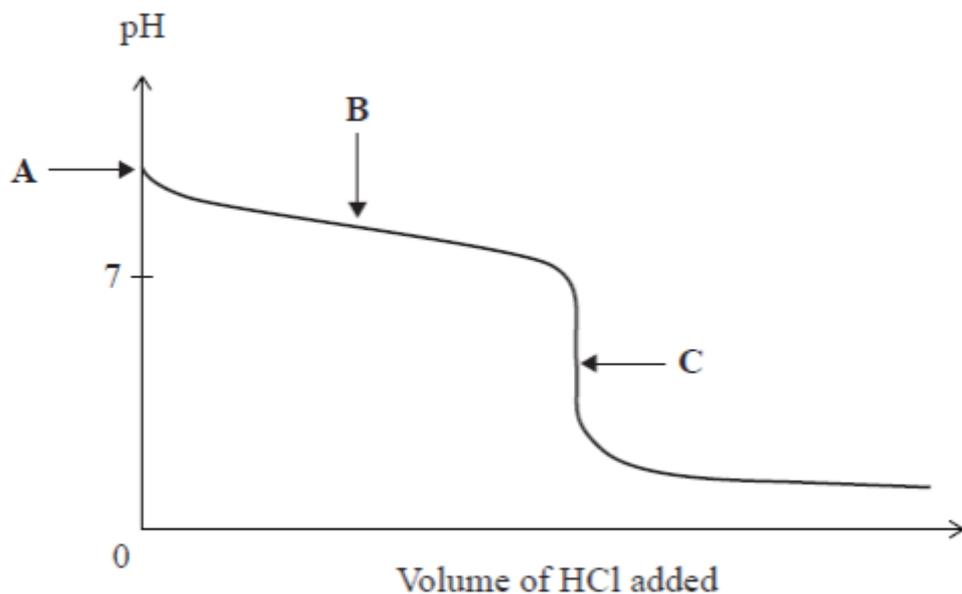
$$\text{pH} = 4.96$$

NCEA 2016 Titrations - (PART THREE)

Excellence
Question

Question 3c: 20.00 mL of 0.320 mol L⁻¹ ammonia, NH₃, is titrated with 0.640 mol L⁻¹ hydrochloric acid, HCl. pK_a(NH₄⁺) = 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

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

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

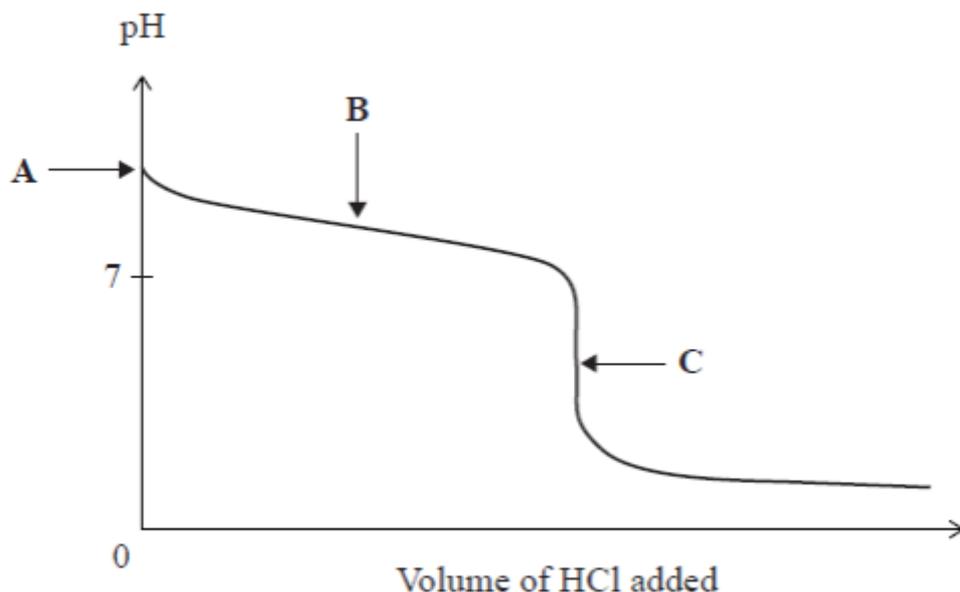
$$\text{therefore } \text{p}K_a = \text{pH}.$$

NCEA 2016 Titrations - (PART FOUR)

Merit
Question

Question 3d: 20.00 mL of 0.320 mol L⁻¹ ammonia, NH₃, is titrated with 0.640 mol L⁻¹ hydrochloric acid, HCl. pK_a(NH₄⁺) = 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 NH₄Cl.

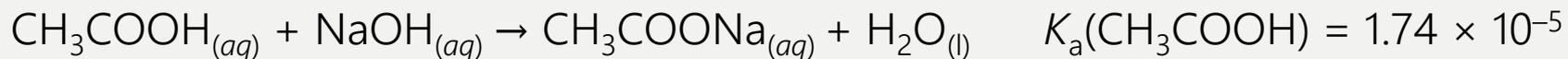
NH₄⁺ solution is acidic since,
$$\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$$

NCEA 2017 Titrations - (PART ONE)

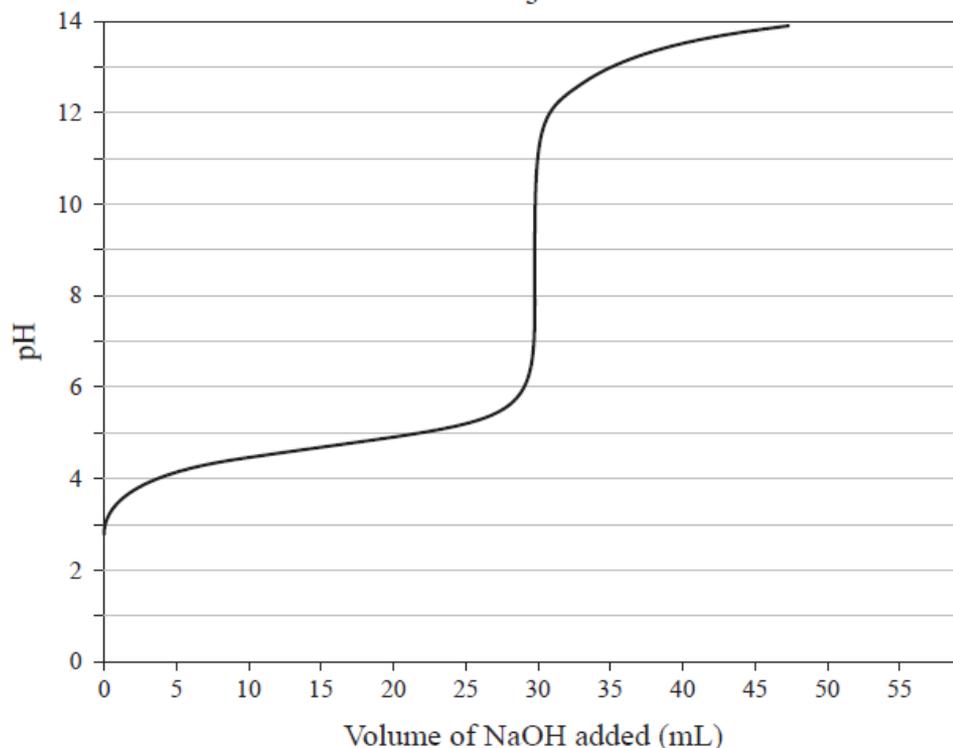
Achieved
Question

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

The equation for the reaction is:



Titration curve for CH_3COOH versus NaOH



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

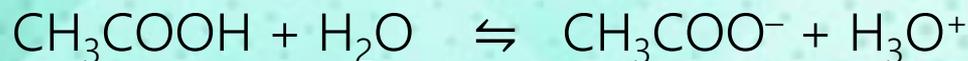
Indicator	$\text{p}K_a$	Tick ONE box below
Methyl yellow	3.1	<input type="checkbox"/>
Bromocresol purple	6.3	<input type="checkbox"/>
Phenolphthalein	9.6	<input checked="" type="checkbox"/>

NCEA 2017 Titrations - (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 CH_3COOH solution is 0.166 mol L^{-1} .



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

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

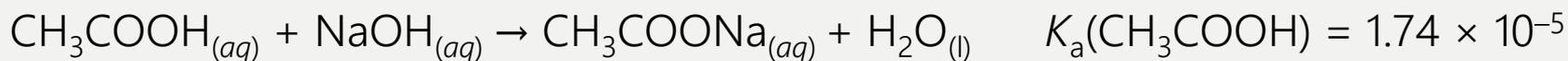
$$[\text{CH}_3\text{COOH}] = 0.166 \text{ mol L}^{-1}$$

NCEA 2017 Titrations - (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⁻¹ NaOH has been added to 20.0 mL of ethanoic acid solution, CH₃COOH_(aq).



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

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

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

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

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

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

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

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

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

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

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

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

$$\text{pH} = 4.47$$

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.

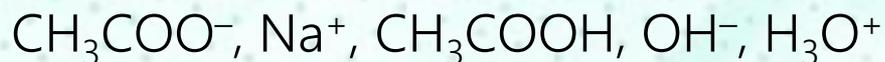
(ii) In a second titration, a 0.166 mol L^{-1} methanoic acid solution, $\text{HCOOH}_{(aq)}$, is titrated with the NaOH solution. The equivalence point pH for this titration is 8.28.

The equivalence point pH for the CH_3COOH 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 OH^- ions than ethanoate ions

OR HCOOH has a larger K_a than CH_3COOH , as it is a stronger acid. As a result, its conjugate base, HCOO^- , is weaker than CH_3COO^- , so the pH will be lower at the equivalence point.

NCEA 2018 Titrations (Part ONE)

Merit
Question

Question: 2. A titration was carried out by adding 0.210 mol L^{-1} hydrochloric acid, HCl, to 25.0 mL of 0.168 mol L^{-1} methanamine, CH_3NH_2 .

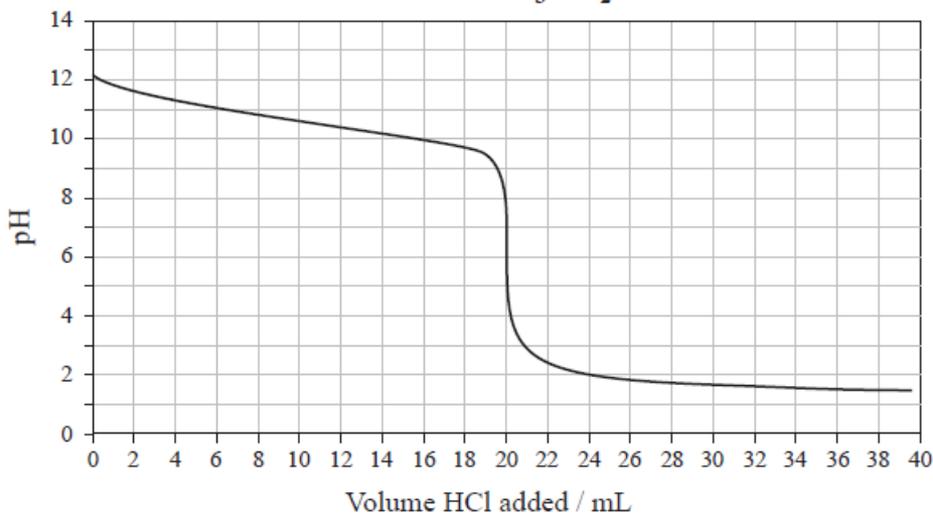
The equation for the reaction is: $\text{HCl} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{NH}_3^+ + \text{Cl}^-$

$p_{K_a}(\text{CH}_3\text{NH}_3^+) = 10.6$ $K_a(\text{CH}_3\text{NH}_3^+) = 2.51 \times 10^{-11}$

(b) (i) List all the species present in the solution at the equivalence point in order of decreasing concentration.

Do not include water.

Titration Curve for CH_3NH_2 versus HCl



$\text{Cl}^- > \text{CH}_3\text{NH}_3^+ > \text{CH}_3\text{NH}_2 = \text{H}_3\text{O}^+ > \text{OH}^-$

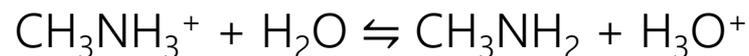
NCEA 2018 Titrations (Part TWO)

Question: 2. A titration was carried out by adding 0.210 mol L^{-1} hydrochloric acid, HCl, to 25.0 mL of 0.168 mol L^{-1} methanamine, CH_3NH_2 .

The equation for the reaction is: $\text{HCl} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{NH}_3^+ + \text{Cl}^-$

$pK_a(\text{CH}_3\text{NH}_3^+) = 10.6$ $K_a(\text{CH}_3\text{NH}_3^+) = 2.51 \times 10^{-11}$

(ii) Calculate the pH at the equivalence point.



$$K_a = 2.51 \times 10^{-11} = \frac{[\text{H}_3\text{O}^+]^2}{\left(0.168 \times \frac{25}{45}\right)}$$

$$[\text{H}_3\text{O}^+] = 1.53 \times 10^{-6} \text{ mol L}^{-1}$$

$$\text{pH} = -\log 1.53 \times 10^{-6} = 5.82$$

Titration Curve for CH_3NH_2 versus HCl

