

## Chemistry AS 91392 C3.6 Aqueous Systems

## Achievement Criteria - Solubility

Demonstrate understanding of equilibrium principles in aqueous systems
Aqueous systems are limited to those involving sparingly soluble ionic solids

## AS 91392

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 $A B, A_{2} B$ and $A B_{2}$ types where neither of the ions $A$ nor $B$ reacts further with water.
Candidates are expected to recognise common strong acids $\left(\mathrm{HCl}, \mathrm{HBr}, \mathrm{HNO}_{3}, \mathrm{H}_{2} \mathrm{SO}_{4}\right)$; strong bases ( KOH , $\mathrm{NaOH})$; weak acids ( $\mathrm{HF}, \mathrm{CH}_{3} \mathrm{COOH}$, and $\mathrm{NH}_{4}{ }^{+}$); weak bases $\left(\mathrm{NH}_{3}, \mathrm{CH}_{3} \mathrm{NH}_{2}\right.$, and $\left.\mathrm{CH}_{3} \mathrm{COO}^{-}\right)$. Less familiar weak acids and bases may be included in the context of appropriate resource information. Values of $K_{\mathrm{b}}$ or $\mathrm{p} K_{\mathrm{b}}$ 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.

## Achievement Criteria - Acids and Bases

Demonstrate understanding of equilibrium principles in aqueous systems
Aqueous systems are limited to those involving acidic and basic solutions (in which proton transfer occurs).
$\square$ acidic and basic solutions (includes buffers)

## AS 91392

- acid/base strength, $K_{\mathrm{a}}\left(\mathrm{p} K_{\mathrm{a}}\right)$
- 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 feactions go to completion

## products

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



Time

## 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 evapourating 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 evapourate into gas at the same rate that gas condenses into a liquid.

open system

closed system


## Changes in Equilibrium

## A system stays in equilibrium unless a change is made

 A change made to a system in equilibrium will either

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

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.

## Aqueous Solutions

When a solid mixes into a liquid and can 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 wil continue to dissolve and precipitate.

## Sparingly Solubility

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


The solubility of a salt is often measured in grams per litre, $\mathrm{g} \mathrm{L}^{-1}$, or moles per litre, $\mathrm{mol} \mathrm{L}^{-1}$. 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.
$\mathrm{Ag}_{2} \mathrm{CrO}_{4(\mathrm{~s})} \leftrightarrow 2 \mathrm{Ag}^{+}{ }_{(\mathrm{aq})}+\mathrm{CrO}_{4}^{2-}{ }_{(\mathrm{aq})}$

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

## Solubility [s] and Concentration

At room temperature the solubility of silver chromate, $\mathrm{Ag}_{2} \mathrm{CrO}_{4}$, is $6.5 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1}$.

What is the concentration of $\mathrm{Ag}^{+}$and $\mathrm{CrO}_{4}{ }^{2-}$ ions $[\mathrm{s}]$ in 500 mL of a saturated solution?

Start with the equation for the dissolving process.
$\mathrm{Ag}_{2} \mathrm{CrO}_{4(\mathrm{~s})} \rightleftharpoons 2 \mathrm{Ag}^{+}{ }_{(\mathrm{aq})}+\mathrm{CrO}_{4}{ }^{2-}{ }_{(\mathrm{aq})}$
The equation shows that for every mole of dissolved solid there are 2 moles of $\mathrm{Ag}^{+}$ions and 1 mole of $\mathrm{CrO}_{4}{ }^{2-}$ ions. Therefore
$\left[\mathrm{Ag}^{+}\right]=2 \times 6.5 \times 10^{-5}=1.3 \times 10^{--9} \mathrm{~mol} \mathrm{~L}^{-1}$
$\left[\mathrm{CrO}_{4}{ }^{2-}\right]=6.5 \times 10^{-5} \mathrm{~mol} \mathrm{~L}{ }^{-1}$
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 $6.5 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1}$ (at room temperature).

## Solubility from $\mathrm{molL}^{-1}$ to $\mathrm{gL}^{-1}$

Example question: What is the solubility $[\mathrm{s}]$ of $\mathrm{Ag}_{2} \mathrm{CrO}_{4}$ in $\mathrm{g} \mathrm{L}^{-1}$ ?
To convert from moles per litre to grams per litre it is necessary to use the molar mass $M\left(\mathrm{Ag}_{2} \mathrm{CrO}_{4}\right)=332 \mathrm{~g} \mathrm{~mol}^{-1}$ and the relationship $\mathrm{m}=\mathrm{n} \times M$. $s=6.5 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1}$.

Since there is $6.5 \times 10^{-5}$ moles in 1 litre the number of grams in 1 litre would be mass $=6.5 \times 10^{-5} \times 332$
$=0.0216$ grams
and the concentration is $0.0216 \mathrm{~g} \mathrm{~L}^{-1}$.


## 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: $\mathrm{K}_{\mathrm{c}}$

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


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. $\mathrm{K}_{\mathrm{c}}=\frac{\left[\mathrm{NH}_{3}\right]^{2}}{\left[\mathrm{~N}_{2}\right] \times\left[\mathrm{H}_{2}\right]^{3}}$

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 $\mathrm{K}_{\mathrm{s}}$

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 $\mathrm{Ca}(\mathrm{OH})_{2}$. For this equilibrium, we have the solubility product expression:

$$
\mathrm{Ca}(\mathrm{OH})_{2(s)} \rightleftharpoons \mathrm{Ca}^{2+}{ }_{(a q)}+2 \mathrm{OH}_{(a q)}^{-}
$$

$$
K_{s}\left(\mathrm{Ca}(\mathrm{OH})_{2}\right)=\left[\mathrm{Ca}^{2+}\right]\left[\mathrm{OH}^{-}\right]^{2}
$$



## Solubility product $\mathrm{K}_{\mathrm{s}}$

Exercise: For each of the following sparingly soluble salts write the ëquation for the solid dissolving, calculate the concentration of each ion [s] and then the expression for the solubility product [Ks].
(a) $\mathrm{CaCO}_{3(5)} 1.3 \times 10^{-4} \mathrm{gL}^{-1}$
(b) $\mathrm{Ag}_{2} \mathrm{~S}_{(\mathrm{s})} 2.8 \times 10^{-3} \mathrm{gL}^{-1}$
(c) $\mathrm{Pbl}_{2(s)} 4.2 \times 10^{-5} \mathrm{gL}^{-1}$
(d) $\mathrm{Fe}(\mathrm{OH})_{3(s)} 6.4 \times 10^{-2} \mathrm{gL}{ }^{-1}$
$\mathrm{A} \rightleftharpoons \mathrm{cC}+\mathrm{dD}$
$\mathrm{K}_{\mathrm{s}}=[C]^{\mathrm{c}} \mathrm{x}[\mathrm{D}]^{\mathrm{d}}$
Remember: The solid salt is not included in the expression only the ions in aqueous state.
[ ] = concentration in $\mathrm{molL}^{-1}$ at equilibrium
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 Ks expression.

## Calculating $\mathrm{K}_{\mathrm{s}}$ : 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. $\quad \mathrm{AB}$ type of salt (ratio of cation to anion $=1: 1$ )

The solubility of $\mathrm{BaSO}_{4}$ is given as $1.05 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1}$ at $25^{\circ} \mathrm{C}$. Calculate the value of $K_{s}$.

$$
\mathrm{BaSO}_{4}(\mathrm{~s}) \quad \rightleftharpoons \mathrm{Ba}^{2+}(\mathrm{aq})+\mathrm{SO}_{4}{ }^{2-}(\mathrm{aq})
$$

From this equation $\left[\mathrm{Ba}^{2+}\right]=\left[\mathrm{SO}_{4}{ }^{2-}\right]=$ solubility, s
$K_{s}\left(\mathrm{BaSO}_{4}\right)=\left[\mathrm{Ba}^{2+}\right] \times\left[\mathrm{SO}_{4}{ }^{2-}\right]=\mathrm{s}^{2}=\left(1.05 \times 10^{-5}\right)^{2}$
$K_{s}=s^{2}$
$=1.10 \times 10^{-10}$
NOTE: This equality is only true if there are no other sources of $\mathrm{Ba}^{2+}$ and $\mathrm{SO}_{4}{ }^{2-}$ present in the solution ie if all the $\mathrm{Ba}^{2+}$ and $\mathrm{SO}_{4}{ }^{2-}$ ions come from the dissolved solid

Calculate the solubility product for $\mathrm{Pbl}_{2}$ at $25^{\circ} \mathrm{C}$, given the solubility at $25^{\circ} \mathrm{C}$ is $1.52 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}$.

$$
\mathrm{Pbl}_{2}(\mathrm{~s}) \quad \rightleftharpoons \quad \mathrm{Pb}^{2+}(\mathrm{aq}) \quad+\quad 2 \mathrm{I}^{-}(\mathrm{aq})
$$

This tells us that

$$
\left[\mathrm{Pb}^{2+}\right]=\text { solubility, } \mathrm{s}=1.52 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}
$$

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

The expression for $K_{s}$ is $K_{s}\left(\mathrm{Pbl}_{2}\right)=\left[\mathrm{Pb}^{2+}\right] \times[1-]^{2}$ and substituting for solubility we get
$K_{s}\left(\mathrm{PbI}_{2}\right)=\left(1.52 \times 10^{-3}\right) \times\left(3.04 \times 10^{-3}\right)^{2}=1.40 \times 10^{-8}$
$K_{s}=4 s^{3}$
NOTE: because $[2 \mathrm{~s}]^{2}$ means everything inside the brackets is squared then expanding it out becomes $2^{2}+s^{2}=4 s^{2}$. The other ion [s] then is multiplied so the whole expression becomes $4 s^{3}$ (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 $25^{\circ} \mathrm{C}$ given that

$$
\begin{array}{r}
\mathrm{FeS}(\mathrm{~s}) \rightleftharpoons \mathrm{Fe}^{2+}(\mathrm{aq})+\mathrm{S}^{2-}(\mathrm{aq}) \\
K_{\mathrm{s}}(\mathrm{FeS})=\left[\mathrm{Fe}^{2+}\right] \times\left[\mathrm{S}^{2-}\right]=6.3 \times 10^{-18}
\end{array}
$$

From the equation it can be seen that, since the only source of ions is from the dissolving of FeS
then $\left[\mathrm{Fe}^{2+}\right]=\left[\mathrm{S}^{2-}\right]=$ solubility, s
$\therefore K_{s}(\mathrm{FeS})=\mathrm{s}^{2}$ and $\mathrm{s}===2.51 \times 10^{-9} \mathrm{~mol} \mathrm{~L}^{-1}$

## Determining S from $\mathrm{K}_{\mathrm{s}}$ (2:1)

Calculate the solubility of zinc hydroxide at $25^{\circ} \mathrm{C}$ given $K_{s}\left(\mathrm{Zn}(\mathrm{OH})_{2}\right)$
$s=\frac{3}{\frac{3}{s}}$
$=2.0 \times 10^{-17}$
The dissolving equation is $\mathrm{Zn}(\mathrm{OH})_{2(\mathrm{~s})} \rightleftharpoons \mathrm{Zn}^{2+}{ }_{(\mathrm{aq})}+2 \mathrm{OH}^{-}{ }_{(\mathrm{aq})}$
This means that $\left[\mathrm{Zn}^{2+}\right]=$ solubility $=s \quad$ and $\quad\left[\mathrm{OH}^{-}\right]=2 x$ solubility $=2 \mathrm{~s}$
The expression for $K_{s}$ is $K_{s}\left(\mathrm{Zn}(\mathrm{OH})_{2}\right)=\left[\mathrm{Zn}^{2+}\right] \times\left[\mathrm{OH}^{-}\right]^{2}$
OR $\quad K_{s}\left(\mathrm{Zn}(\mathrm{OH})_{2}\right)=(\mathrm{s}) \times(2 \mathrm{~s})^{2}=4 \mathrm{~s}^{3}$
It is therefore possible to use this expression to solve for the solubility, s.

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

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

$$
\begin{aligned}
& {\left[\mathrm{Zn}^{2+}\right]=\text { solubility }=1.71 \times 10^{-6} \mathrm{~mol} \mathrm{~L}^{-1}} \\
& {\left[\mathrm{OH}^{-}\right]=2 \mathrm{~s}=2 \times 1.71 \times 10^{-6}=3.42 \times 10^{-6} \mathrm{~mol} \mathrm{~L}^{-1}}
\end{aligned}
$$

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

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

1. Write the ionic equation and expression
2. Calculate concentration (in $\mathrm{molL}^{-1}$ ) Use $\mathrm{n}=\mathrm{m} / \mathrm{M}$ and then $\mathrm{c}=\mathrm{n} / \mathrm{v}$ (remember volume $=\mathrm{L}$ and Mass $=\mathrm{g}$ ) $\quad$ Assume concentration (c) $=\mathrm{s}$
3. Calculate $\mathrm{Ks} \quad 1: 1$ salt $\mathrm{Ks}=[\mathrm{s}][\mathrm{s}]\left(\right.$ or $\left.\mathrm{s}^{2}\right) \quad 2: 1$ salt $\mathrm{Ks}=[2 \mathrm{~s}]^{2}[\mathrm{~s}]\left(\right.$ or $\left.4 \mathrm{~s}^{3}\right)$

Other questions may require you to calculate mass (of salt) given $\mathrm{Ks} \mathrm{or} \mathrm{s} .\mathrm{For} \mathrm{example:}$
Silver carbonate, $\mathrm{Ag}_{2} \mathrm{CO}_{31}$ is a sparingly soluble salt. $\quad K_{5}\left(\mathrm{Ag}_{2} \mathrm{CO}_{3}\right)=8.10 \times 10^{-12}$ at $25^{\circ} \mathrm{C}$ $M\left(\mathrm{Ag}_{2} \mathrm{CO}_{3}\right)=276 \mathrm{~g} \mathrm{~mol}^{-1}$
Calculate the mass of $\mathrm{Ag}_{2} \mathrm{CO}_{3}$ that will dissolve in 50 mL of water to make a saturated solution at $25^{\circ} \mathrm{C}$.

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

## Summary of solubility calculations - Q1

Question: Calculate $\mathrm{K}_{\mathrm{s}}$
Starting information:
Mass, Molar mass and Volume
Calculate c
$\mathrm{n}=\mathrm{m} / \mathrm{M}$ and then $\mathrm{c}=\mathrm{n} / \mathrm{v}$

Question: Calculate mass

## Starting information:

Ks and Molar Mass

Calculate s

$$
1: 1 \mathrm{~s}=\sqrt{ } \mathrm{Ks} \quad 2: 1 \quad \mathrm{~s}=3 \sqrt{\mathrm{~K}} / 4
$$

Assume concentration (c) =s

Calculate Ks
1:1 salt $\mathrm{Ks}=[\mathrm{s}][\mathrm{s}]$ (or s${ }^{2}$ )
2:1 salt Ks = [2s] ${ }^{2}[\mathrm{~s}]\left(\right.$ or $\left.4 s^{3}\right)$

Calculate Mass

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

then $m=n \times M$

## Adding or removing products

# Neutralisation <br> i.e. adding acid to $\mathrm{CO}_{3}{ }^{2-}$ ions <br> Forming complex ions <br>  <br> Increase solubility <br> Salt <br> $\rightleftharpoons$ ions <br> Adding more product <br> <br> decrease solubility <br> <br> decrease solubility <br> i.e. adding base ( pH below 10) to increase $\mathrm{OH}^{-}$ions 

Increasing solubility
Neutralisation
decreasing solubility
Adding more product

## Analysing the $\mathrm{K}_{\mathrm{s}}$ value

The $\mathrm{K}_{\mathrm{s}}$ value is an indication of position of the equilibrium. A small $\mathrm{K}_{\mathrm{s}}$ indicates more reactants (solid salt) therefore less solubility. A larger $\mathrm{K}_{\mathrm{s}}$ indicates more products (ions) therefore more solubility


Some questions will ask you to discuss the solubility of a system in different conditions. The conditions will impact the concentration of the products, either adding or removing. In all cases link this to a shift in the equilibrium position. A shift to the right causes increased solubility. A shift to the left causes decreased solubility.

## Effects of Acid on Solubility

If the salt contains a carbonate i.e. $\mathrm{Ag}_{2} \mathrm{CO}_{3}$ which is sparingly soluble, it will dissociate into its ions - one ion being a cation and the other the anion carbonate.

$$
\mathrm{Ag}_{2} \mathrm{CO}_{3} \rightleftharpoons \mathrm{Ag}^{+}+\mathrm{CO}_{3}^{2-}
$$

## 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 $\mathrm{Ag}^{+}$which reacts with $\mathrm{NH}_{3}$ or OH - to produce a complex ion such as $\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}\right]^{+}$

## 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 SOLUBHLITY

If a sparingly soluble salt conntains hydroxide i.e. $\mathrm{Zn}(\mathrm{OH})_{2}$, 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

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

## Possible Complex Ions

The following complex ion formula will be provided in the Resource Booklet when sitting Examinations

| $\left[\mathrm{Ag}(\mathrm{CN})_{2}\right]^{-}$ | $\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$ |
| :--- | :---: |
| $\left[\mathrm{Al}(\mathrm{OH})_{4}\right]^{-}$ | $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$ |
| $\left[\mathrm{Pb}(\mathrm{OH})_{4}\right]^{2-}$ | $\left[\mathrm{Zn}(\mathrm{OH})_{4}\right]^{2-}$ |
| $\left[\mathrm{Zn}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$ | $\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}$ |
| $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$ |  |

## Summary of Equilibrium changes in Solubility - Q2

$$
\left.\mathrm{Zn}(\mathrm{OH})_{2(s)} \rightleftharpoons \mathrm{Zn}^{2+}{ }_{(a q)}+2 \mathrm{OH}_{(a q)}^{-}\right)
$$

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 $\mathrm{OH}^{-}$


Total OH - concentration increases, therefore more product.

Reverse reaction increases
Solubility decreases
pH is above 10


Complex ion forms, and removes product., by removing $\mathrm{Zn}^{2+}$ ions.

Forward reaction increases
Solubility increases

Remove product - solubility increases. Add to product - solubility decreases

Question: 2a: In an experiment, a saturated solution was made by dissolving $1.44 \times 10^{-3} \mathrm{~g}$ of $\mathrm{Ag}_{2} \mathrm{CrO}_{4}$ in water, and making it up to a volume of 50.0 mL .
$\mathrm{M}\left(\mathrm{Ag}_{2} \mathrm{CrO}_{4}\right)=332 \mathrm{~g} \mathrm{~mol}^{-1}$

$$
K_{\mathrm{s}}=\left[\mathrm{Ag}^{+}\right]^{2}\left[\mathrm{CrO}_{4}{ }^{2-}\right]
$$

(a) Write the $K_{5}$ expression for $\mathrm{Ag}_{2} \mathrm{CrO}_{4(s)}$.

## NCEA 2013 solubility

Question: 2b: In an experiment, a saturated solution was made by dissolving $1.44 \times 10^{-3} \mathrm{~g}$ of $\mathrm{Ag}_{2} \mathrm{CrO}_{4}$ in water, and making it up to a volume of 50.0 mL . $\quad \mathrm{M}\left(\mathrm{Ag}_{2} \mathrm{CrO}_{4}\right)=332 \mathrm{~g} \mathrm{~mol}^{-1}$
(i) Calculate the solubility of $\mathrm{Ag}_{2} \mathrm{CrO}_{4(s)^{\prime}}$, and hence give the $\left[\mathrm{Ag}^{+}\right]$and $\left[\mathrm{CrO}_{4}{ }^{2-}\right]$ in the solution.
$K_{\mathrm{s}}=\left[\mathrm{Ag}^{+}\right]^{2}\left[\mathrm{CrO}_{4}{ }^{2-}\right]$
$n\left(\mathrm{Ag}_{2} \mathrm{CrO}_{4}\right)=\frac{1.44 \quad 10^{3}}{332}$

$$
=4.33 \quad 10{ }^{6} \mathrm{~mol} \text { in } 50 \mathrm{~mL}
$$

$\left[\mathrm{Ag}_{2} \mathrm{CrO}_{4}\right]=\frac{4.3310^{6}}{50 \quad 10^{3}}$

$$
=8.67 \quad 10^{5} \mathrm{~mol} \mathrm{~L}^{1}
$$

$\left[\mathrm{Ag}^{+}\right]=8.67 \quad 10^{5} \quad 2=1.73 \quad 10^{4} \mathrm{~mol} \mathrm{~L}^{1}$
$\left[\mathrm{CrO}_{4}^{2}\right]=8.67 \quad 10{ }^{5} \mathrm{~mol} \mathrm{~L}^{1}$
(ii) Determine the $\mathrm{Ks}\left(\mathrm{Ag}_{2} \mathrm{CrO}_{4}\right)$.

$$
\begin{aligned}
& K_{\mathrm{s}}=\left(\begin{array}{ll}
1.73 & 10^{4}
\end{array}\right)^{2}\left(\begin{array}{ll}
8.67 & 10^{5}
\end{array}\right) \\
& =2.61 \quad 10^{12}
\end{aligned}
$$

## NCEA 2014 solubility

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

$$
\mathrm{PbCl}_{2(s)} \rightleftharpoons \mathrm{Pb}^{2+}{ }_{(a q)}+2 \mathrm{Cl}_{(a q)}
$$

Question: 2a: (ii) Write the expression for $K_{\mathrm{s}}\left(\mathrm{PbCl}_{2}\right)$.

$$
K_{\mathrm{s}}=\left[\mathrm{Pb}^{2+}\right]\left[\mathrm{Cl}^{-}\right]^{2}
$$

Question: 2a: (iii) Calculate the solubility (in $\mathrm{mol}^{-1}$ ) of lead(II) chloride in water at $25^{\circ} \mathrm{C}$, and give the $\left[\mathrm{Pb}^{2+}\right]$ and $\left[\mathrm{Cl}^{-}\right]$in the solution. $K_{\mathrm{s}}\left(\mathrm{PbCl}_{2}\right)=1.70 \times 10^{-5}$ at $25^{\circ} \mathrm{C}$

$$
\begin{aligned}
& {\left[\mathrm{Pb}^{2+}\right]=x \quad\left[\mathrm{Cl}^{-}\right]=} \\
& 2 x \\
& K_{\mathrm{s}}=4 x^{3} \\
& x=\sqrt[3]{\frac{K_{\mathrm{s}}}{4}} \\
& =\sqrt[3]{\frac{1.7010^{5}}{4}} \\
& =1.62 \quad 10^{2} \mathrm{~mol} \mathrm{~L}^{1}
\end{aligned}
$$

$$
\left[\mathrm{Pb}^{2+}\right]=1.62 \times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1}
$$

$$
\left[\mathrm{Cl}^{-}\right]=3.24 \times 10^{-} \mathrm{mol} \mathrm{~L}^{-1}
$$

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

Write the equation for the equilibrium occurring in a saturated solution of $\mathrm{CaCO}_{3}$.

$$
\mathrm{CaCO}_{3}(\mathrm{~s}) \rightleftharpoons \mathrm{Ca}^{2+}(a q)+\mathrm{CO}_{3}^{2-}(a q)
$$

Question: 2a: (ii) Write the expression for $\mathrm{Ks}\left(\mathrm{CaCO}_{3}\right)$.

$$
K_{\mathrm{s}}=\left[\mathrm{Ca}^{2+}\right]\left[\mathrm{CO}_{3}{ }^{2-}\right]
$$

Question: 2a: (iii) Calculate the solubility product of $\mathrm{CaCO}_{3}, \mathrm{~K}_{\mathrm{s}}\left(\mathrm{CaCO}_{3}\right)$.
The solubility of $\mathrm{CaCO}_{3}$ is $5.74 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1}$.

## $K_{\mathrm{s}}\left(\mathrm{CaCO}_{3}\right)=\left(5.74 \times 10^{-5}\right)^{2}=3.29 \times 10^{-9}$

## NCEA 2016 Solubility

Question: 1a: Silver carbonate, $\mathrm{Ag}_{2} \mathrm{CO}_{3}$, is a sparingly soluble salt. $K_{5}\left(\mathrm{Ag}_{2} \mathrm{CO}_{3}\right)=8.10 \times 10^{-12}$ at $25^{\circ} \mathrm{C} \quad M\left(\mathrm{Ag}_{2} \mathrm{CO}_{3}\right)=276 \mathrm{~g} \mathrm{~mol}^{-1}$
(a) Write the solubility product expression, $K_{5^{\prime}}$ for silver carbonate $\left(\mathrm{Ag}_{2} \mathrm{CO}_{3}\right)$.

## NCEA 2016 Solubility

Question: 1b: Silver carbonate, $\mathrm{Ag}_{2} \mathrm{CO}_{3}$, is a sparingly soluble salt.
$K_{5}\left(\mathrm{Ag}_{2} \mathrm{CO}_{3}\right)=8.10 \times 10^{-12}$ at $25^{\circ} \mathrm{C} \quad M\left(\mathrm{Ag}_{2} \mathrm{CO}_{3}\right)=276 \mathrm{~g} \mathrm{~mol}^{-1}$
Calculate the mass of $\mathrm{Ag}_{2} \mathrm{CO}_{3}$ that will dissolve in 50 mL of water to make a saturated solution at $25^{\circ} \mathrm{C}$.

$$
\begin{aligned}
& \text { Let } s=\text { solubility } \\
& {\left[\mathrm{Ag}^{+}\right]=2 s} \\
& {\left[\mathrm{CO}_{3}{ }^{2-}\right]=s} \\
& \quad K_{s}=4 s^{3} \\
& s=1.27 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1} \\
& n=c \times v=6.33 \times 10^{-6} \mathrm{~mol} \\
& m=n \times M=1.75 \times 10^{-3} \mathrm{~g}
\end{aligned}
$$

## OR

$g L^{-1}=c \times M=0.0349 \mathrm{~g} \mathrm{~L}^{-1}$
so mass in $50 \mathrm{~mL}=$
$\frac{0.0349 \quad 50}{1000}$
$=1.75 \times 1^{-3} \mathrm{~g}$

## Question 1b:

(i) Write the equation for the equilibrium occurring in a saturated solution of copper(II) hydroxide, $\mathrm{Cu}(\mathrm{OH})_{2}$.
(ii) Write the expression for $K_{s}\left(\mathrm{Cu}(\mathrm{OH})_{2}\right)$.
(iii) Calculate the solubility of $\mathrm{Cu}(\mathrm{OH})_{2}$ in water at $25^{\circ} \mathrm{C}$.
$K_{s}\left(\mathrm{Cu}(\mathrm{OH})_{2}\right)=4.80 \times 10^{-20}$
Let $s=$ solubility
$\left[\mathrm{Cu}^{2+}\right]=s$
[OH-]2 $=(2 s)^{2}$
$K s=4 s^{3}$
$4 s^{3}=4.80 \times 10^{-20}$
So; $s=2.29 \times 10^{-7} \mathrm{~mol} \mathrm{~L}^{-1}$

## NCEA 2018 Solubility

Question: 1b (i). Write the equation for the equilibrium occurring in a saturated solution of calcium fluoride, $\mathrm{Ca} \mathrm{F}_{2}$.

Question: 1b (ii). Calculate the solubility of $\mathrm{Ca} \mathrm{F}_{2}$ in water at $25^{\circ} \mathrm{C}$.
$K_{\mathrm{s}}\left(\mathrm{Ca} \mathrm{F}_{2}\right)=3.20 \times 10^{-11}$

$$
\begin{aligned}
& \mathrm{CaF}_{2} \rightleftharpoons \mathrm{Ca}^{2+}+2 \mathrm{~F}^{-} \\
& \mathrm{K}_{\mathrm{s}}=\left[\mathrm{Ca}^{2+}\right]\left[\mathrm{F}^{-}\right]^{2}
\end{aligned}
$$

Let solubility be ' $s$ ':
$\left[\mathrm{Ca}^{2+}\right]=s \quad\left[\mathrm{~F}^{-}\right]=2 s$
$K_{\mathrm{s}}=4 s^{3}$
$s=\sqrt[3]{\left(\frac{3.20 \times 10^{-11}}{4}\right)}$
$=2.00 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1}$

## NCEA 2019 Solubility

Question: 1a (i). Write the equation for the equilibrium occurring in a saturated solution of zinc hydroxide, $\mathrm{Zn}(\mathrm{OH})_{2}$.
(ii) Write the expression for $K_{\mathrm{s}}\left(\mathrm{Zn}(\mathrm{OH})_{2}\right)$.
(iii) Calculate the solubility of $\mathrm{Zn}(\mathrm{OH})_{2}$ in water at $25^{\circ} \mathrm{C}$, and give the $\left[\mathrm{Zn}^{2+}\right]$ and $\left[\mathrm{OH}^{-}\right]$in the solution.
$K_{\mathrm{s}}\left(\mathrm{Zn}(\mathrm{OH})_{2}\right)=3.80 \times 10^{-17}$
$\mathrm{Zn}(\mathrm{OH})_{2} \rightleftharpoons \mathrm{Zn}^{2+}+2 \mathrm{OH}^{-}$
$K_{\mathrm{s}}=\left[\mathrm{Zn}^{2+}\right]\left[\mathrm{OH}^{-}\right]^{2}$
Let solubility be ' $s$ ':
$\left[\mathrm{Zn}^{2+}\right]=s \quad\left[\mathrm{OH}^{-}\right]=2 s$
$K_{\mathrm{s}}=4 s^{3}$
$4 s^{3}=3.80 \times 10^{-17}$
$s=2.12 \times 10^{-6} \mathrm{~mol} \mathrm{~L}^{-1}$
$\left[\mathrm{Zn}^{2+}\right]=2.12 \times 10^{-6} \mathrm{~mol} \mathrm{~L}^{-1}$
$\left[\mathrm{OH}^{-}\right]=4.24 \times 10^{-6} \mathrm{~mol} \mathrm{~L}^{-1}$

## NCEA 2020 Solubility

Question: 2a (i). Write the equation for the equilibrium occurring in a saturated solution of lead bromide, $\mathrm{PbBr}_{2}$.
(ii) Write the expression for $\mathrm{K}_{5}\left(\mathrm{PbBr}_{2}\right)$.
(iii) Calculate the solubility of $\mathrm{PbBr}_{2}$ in water at $25^{\circ} \mathrm{C} . \quad \mathrm{K}_{5}\left(\mathrm{PbBr}_{2}\right)=2.10 \times 10^{-6}$
$\mathrm{PbBr}_{2} \rightleftharpoons \mathrm{~Pb}^{2+}+2 \mathrm{Br}$

$$
K_{\mathrm{s}}=\left[\mathrm{Pb}^{2+}\right]\left[\mathrm{Br}^{2}\right]^{2}
$$

Let solubility be 's':

$$
\begin{aligned}
& {\left[\mathrm{Pb}^{2+}\right]=s \quad\left[\mathrm{Br}^{-}\right]=2 s} \\
& K_{\mathrm{s}}=4 s^{3} \\
& 4 s^{3}=2.10 \times 10^{-6} \\
& s=8.07 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}
\end{aligned}
$$



## NCEA 2020 Solubility

Question: 2c (ii). Calculate the solubility of a saturated solution of nickel hydroxide at pH 8.25 .
$\mathrm{K}_{\mathrm{s}}\left(\mathrm{Ni}(\mathrm{OH})_{2}\right)=6.00 \times 10^{-16}$

$$
\begin{aligned}
& \mathrm{Ni}(\mathrm{OH})_{2} \rightleftharpoons \mathrm{Ni}^{2+}+2 \mathrm{OH}^{-} \quad K_{\mathrm{s}}=\left[\mathrm{Ni}^{2+}\right]\left[\mathrm{OH}^{-}\right]^{2} \\
& {\left[\mathrm{OH}^{-}\right]=\mathrm{K}_{\mathrm{w}} /\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1 \times 10^{-14} / 10^{-8.25}=1.78 \times 10^{-6} \mathrm{~mol} \mathrm{~L}^{-1}} \\
& \mathrm{~K}_{\mathrm{s}}=\left[\mathrm{Ni}^{2+}\right]\left[\mathrm{OH}^{-}\right]^{2} \\
& 6.00 \times 10^{-16}=\left[\mathrm{Ni}^{2+}\right] \times\left(1.78 \times 10^{-6}\right)^{2} \\
& {\left[\mathrm{Ni}^{2+}\right]=1.90 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1}}
\end{aligned}
$$

## NCEA 2013 solubility and Equilibrium

Question: 2c: In another experiment, 0.0100 g of $\mathrm{Ag}_{2} \mathrm{CrO}_{4}$ in beaker A was made up to a volume of 50.0 mL with water. In beaker $\mathrm{B}, 0.0100 \mathrm{~g}$ of $\mathrm{Ag}_{2} \mathrm{CrO}_{4}$ was made up to a volume of 50.0 mL with $0.100 \mathrm{~mol} \mathrm{~L}^{-1}$ ammonia solution. Compare and contrast the solubility of $\mathrm{Ag}_{2} \mathrm{CrO}_{4}$ in beaker A and beaker B.


Beaker A


Beaker B

Dissolving 0.0100 g of silver chromate in 50 mL water will result in solid being present, as the required amount to make a saturated solution is $1.44 \times 10^{-3} \mathrm{~g}$ 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 $\mathrm{Ag}_{2} \mathrm{CrO}_{4}$ will dissociate completely and form an equilibrium.
$\mathrm{Ag}_{2} \mathrm{CrO}_{4} \rightleftharpoons 2 \mathrm{Ag}^{+}+\mathrm{CrO}_{4}{ }^{2-}$
$\mathrm{Ag}^{+}+2 \mathrm{NH}_{3} \rightarrow\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}\right]^{+}$
The silver ion will then react further with $\mathrm{NH}_{3}$, removing it from the above equilibrium. Thus, more $\mathrm{Ag}_{2} \mathrm{CrO}_{4}$ will dissolve to re-establish equilibrium.

## NCEA 2014 solubility and equilibrium

Question: 2 c : The solubility of zinc hydroxide, $\mathrm{Zn}(\mathrm{OH})_{2}$, can be altered by changes in pH . Some changes in pH may lead to the formation of complex ions, such as the zincate ion, $\left[\mathrm{Zn}(\mathrm{OH})_{4}\right]^{--}$
Use equilibrium principles to explain why the solubility of zinc hydroxide increases when the pH is less than 4 or greater than 10.
$\mathrm{Zn}(\mathrm{OH})_{2}(s) \rightleftharpoons \mathrm{Zn}^{2+}(a q)+2 \mathrm{OH}^{-}(a q) \quad$ When pH is less than $4 /$ low, $\left[\mathrm{OH}^{-}\right]$is decreased due to the reaction with $\mathrm{H}_{3} \mathrm{O}^{+}$to form water,
$\mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}$ so equilibrium shifts to the right to produce more [ $\mathrm{OH}^{-}$], therefore more $\mathrm{Zn}(\mathrm{OH})_{2}$ will dissolve.

When pH is greater than 10 / high, then more $\mathrm{OH}^{-}$is available and the complex ion (zincate ion) will form.
$\mathrm{Zn}(\mathrm{OH})_{2}(\mathrm{~s})+2 \mathrm{OH}^{-} \rightarrow\left[\mathrm{Zn}(\mathrm{OH})_{4}\right]^{2-} \quad \mathrm{OR} \mathrm{Zn} 2+4 \mathrm{OH}^{-} \rightarrow\left[\mathrm{Zn}(\mathrm{OH})_{4}\right]^{2-}$
This decrease in $\left[\mathrm{Zn}^{2+}\right]$ causes the position of equilibrium to shift further to the right, therefore more $\mathrm{Zn}(\mathrm{OH})_{2}$ 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 $\mathrm{CaCO}_{3}$ is higher in an acidic solution.
Use an equation to support your explanation.

The $\mathrm{H}_{3} \mathrm{O}^{+}$from the acidic solution reacts with the $\mathrm{CO}_{3}{ }^{2-}$. This reduces $\left[\mathrm{CO}_{3}{ }^{2-}\right]$, causing the equilibrium to shift towards the products / RHS to replace some of the lost $\mathrm{CO}_{3}{ }^{2-}$. Therefore more solid $\mathrm{CaCO}_{3}$ will dissolve.

$$
2 \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{CO}_{3}^{2-} \rightarrow 3 \mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}
$$

## NCEA 2016 Solubility and equilibrium

Question: 1c: Explain how the solubility of $\mathrm{Ag}_{2} \mathrm{CO}_{3}$ will change if added to 50 mL of a $1.00 \mathrm{~mol} \mathrm{~L}^{-1}$ ammonia, $\mathrm{NH}_{3}$, solution.

Support your answer with balanced equations.
$\mathrm{Ag}_{2} \mathrm{CO}_{3(\mathrm{~s})} \rightarrow 2 \mathrm{Ag}^{+}{ }_{(\mathrm{aq})}+\mathrm{CO}_{3}{ }^{2-}{ }_{(\mathrm{aq})}$
$\mathrm{Ag}^{+}{ }_{(\mathrm{aq})}+2 \mathrm{NH}_{3(\mathrm{aq})} \leftrightharpoons\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}\right]_{(\mathrm{aq})}$
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

## NCEA 2017 Solubility and equilibrium

## Question 1b:

(i) 40.0 mL of $0.150 \mathrm{~mol} \mathrm{~L}-1 \mathrm{HBr}$ 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.
$\mathrm{AgBr} \leftrightharpoons \mathrm{Ag}^{+}+\mathrm{Br}^{-}$
Br is a common ion / added to solution
An increase in $[\mathrm{Br}]$ will result in the reverse reaction being favoured, to restore equilibrium / minimise the change.

This results in a decrease in $\left[\mathrm{Ag}^{+}\right]$(since $\mathrm{Ag}^{+}$reacts with some of the added Br to help use it up) / AgBr becomes less soluble, (until $\left[\mathrm{Ag}^{+}\right][\mathrm{Br}]$ is again equal to Ks .)

## NCEA 2017 Solubility and equilibrium

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

When copper(II) hydroxide is dissolved in an acidic solution, the $\mathrm{H}_{3} \mathrm{O}^{+}$ions neutralise
the $\mathrm{OH}^{-}$ions $/ \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}$
A decrease in $\left[\mathrm{OH}^{-}\right]$will result in the forward reaction being favoured, to restore equilibrium / minimise the change.

This causes more solid $\mathrm{Cu}(\mathrm{OH})_{2}$ to dissolve, i.e. the solubility of $\mathrm{Cu}(\mathrm{OH})_{2}$ increases /
so that $\left[\mathrm{Cu}^{2+}\right]\left[\mathrm{OH}^{-}\right]$will again equal K .

## NCEA 2018 Solubility and Equilibrium

Question: 1c. Explain the effect of the following on the solubility of iron(III) hydroxide, $\mathrm{Fe}(\mathrm{OH})_{3}$, in water.
Include relevant equation(s) in your answer. No calculations are necessary.
(i) pH lowered below 4

In a saturated solution:
$\mathrm{Fe}(\mathrm{OH})_{3} \rightleftharpoons \mathrm{Fe}^{3+}+3 \mathrm{OH}^{-}$
As the pH is lowered, $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$increases. The $\mathrm{H}_{3} \mathrm{O}^{+}$will remove and neutralise $\mathrm{OH}^{-} /$
$\mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}$
A decrease in $\left[\mathrm{OH}^{-}\right]$will result in the forward reaction being favoured, to restore equilibrium / minimise the change.

This causes more solid $\mathrm{Fe}(\mathrm{OH})_{3}$ to dissolve, i.e. the solubility of $\mathrm{Fe}(\mathrm{OH})_{3}$ increases / so that $\left[\mathrm{Fe}^{3+}\right]\left[\mathrm{OH}^{-]}\right.$will again equal $K_{s}$.

## NCEA 2018 Solubility and Equilibrium

Question: 1c. Explain the effect of the following on the solubility of iron(III) hydroxide, $\mathrm{Fe}(\mathrm{OH})_{3}$, 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 $\mathrm{Fe}^{3+}$ ions:
$\mathrm{Fe}^{3+}+\mathrm{SCN}^{-} \rightarrow[\mathrm{FeSCN}]^{2+}$
Since the $\mathrm{Fe}^{3+}$ are removed from the equilibrium, more $\mathrm{Fe}(\mathrm{OH})_{3}$ dissolves to replace some of the $\mathrm{Fe}^{3+}$, i.e. equilibrium will shift towards the products / speed up the forward reaction. As a result, the solubility of $\mathrm{Fe}(\mathrm{OH})_{3}$ increases.

## NCEA 2018 Solubility and Equilibrium

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, $\mathrm{AgNO}_{3}$, solution is added to a saturated solution of AgCl ?

Explain your answer.
$K s=\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right]$
The $\mathrm{Ag}^{+}$is a common ion. By increasing $\left[\mathrm{Ag}^{+}\right]$, the equilibrium will shift towards the reactants to use up some of the extra $\mathrm{Ag}^{+}$, so more solid AgCl will form, i.e. the solubility of AgCl will decrease.

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

## NCEA 2019 Solubility and Equilibrium

Question: 1b Use equilibrium principles to explain why the solubility of $\mathrm{Zn}(\mathrm{OH})_{2}$ increases when an excess of dilute sodium hydroxide, NaOH , is added.

Include relevant equation(s) in your answer.
$\mathrm{Zn}(\mathrm{OH})_{2} \rightleftharpoons \mathrm{Zn}^{2+}+2 \mathrm{OH}^{-}$
When the $\mathrm{OH}^{-}$ions are in excess, the $\mathrm{Zn}^{2+}$ ions can form a complex ion:
$\mathrm{Zn}^{2+}+4 \mathrm{OH}^{-} \rightarrow\left[\mathrm{Zn}(\mathrm{OH})_{4}\right]^{2-}$
A decrease in $\left[\mathrm{Zn}^{2+}\right]$ will result in the forward reaction being favoured, to restore equilibrium / minimise the change.

This causes more solid $\mathrm{Zn}(\mathrm{OH})_{2}$ to dissolve / the solubility of $\mathrm{Zn}(\mathrm{OH})_{2}$
 increases / so that $\left[\mathrm{Zn}^{2+}\right]\left[\mathrm{OH}^{-}\right]$will again equal $K_{s}$.

## NCEA 2020 Solubility and Equilibrium

Question: 2c (i) Explain the effect of the following on the solubility of nickel hydroxide, $\mathrm{Ni}(\mathrm{OH})_{2}$, in water.
Include relevant equation(s) in your answer. No calculations are necessary.

- Ammonia solution, $\mathrm{NH}_{3(\mathrm{aq})}$, is added:
$\mathrm{Ni}(\mathrm{OH})_{2} \rightleftharpoons \mathrm{Ni}^{2+}+2 \mathrm{OH}^{-}$
When ammonia solution is added, the $\mathrm{Ni}^{2+}$ ions ar removed from the saturated solution to form a complex ion, as shown below:
$\mathrm{Ni}^{2+}+6 \mathrm{NH}_{3} \rightarrow\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}$
To restore the equilibrium, more solid $\mathrm{Ni}(\mathrm{OH})_{2}$ dissolves to replace some of the $\mathrm{Ni}^{2+}$ / increase

$\left[\mathrm{Ni}^{2+}\right]$. Therefore the solubility of $\mathrm{Ni}(\mathrm{OH})_{2}$ increases.


## NCEA 2020 Solubility and Equilibrium

Question: 2c (i) Explain the effect of the following on the solubility of nickel hydroxide, $\mathrm{Ni}(\mathrm{OH})_{2}$, in water.

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

- The pH is decreased below 4 :

$$
\mathrm{Ni}(\mathrm{OH})_{2} \rightleftharpoons \mathrm{Ni}^{2+}+2 \mathrm{OH}^{-}
$$

When the pH is decreased below $\mathrm{pH} 4,\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ increases. The $\mathrm{H}_{3} \mathrm{O}^{+}$remove the $\mathrm{OH}^{-}$from the equilibrium according to the neutralisation equation below:


$$
\mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}
$$

To restore the equilibrium, more solid $\mathrm{Ni}(\mathrm{OH})_{2}$ dissolves to replace some of the $\mathrm{OH}^{-}$/ increase
$\left[\mathrm{OH}^{-}\right]$. Therefore the solubility of $\mathrm{Ni}(\mathrm{OH})_{2}$ increases.

## Ionic product

 products and reactants is called Q.In any solution, whether it is saturated ornot, such as AgCl the product formed $\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right]$is called the ionic product and can not exceed the $\mathrm{K}_{\mathrm{s}}$. If either $\mathrm{Ag}^{+}$ions or $\mathrm{Cl}^{-}$ions are added from another source, such as by adding NaCl , and the new concentrations of ions exceed the $\mathrm{K}_{\mathrm{s}}$ then a precipitate will form.

## Example

What is the minimum concentration of $\mathrm{Cl}^{-}$ions to give a precipitate of AgCl ? $\mathrm{c}\left(\mathrm{AgNO}_{3}\right)=0.01 \mathrm{molL}^{-1} \quad \mathrm{~K}_{\mathrm{s}}=2 \times 10^{-10}$
If IP $>\mathrm{Ks}$ then precipitate will form

1. $\mathrm{AgCl}_{(\mathrm{s})} \rightleftharpoons \mathrm{Ag}^{+}{ }_{(\mathrm{aq})}+\mathrm{Cl}_{(\mathrm{aq})}$
2. $\mathrm{K}_{\mathrm{s}}=\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right] \quad \mathrm{K}_{\mathrm{s}}=[0.01][\mathrm{Cl}]$
3. Rearrange $\mathrm{K}_{\mathrm{s}}=\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right]$

$$
[\mathrm{Cl}]=\frac{\mathrm{K}_{\mathrm{s}}}{[0.01]} \quad \frac{=2 \times 10^{-10}}{0.01} \quad=2 \times 10^{-8}
$$

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

## 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

$$
\mathrm{AgCl}(\mathrm{~s}) \rightleftharpoons \mathrm{Ag}^{+}(\mathrm{aq}) \quad+\mathrm{Cl}^{-}(\mathrm{aq})
$$

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

extra Clions present in sea water

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

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

$\left[\mathrm{Ag}^{+}\right]=$solubility, $s$ of the AgCl since the only source of silver ions is from dissolved AgCl . $\left[\mathrm{Cl}^{-}\right]=0.0025+\mathrm{s} \quad$ since the final concentration of $\mathrm{Cl}^{-}$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 $\left[\mathrm{Cl}^{-}\right]=0.0025$

$$
\begin{aligned}
& \text { Ks }(\mathrm{AgCl})=s \times 0.0025=1.6 \times 10^{-10} \\
& \text { and } \quad s=\frac{1.6 \times 10^{-10}}{0.0025}
\end{aligned}
$$

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

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

## Summary of Common ion calculations - Q3

$\mathrm{Q}=$ ratio of the concentrations of products and reactants.
Ks is the maximum concentration of ions the solution can hold (at a given temperature)

1:1 salt

$$
\mathrm{Q}=(\mathrm{c}) \times(\mathrm{c})
$$

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



## NCEA 2014 common ion effect

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

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. $K_{\mathrm{s}}\left(\mathrm{PbCl}_{2}\right)=1.70 \times 10^{-5} \mathrm{M}\left(\mathrm{Pb}\left(\mathrm{NO}_{3}\right)_{2}\right)=331 \mathrm{~g} \mathrm{~mol}^{-1}$

$$
\begin{aligned}
& n\left(\mathrm{~Pb}\left(\mathrm{NO}_{3}\right)_{2}\right)=\frac{2.00 \mathrm{~g}}{331 \mathrm{~g} \mathrm{~mol}^{1}} \\
& =6.04 \times 10^{-3} \mathrm{~mol} \\
& \therefore\left[\mathrm{~Pb}^{2+}\right]=6.04 \times 10^{-3} \mathrm{~mol} / 0.500 \mathrm{~L} \\
& =1.21 \times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1} \\
& Q=\left(1.21 \times 10^{-2}\right) \times(0.440)^{2} \\
& =2.34 \times 10^{-3} \\
& \text { As } Q>K_{s^{\prime}} \text { a precipitate will form. }
\end{aligned}
$$

Question: 2c: Show, by calculation, that a precipitate of lead(II) hydroxide, $\mathrm{Pb}(\mathrm{OH})_{2}$, will form when 25.0 mL of a sodium hydroxide solution, NaOH , at pH 12.6 is added to 25.0 mL of a $0.00421 \mathrm{~mol}^{-1}$ lead(II) nitrate, $\mathrm{Pb}\left(\mathrm{NO}_{3}\right)_{2}$, solution. $K_{5}\left(\mathrm{~Pb}(\mathrm{OH})_{2}\right)=8.00 \times 10^{-17}$ at $25^{\circ} \mathrm{C}$

## The ratio of the concentrations of

 products and reactants is called Q.$$
\begin{aligned}
& \mathrm{Pb}(\mathrm{OH})_{2} \rightleftharpoons \mathrm{~Pb}^{2+}+2 \mathrm{OH}^{-} \\
& Q=\left[\mathrm{Pb}^{2+}\right]\left[\mathrm{OH}^{-}\right]^{2} \\
& {\left[\mathrm{~Pb}^{2+}\right]=0.5 \times 0.00421=2.105 \times 10^{-3}} \\
& {\left[\mathrm{OH}^{-}\right]=0.5 \times 0.0398=1.99 \times 10^{-2}} \\
& Q=\left(2.105 \times 10^{-3}\right) \times\left(1.99 \times 10^{-2}\right)^{2} \\
& Q=8.34 \times 10^{-7}
\end{aligned}
$$

$$
\begin{array}{|l|}
\hline \mathrm{pH}=12.6 \\
\mathrm{pOH}=1.4 \\
{\left[\mathrm{OH}^{-}\right]=0.0398} \\
\hline
\end{array}
$$

Since $Q>K_{s^{\prime}}$ a precipitate of $\mathrm{Pb}(\mathrm{OH})_{2}$ will form.

Question: 1d: Show by calculation whether a precipitate of $\mathrm{Ag}_{2} \mathrm{CO}_{3}$ will form when 20.0 mL of $0.105 \mathrm{~mol}^{-1}$ silver nitrate, $\mathrm{AgNO}_{3}$, solution is added to 35.0 mL of a $0.221 \mathrm{~mol} \mathrm{~L}{ }^{-1}$ sodium carbonate, $\mathrm{Na}_{2} \mathrm{CO}_{3}$, solution.
$K_{5}\left(\mathrm{Ag}_{2} \mathrm{CO}_{3}\right)=8.10 \times 10^{-12}$ at $25^{\circ} \mathrm{C}$
$\mathrm{AgNO}_{3}$ dilution: $\quad \frac{20}{55} \quad 0.105=0.0382$
$\mathrm{Na}_{2} \mathrm{CO}_{3}$ dilution: $\quad \frac{35}{55} 0.221=0.141$
Q / I.P. $=[0.03818]^{2}[0.1406]=2.06 \times 10^{-4}$
As Q / I.P. > $K_{s^{\prime}}$ a precipitate will form.

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

$$
K_{\mathrm{s}}=\left[\mathrm{Ag}^{+}\right]^{2}\left[\mathrm{CO}_{3}{ }^{2-}\right]
$$

Question 1 b (iii) : 40.0 mL of $0.150 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{HBr}$ solution was added to 25.0 mL of a saturated silver bromide, AgBr , solution.

Calculate the concentration of the silver ions, $\mathrm{Ag}^{+}$, after the HBr solution has been added.
$K s(\mathrm{AgBr})=5.00 \times 10^{-13}$
Assume the concentration of $\mathrm{Br}^{-}$in the original saturated solution of

AgBr is insignificant.
$\mathrm{AgBr} \leftrightharpoons \mathrm{Ag}^{+}+\mathrm{Br}^{-}$
$\mathrm{Ks}(\mathrm{AgBr})=\left[\mathrm{Ag}^{+}\right][\mathrm{Br}-]$
The ratio of the concentrations of products and reactants is called Q.
$5 \times 10^{-13}=\left[\mathrm{Ag}^{+}\right] \times \underline{0.150 \times 40}$
65
$\left[\mathrm{Ag}^{+}\right]=5.42 \times 10^{-12} \mathrm{~mol} \mathrm{~L}^{-1}$

## NCEA 2018 Common Ion Effect

Question: 3a (iii). Show by calculation whether a precipitate of AgCl will form when 70.0 mL of $0.0220 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{AgNO}_{3}$ is added to 50.0 mL of $0.0550 \mathrm{~mol} \mathrm{~L}^{-1}$ sodium chloride, NaCl .
$K_{\mathrm{s}}(\mathrm{AgCl})=1.80 \times 10^{-10}$

Dilution: volume / total volume of solutions

Final $\left[\mathrm{Ag}^{+}\right]=70 / 120 \times 0.0220=0.0128 \mathrm{~mol} \mathrm{~L}^{-1}$
Final $\left[\mathrm{Cl}^{-}\right]=50 / 120 \times 0.0550=0.0229 \mathrm{~mol} \mathrm{~L}^{-1}$ $Q=\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right]=0.0128 \times 0.0229=2.94 \times 10^{-4}$ Since $\mathrm{Q}>K_{\mathrm{s}^{\prime}} \mathrm{AgCl}$ will form a precipitate.


## NCEA 2019 Common Ion Effect

Question: 1a (iv). The presence of a common ion decreases the solubility of a sparingly soluble solid, such as $\mathrm{Zn}(\mathrm{OH})_{2}$.

Calculate the concentration of the hydroxide ions, $\mathrm{OH}^{-}$, in solution after 25.0 mL of $0.210 \mathrm{~mol} \mathrm{~L}^{-1}$ zinc chloride, $\mathrm{ZnCl}_{2}$, solution was added to 25.0 mL of a saturated $\mathrm{Zn}(\mathrm{OH})_{2}$ solution.

$$
K_{s}\left(\mathrm{Zn}(\mathrm{OH})_{2}\right)=3.80 \times 10^{-17}
$$

(0.210/2) due to dilution factor from adding two solutions together.
$K_{\mathrm{s}}=\left[\mathrm{Zn}^{2+}\right]\left[\mathrm{OH}^{-}\right]^{2}$

$3.80 \times 10^{-17}=(0.210 / 2) \times\left[\mathrm{OH}^{-}\right]^{2}$
$\left[\mathrm{OH}^{-}\right]=1.90 \times 10^{-8} \mathrm{~mol} \mathrm{~L}^{-1}$

## NCEA 2019 Common Ion Effect

Question: 1c Determine whether a precipitate of $\mathrm{Zn}(\mathrm{OH})_{2}$ will form when 30.0 mL or sodium hydroxide solution, NaOH , at pH 13.1 is added to 20.0 mL of $0.0242 \mathrm{~mol} \mathrm{~L}^{-1}$ zinc nitrate, $\mathrm{Zn}\left(\mathrm{NO}_{3}\right)^{2}$.
$K_{s}\left(\mathrm{Zn}(\mathrm{OH})_{2}\right)=3.80 \times 10^{-17}$
Dilution: volume / total volume
[ $\mathrm{OH}^{-}$] calculated by $\mathrm{K}_{\mathrm{w}} / 10^{\mathrm{pH}}$

$$
\left[\mathrm{Zn}^{2+}\right]=20 / 50 \times 0.0242=9.68 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}
$$

$$
[\mathrm{OH}-]=30 / 50 \times 1 \times 10^{-14} / 10^{-13.1}=0.0755 \mathrm{~mol} \mathrm{~L}^{-1}
$$

$$
\begin{array}{ll}
\text { IP }=\left[\mathrm{Zn}^{2+}\right]\left[\mathrm{OH}^{-}\right]^{2}=9.68 \times 10^{-3} \times(0.0755)^{2} & \text { IP has no units but must be to } \\
=5.52 \times 10^{-5}\left(5.53 \times 10^{-5}\right) \quad 3 \mathrm{sgf}
\end{array}
$$

Since IP $>K_{s^{\prime}}$ a precipitate of $\mathrm{Zn}(\mathrm{OH})_{2}$ will form.

Must state this to get Excellence

## NCEA 2020 Common lon Effect

Question: 2 b Determine whether a precipitate of lead bromide, $\mathrm{PbBr}_{2}$, will form when 125 mL of $0.0365 \mathrm{~mol} \mathrm{L-1}$ lead nitrate, $\mathrm{Pb}\left(\mathrm{NO}_{3}\right)_{2}$, is added to 175 mL of $0.00262 \mathrm{~mol} \mathrm{~L}^{-1}$ magnesium bromide, $\mathrm{MgBr}_{2}$.

$$
\mathrm{K}_{5}\left(\mathrm{PbBr}_{2}\right)=2.10 \times 10^{-6}
$$



Dilution: volume / total volume $\times 2 \mathrm{~mol} \mathrm{Br}^{-}$per 1 mol $\mathrm{MgBr}_{2}$

$$
\left[\mathrm{Pb}^{2+}\right]=125 / 300 \times 0.0365=1.52 \times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1}
$$

$$
[\mathrm{Br}-]=175 / 300 \times 2 \times 0.00262=3.06 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}
$$

$$
\begin{aligned}
& \mathrm{IP}=\left[\mathrm{Pb}^{2+}\right]\left[\mathrm{Br}^{-}\right]^{2}=\left(1.52 \times 10^{-2}\right) \times\left(3.06 \times 10^{-3}\right)^{2} \\
& =1.42 \times 10^{-7}
\end{aligned}
$$

Since IP $<K_{s^{\prime}}$ no precipitate of $\mathrm{PbBr}_{2}$ will form.

Must state this to get Excellence

## Solubility Key concepts

## $\mathrm{Ks} / \mathrm{s}$ calculations

Solubility expressions
equations

| $\mathrm{CA} \rightleftharpoons \mathrm{C}^{+}+\mathrm{A}^{-}$ |
| :--- |
| $\mathrm{C}_{2} \mathrm{~A} \rightleftharpoons 2 \mathrm{C}^{+}+\mathrm{A}^{-}$ |
| $\mathrm{CA}_{2} \rightleftharpoons \mathrm{C}^{+}+2 \mathrm{~A}^{-}$ |

Equilibrium effects

| Acids increase solubility if the salt contains a carbonate |  |
| :---: | :---: |
| Bases increase solubility if the salt contains a cation that forms a  <br> complex ion  <br>   <br> When pH is above 10  <br> \begin{tabular}{rl\|}
\hline
\end{tabular}  This occurs when pH is above 4 but below 10 |  |


| $\mathrm{K}_{5}(C A)=[C][A]$ |
| :--- |
| $\mathrm{K}_{5}\left(\mathrm{C}_{2} A\right)=[C]^{2}[A]$ |
| $\mathrm{Ks}\left(\mathrm{CA}_{2)}=[C][A]^{2}\right.$ |

$$
C=\text { cation } A=\text { anion }
$$

Common ion effect

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

If IP $>$ Ks then precipitate
If IP < Ks then no precipitate

```
IP = ionic product
Ks = solubility product
```


## Acids - their characteristics

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

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

## Acids - their characteristics

An Acid donates its Hydrogen ion $\left(\mathrm{H}^{+}\right)$, which is really just a proton - the electron remains behind.
Common acids (that you need to know) include:
Strong acids: $\mathrm{HNO}_{3}$ - nitric acid, HCl - hydrochloric acid, $\mathrm{H}_{2} \mathrm{SO}_{4}$ - sulfuric acid, HBr - Hydrobromic acid
Weak acids: $\mathrm{CH}_{3} \mathrm{COOH}$ - ethanoic acid, HF - Hydrofluoric acid, and $\mathrm{NH}_{4}{ }^{+}-$ ammonium


## Bases - their characteristics

## Bases are a family of Chemicals that can

 remove acid particles $\left(\mathrm{H}^{+}\right)$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 $\mathrm{OH}^{-}$ions.

## Bases - their characteristics

6446
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: $\mathrm{NH}_{3}$ - ammonia, $\mathrm{CH}_{3} \mathrm{NH}_{2}$ - methylamine and $\mathrm{CH}_{3} \mathrm{COO}^{-}$- 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.


Acid-Base reactions involve the transfer of Hydrogen ions, $\mathrm{H}^{+}$
A hydrogen ion, $\mathrm{H}^{+}$is simply a lone proton (an H with the electron removed) In water (or aqueous solutions ) $\mathrm{H}^{+}$ions exist as an $\mathrm{H}_{3} \mathrm{O}^{+}$ion, called hydronium.

Acids are substances that donate protons $\left(\mathrm{H}^{+}\right)$in solution
$\mathrm{HCl}_{(\mathrm{g})}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightarrow \quad \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}+\mathrm{Cl}^{-}{ }_{(\mathrm{aq})}$
HCl gas dissolved in water
HCl has donated a $\mathrm{H}^{+}$so is acting as an acid
$\mathrm{H}_{2} \mathrm{O}$ has accepted a $\mathrm{H}^{+}$so it is acting as a base

Solution becomes acidic since $\mathrm{H}_{3} \mathrm{O}^{+}$ ions form

Bases are substances that accept protons $\left(\mathrm{H}^{+}\right)$in solution
$\mathrm{NH}_{3(\mathrm{~g})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightarrow \quad \mathrm{NH}_{4}{ }^{+}{ }_{(\mathrm{aq})}+\mathrm{OH}^{-}{ }_{(\mathrm{aq})}$
$\mathrm{NH}_{3}$ gas dissolved in water
$\mathrm{NH}_{3}$ has accepted a $\mathrm{H}^{+}$so it is acting as a base
$\mathrm{H}_{2} \mathrm{O}$ has donated a $\mathrm{H}^{+}$so is acting as an acid

Solution becomes basic since $\mathrm{OH}^{-}$ions form.

## Brensted-Lowry acids and bases summary

Proton donation to a water molecule forms $\mathrm{H}_{3} \mathrm{O}^{+}$(hydronium) ions.
\(\underset{\substack{acid <br>

proton donor}}{\mathrm{HA}(a q)}+\underset{\)|  base  |
| :--- |
|  proton acceptor  |$}{\mathrm{H}_{2} \mathrm{O}(\mathrm{l})} \longrightarrow$




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

B(aq)
base

$$
+\quad \mathrm{H}_{2} \mathrm{O}(l)
$$

acid
proton acceptor
proton donor

$\mathrm{NH}_{3}$

$\mathrm{BH}^{+}(a q)+\mathrm{OH}^{-}(a q)$ acid base

## Amphiprotic substances

An amphiprotic substance is a substance that can donate or accept a proton, $\mathrm{H}^{+}$
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, $\mathrm{H}_{2} \mathrm{O}, \mathrm{HCO}_{3}^{-}, \mathrm{HSO}_{4}^{-}, \mathrm{HPO}_{4}{ }^{2-}$ and $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$

| Name <br> of amphiprotic <br> species | Chemical <br> formula | Able to donate a proton, $\mathrm{H}^{+}$ | Able to accept a proton, $\mathrm{H}^{+}$ |
| :--- | :--- | :--- | :--- |
| Water | $\mathrm{H}_{2} \mathrm{O}$ | $\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}(\mathrm{aq})$ | $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})+\mathrm{H}^{+}(\mathrm{aq}) \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ |
| Hydrogen <br> carbonate ion | $\mathrm{HCO}_{3}^{-}$ | $\mathrm{HCO}_{3}^{-}(\mathrm{aq}) \rightarrow \mathrm{H}^{+}(\mathrm{aq})+\mathrm{CO}_{3}^{2-}(\mathrm{aq})$ | $\mathrm{HCO}_{3}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq}) \rightarrow \mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq})$ |
| Hydrogen sulfate <br> ion | $\mathrm{HSO}_{4}^{-}$ | $\mathrm{HSO}_{4}^{-}(\mathrm{aq}) \rightarrow \mathrm{H}^{+}(\mathrm{aq})+\mathrm{SO}_{4}^{2-}(\mathrm{aq})$ | $\mathrm{HSO}_{4}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq}) \rightarrow \mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})$ |
| Dihydrogen <br> phosphate ion | $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$ | $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}(\mathrm{aq}) \rightarrow \mathrm{H}^{+}(\mathrm{aq})+\mathrm{HPO}_{4}^{2-}(\mathrm{aq})$ | $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq}) \rightarrow \mathrm{H}_{3} \mathrm{PO}_{4}(\mathrm{aq})$ |

## 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 $\mathrm{H}+$ ions (protons) break away from the original acid molecule in water. A weak acid only partially dissociates and loses just some of it's 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 $\mathrm{H}^{+}$ion. A weak base is a compound where only some of the molecules will accept a $\mathrm{H}^{+}$ion. Most weak base molecules remain un reacted.

Note: For strong alkalis, all of the $\mathrm{OH}^{-}$ 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 $\mathrm{H}^{+}$ ions. Strong acids will have a low $\mathrm{pH}(0-3)$ and include $\mathrm{HNO}_{3}, \mathrm{HCl}, \mathrm{H}_{2} \mathrm{SO}_{4}$, and HBr

Weak acids will have a higher pH (4-6). They are mostly organic acids and include $\mathrm{CH}_{3} \mathrm{COOH}, \mathrm{HF}$ and $\mathrm{NH}_{4}{ }^{+}$

## Strong acids

Donate protons $\left(\mathrm{H}^{+}\right)$in aqueous solution to become completely dissociated.
$\mathrm{HCl}_{(\mathrm{g})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq)}}+\mathrm{Cl}^{-}{ }_{(\mathrm{aq})}$
HCl gas dissolved in water
HCl has donated an $\mathrm{H}^{+}$so is acting as an acid
$\mathrm{H}_{2} \mathrm{O}$ has accepted an $\mathrm{H}^{+}$so it is acting as a base

Solution contains virtually no intact HCl molecules after reaction.

## Weak acids

Donate protons $\left(\mathrm{H}^{+}\right)$in aqueous solution to become partially dissociated.
$\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{l})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}{ }_{(\mathrm{aq})}+\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}$
$\mathrm{CH}_{3} \mathrm{COOH}$ dissolved in water
Only some of the acetic acid molecules dissociate into acetate ions $\left(\mathrm{CH}_{3} \mathrm{COO}^{-}\right)$

Because the acetate ion is a strong base (conjugate pairs) it will readily accept $\mathrm{H}^{+}$ (from $\mathrm{H}_{3} \mathrm{O}^{+}$) and become acetic acid.

Solution contains mostly intact $\mathrm{CH}_{3} \mathrm{COOH}$ 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 $\mathrm{H}^{+}$ions would join with available water to form hydronium ions


The strength of a base is determined by how readily it will accept $\mathrm{H}^{+}$ions. Strong bases will have a high $\mathrm{pH}(12-14)$ and include NaOH and KOH . Weak acids will have a lower $\mathrm{pH}(8-11)$. They include $\mathrm{NH}_{3}, \mathrm{CH}_{3} \mathrm{NH}_{2}$ and $\mathrm{CH}_{3} \mathrm{COO}^{-}$

## Strong Bases

Completely accept protons $\left(\mathrm{H}^{+}\right)$in aqueous solution
$\mathrm{NaOH}_{(\mathrm{s})} \xrightarrow{\mathrm{H}_{2} \mathrm{O}} \mathrm{Na}^{+}{ }_{(\mathrm{aq)}}+\mathrm{OH}^{-}{ }_{(\mathrm{aq})}$
NaOH completely dissociates
The OH - ions will readily accept $\mathrm{H}^{+}$ ions.

Solution contains very few intact NaOH molecules after reaction.

## Weak Bases

Partially accept protons $\left(\mathrm{H}^{+}\right)$in aqueous solution
$\mathrm{NH}_{3(\mathrm{~g})}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{NH}_{4}{ }^{+}{ }_{(\mathrm{aq})}+\mathrm{OH}^{-}{ }_{(\text {aq })}$
Only some of the ammonia molecules dissociate into ammonium ions $\left(\mathrm{NH}_{4}{ }^{+}\right)$

Because ammonium is a reasonably strong acid (conjugate pairs) it will readily donate $\mathrm{H}^{+}$and become ammonia. Solution contains mostly intact $\mathrm{NH}_{3}$ molecules.

## Conjugate pairs

If 2 species differ by just 1 proton they are classed as a conjugate acild-base pair.
Examples of acid-base pairs are $\mathrm{H}_{2} \mathrm{SO}_{4} / \mathrm{HSO}_{4}^{-}$and $\mathrm{NH}_{4}{ }^{+} / \mathrm{NH}_{3}$. The acid is always the species with the additional proton. It can also be said that $\mathrm{NH}_{3}$ is the conjugate base of $\mathrm{NH}_{4}{ }^{+}$.

| Base | Conjugate Acid |  |
| :--- | :--- | :---: |
| $\mathrm{H}_{2} \mathrm{O}$ | water | $\mathrm{H}_{3} \mathrm{O}^{+}$ |
| $\mathrm{SO}_{4}{ }^{2-} \quad$ sulfate ion | $\mathrm{HSO}_{4}{ }^{-}$ |  |
| $\mathrm{NH}_{3}$ | ammonia | $\mathrm{NH}_{4}{ }^{+}$ |
| $\mathrm{OH}^{-}$ | hydroxide ion | $\mathrm{H}_{2} \mathrm{O}$ |
| $\mathrm{HCO}_{3}{ }^{-}$ | hydrogen carbonate ion | $\mathrm{H}_{2} \mathrm{CO}_{3}$ |
| $\mathrm{CO}_{3}{ }^{2-}$ | carbonate ion | $\mathrm{HCO}_{3}{ }^{-}$ |

## Transfer of hydrogen ions in conjugate pairs



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 $\left(\mathrm{H}^{+}\right)$
The conjugate base produced, X -, is formed from the remainder of the acid after it has donated a proton.

transfer of $\mathrm{H}^{+}$
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.

transfer of $\mathrm{H}^{+}$


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



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 $\mathrm{Cl}^{-}$to reaccept a proton. Consequently, $\mathrm{Cl}^{-}$is a very weak base. A strong base like the $\mathrm{H}^{-}$ion accepts a proton and holds it so firmly that there is no tendency for the conjugate acid $\mathrm{H}_{2}$ to donate a proton. Hence, $\mathrm{H}_{2}$ is a very weak acid.

## Weak and strong acids

$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}+\right]$
Weak acid - less than $5 \%$ dissociation

| $\mathrm{HA}_{(\text {(aq) }}+$ | $\mathrm{H}_{2} \mathrm{O}_{(\text {aq) }}$ | $\leftrightharpoons$ | $\mathrm{A}^{(a q)}$ | + |  | $\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a \mathrm{aq})}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\dagger$ | $\uparrow$ |  |  |  |  | $\uparrow$ |
| Acid (weak) | water |  | conjugate |  |  | ium |

Strong acid - complete dissociation
$H X_{(a q)}+$
$\mathrm{H}_{2} \mathrm{O}_{(\mathrm{aq})}$
$\mathrm{X}^{-}{ }_{(\mathrm{aq})}+\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}$

Where $\mathrm{c}(\mathrm{HX})=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
Initial concentration of HX is equal to final concentration of $\mathrm{H}_{3} \mathrm{O}^{+}$
so $\mathrm{pH}=-\log \mathrm{c}(\mathrm{HX})$

## Summary of Dissociation equations and Equilibrium expressions - Q4

## Weak Acids

$\mathrm{HF}, \mathrm{CH}_{3} \mathrm{COOH}$, and $\mathrm{NH}_{4}{ }^{+}$
Write an equation using:

## Weak Bases

## $\mathrm{NH}_{3}, \mathrm{CH}_{3} \mathrm{NH}_{2}$, and $\mathrm{CH}_{3} \mathrm{COO}^{-}$

Write an equation using:

$$
\mathrm{B}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(0)} \leftrightharpoons \mathrm{OH}_{(a q)}^{-}+\mathrm{BH}^{+}{ }_{(q q)}
$$

Assume $\mathrm{H}_{2} \mathrm{O}$ has no change in concentration

Write an expression using:

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}
$$

Write an expression using:

$$
\mathrm{K}_{\mathrm{b}}=\left[\mathrm{OH}^{-}\right]\left[\mathrm{BH}^{+}\right]
$$

[B]

## 2015 dissociation equations - NCEA Case Study

Question: 1a: (i) Methylammonium chloride, $\mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl}$, dissolves in water to form a weakly acidic solution.
$\mathrm{Ka}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=2.29 \times 10^{-11}$
(a) (i) Write an equation to show $\mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl}$ dissolving in water.
$\mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl}(\mathrm{s}) \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq}) \quad \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{3} \mathrm{O}^{+}$

## 2014 dissociation equations - NCEA Case Study

Question: 1a: When chlorine gas is added to water, the equation for the reaction is:

$$
\mathrm{Cl}_{2(g)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightleftharpoons \mathrm{HCl}_{(a q)}+\mathrm{HOCl}_{(a q)}
$$

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

$$
\mathrm{HOCl}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{OCl}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

## NCEA 2016 dissociation equations

Question: 2a: (i) Ethanamine, $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}$, is a weak base. $\mathrm{p} \mathrm{K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}\right)=10.6 \mathrm{~K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}\right)=2.51 \times 10^{-11}$
(a) Write an equation to show the reaction of ethanamine with water.
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{3}^{+}+\mathrm{OH}^{-}$

## NCEA 2017 dissociation equations

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:

$$
\begin{array}{lll}
\mathrm{HF}+\mathrm{H}_{2} \mathrm{O} & \leftrightharpoons & \mathrm{~F}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} \\
\mathrm{HBr}+\mathrm{H}_{2} \mathrm{O} & \rightarrow & \mathrm{Br}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}
\end{array}
$$

## Kw - the ionic product for water

$\mathrm{K}_{\mathrm{w}}$ is ionic product for water and an equilibrium constant based on the reaction of water molecules transferring $\mathrm{H}^{+}$in an acid base reaction to create $\mathrm{OH}^{-}$and $\mathrm{H}_{3} \mathrm{O}^{+}$in equal quantities. The rate of reaction from reactants to products is the same as products to reactants once equilibrium is reached.
$\mathrm{K}_{\mathrm{c}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{O}\right]^{2}}$ from $\quad 2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightleftharpoons \underset{\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\text {aq })}+\mathrm{OH}^{-}{ }_{(\text {aq) }}}{\left(\Delta_{\mathrm{r}} \mathrm{H}=+\mathrm{ve}\right)}$
Or $\mathrm{K}_{\mathrm{c}} \times\left[\mathrm{H}_{2} \mathrm{O}\right]^{2}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]$
Because the concentration of water is so large it does not change
$\rightarrow$ considered constant
So $\mathrm{K}_{\mathrm{c}} \times\left[\mathrm{H}_{2} \mathrm{O}\right]^{2}$ is also constant - called $\mathrm{K}_{\mathrm{w}}$
As $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \times\left[\mathrm{OH}^{-}\right]$always equals $1 \times 10^{-14}$ then so does $\mathrm{K}_{\mathrm{w}}$
Temperature increase causes an increase in Kw as the reaction is endothermic this favours the forward reaction (Le Chateliers Principle)

## Using $\mathrm{K}_{\mathrm{w}}$ to Calculate $\left[\mathrm{OH}^{-}\right.$] or $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right.$]

The product $\left[\mathrm{OH}^{-}\right] \times\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$is a constant value (at the same temperature)

## IONIC PRODUCT $\mathrm{K}_{\mathrm{w}}=\left[\mathrm{OH}^{-}\right] \times\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1 \times 10^{-14}$

e.g. If solution $A$ has $[\mathrm{OH}-]=1 \times 10^{-1} \mathrm{molL}^{-1}$ find $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{1 \times 10^{-14}}{1 \times 10^{-1}}=1 \times 10^{-13} \mathrm{molL}^{-1}} \\
& {\left[\mathrm{OH}^{-}\right]=\frac{1 \times 10^{-14}}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]} \quad \text { or } \quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{1 \times 10^{-14}}{\left[\mathrm{OH}^{-}\right]}}
\end{aligned}
$$



Hydronium ion,
$\mathrm{H}_{3} \mathrm{O}^{+}$

## Acidity constant

An acid dissociation constantt, Ka, (also known as acidity constant) is a quantitative measure of the strength of an acid in solution.

It is the equilibrium constant for a chemical reaction known as dissociation in the context of acid-base reactions.

The equilibrium can be written symbolically as:

$$
\begin{aligned}
& \mathrm{HA} \rightleftharpoons \mathrm{H}^{\oplus}+\mathbf{A}^{\ominus} \\
& \text { Acid } \\
& \text { Proton Conjugate } \\
& \text { Base }
\end{aligned}
$$

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 $\longrightarrow$

Small
$\left(K<10^{-3}\right)$
000000
0000000
0000000
000000
Reactants $\quad$ Products

Mostly reactants

Intermediate

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



Significant amounts of reactants and products

Mostly products


Composition of equilibrium mixture

## Acidity constant

From the equation:

$$
\mathrm{HA}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{~A}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

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

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}
$$

We can also assume that the concentration of $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{A}^{-}$are the same, as one mole of $\mathrm{H}_{3} \mathrm{O}^{+}$forms every time one mole of $\mathrm{A}^{-}$is created

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

## Analysing the $\mathrm{K}_{\mathrm{a}}$ value

The $K_{a}$ value is an indication of position of the equilibrium. A small $K_{a}$ indicates more reactants, so less dissociation of the acid, and therefore a weaker acid. A larger $\mathrm{K}_{\mathrm{a}}$ indicates more products ( $\mathrm{H}_{3} \mathrm{O}^{+}$ions and conjugate base), so more dissociation of acid, and therefore a stronger acid
Less $\mathrm{H}_{3} \mathrm{O}^{+}$

Some questions will ask you, when comparing two acids, to discuss the link between Ka, level of dissociation, the relative amount of $\mathrm{H}_{3} \mathrm{O}^{+}$ions produced and therefore the pH and strength of the acids

## Acidity constant - assumptions

Acidity constant $=\mathrm{K}_{\mathrm{a}}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{A}^{-}\right]$hydronium concentration $=$conjugate base concentration
$\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}}{[\mathrm{HA}]}$
$\rightarrow$ if $\mathrm{K}_{\mathrm{a}}$ small then $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right.$] much smaller than [HA] - very little dissociation [HA] can then be assumed to be equal to $c(H A)$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{\mathrm{K}_{\mathrm{a}} \times \mathrm{C}(\mathrm{HA})}
$$

## 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 $c(H A)$. ie $[H A]=$ $c(H A)-\left[H_{3} \mathrm{O}^{+}\right]$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 $\mathrm{HNO}_{2}$ in 1.0 L of water.

$$
\mathrm{HNO}_{2}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \leftrightharpoons \mathrm{H}^{+}{ }_{\text {(aq) }}+\mathrm{NO}_{2}^{-}{ }^{-}{ }_{\text {aq) }}
$$

Initial concentration
Equilibrium concentration

$$
\mathrm{K}_{\mathrm{a}}=10^{-3.29}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{NO}_{2}^{-}\right]}{\left[\mathrm{HNO}_{2}\right]}
$$

$$
=\quad x^{2}
$$

(0.01-x)

# Acidity constant for degree of dissociation > $1 \%$ 



Initial concentration
0.01

Equilibrium concentration
(0.01-x)
$x \quad x$

$$
\mathrm{K}_{\mathrm{a}}=10^{-3.29}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{NO}_{2}^{-}\right]}{\left[\mathrm{HNO}_{2}\right]}
$$

$$
=\quad x^{2}
$$

(0.01-x)

| Solve the quadratic equation: | Solve by approximation: |
| :--- | :--- |
| $10^{-5.29}-10^{-3.29} \mathrm{x}=\mathrm{x}^{2}$  <br> $\mathrm{X}^{2}+10^{-3.29} \mathrm{x}-10^{-5.29}=0$ Assume that $(0.01-\mathrm{x})=0.01$ <br> $\mathrm{X}=0.002$ $10^{-3.29}=\frac{\mathrm{x}^{2}}{10^{-2}}$ <br> $\left[\mathrm{NO}_{2}\right]=\left[\mathrm{H}^{+}\right]=2 \times 10^{-3}=\left(10^{0.03}\right)\left(10^{-3}\right)=10^{-2.7}$ $\mathrm{X}^{2}=10^{-5.29}$ <br> $\left[\mathrm{HNO}_{3}\right]=8 \times 10^{-3}$  <br> $\mathrm{pH}=2.7$ $\mathrm{X}=10^{-2.65}$ <br> $\mathrm{pH}=2.7$  |  |

$\mathrm{pK}_{\mathrm{a}}=-\log \mathrm{K}_{\mathrm{a}}$

## $\rightarrow$ larger pKa more reactants

$\rightarrow$ negative for strong acids (HX)
$\rightarrow$ gets larger $(3-13)$ as acids get weaker - less dissociation
Strong acid
Weak acid
pKa value 0


The $\mathrm{pK}_{\mathrm{a}}$ is used to get a clear idea about the strength, or level of dissociation, of an acid, in a similar way to the pH scale. It can easily be

$$
K_{a}=10-\mathrm{pKa}
$$ converted to Ka to use in calculations. $\mathrm{pK}_{\mathrm{a}}$ have no units attached.

## pH calculations - Weak acid

1. Convert $\mathrm{p} \hat{K}_{\mathrm{a}}$ to $\mathrm{K}_{\mathrm{a}}$
(if required)

$$
\mathrm{K}_{\mathrm{a}}=10^{-\mathrm{Pka}}
$$

2. Calculate $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{\mathrm{K}_{\mathrm{a}} \times \mathrm{c}(\mathrm{HA})}
$$

3. Calculate pH
(start here if strong acid)
$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$

## pH calculations - Weak acid

$$
\begin{gathered}
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{\mathrm{K}_{\mathrm{a}} \mathrm{x}[\mathrm{HA}]}} \\
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
\end{gathered}
$$

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}
$$

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

## Use when

$\rightarrow$ given Ka (acid dissociation constant)
$\rightarrow$ given c(HA) - initial concentration of acid, as concentration at equilibrium [HA] and at the start c(HA)
is the same
$\rightarrow$ weak acid, HA

$$
\mathrm{HA}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{~A}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

Use this equation to compare number of mols.

As weak acids are diluted they become "stronger" as degree of dissociation ( $\mathrm{a}=\left[\mathrm{H}^{+}\right] / \mathrm{c}_{\mathrm{HA}}$ ) increases. (At infinite dilution a weak acid is $100 \%$ dissociated) This is because in the equilibrium $\mathrm{HA}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{A}^{-}$, adding water dilutes all concentrations equally in the expression $\mathrm{K}_{\mathrm{a}}=$ $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \times\left[\mathrm{A}^{-}\right] / \mathrm{HA}$ so to keep K constant, the equilibrium position needs to shift to the right.

## Bases

$\mathrm{B}_{(\mathrm{aq)}}+$ Base
$+$ water
$\mathrm{BH}^{+}+\mathrm{OH}^{-}$
conjugate acid hydroxide

Strong base - completely dissociates (accepts all $\mathrm{H}^{+}$ions)
$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1 \times 10^{-14} /\left[\mathrm{OH}^{-}\right]$
Strong bases will have a conjugate weak acid
Weak base - partly dissociates (accepts few $\mathrm{H}^{+}$ions)
[B] assumed to be same as $C(B)$ - initial concentration
$\mathrm{K}_{\mathrm{b}}$ is small if $\mathrm{K}_{\mathrm{a}}$ is large - weak base and strong acid
$\mathrm{K}_{\mathrm{b}}$ is large if $\mathrm{K}_{\mathrm{a}}$ is small - strong base and weak acid

## pH calculations - Weak base

1. Convert $\mathrm{pK}_{\mathrm{a}}$ to $\mathrm{K}_{\mathrm{a}}$ (if required)

## $K_{a}=10^{- \text {-pa }}$

Note the $K_{a}$ is for the conjugate acid
2. Rearrange expression
3. Calculate $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$

4. Calculate pH

$$
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
$$

## pH Calculations - Q5

Convert $\mathrm{pK}_{\mathrm{a}}$ to $\mathrm{K}_{\mathrm{a}}$

$$
\mathrm{K}_{\mathrm{a}}=10-\mathrm{pKa}
$$

If given Weak Acid
If given Weak Base
$\mathrm{HF}, \mathrm{CH}_{3} \mathrm{COOH}$, and $\mathrm{NH}_{4}{ }^{+}$
$\mathrm{NH}_{3}, \mathrm{CH}_{3} \mathrm{NH}_{2}$, and $\mathrm{CH}_{3} \mathrm{COO}^{-}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{ } K_{a} \times \mathrm{C}(\mathrm{HA})$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\mathrm{V}\left(K_{\mathrm{a}} \times K_{\mathrm{w}} \div[\mathrm{B}]\right)
$$

$$
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
$$

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

A $0.100 \mathrm{~mol} \mathrm{~L}-1$ 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 $\mathrm{p} K_{\mathrm{a}}\left(\operatorname{larger} K_{\mathrm{a}}\right)$ than hypochlorous acid.
So HF will therefore have a higher $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$. As $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$increases, the pH decreases, so HF will have a lower pH than HOCl .
$(\mathrm{pH} \mathrm{HF}=2.09, \mathrm{HOCl}=4.27)$
$\rightarrow$ larger pKa more reactants, the weaker the acid

## NCEA 2015 pH calculations

Question: 1a: (iv) Calculate the pH of $0.0152 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl}$ solution. $\mathrm{Ka}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=2.29 \times 10^{-11}$

$$
\begin{aligned}
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] } & =\sqrt{K_{\mathrm{a}}} \times \mathrm{HA} \\
& =5.90 \times 10^{7}
\end{aligned}
$$

$$
\mathrm{pH}=6.23
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{\mathrm{K}_{\mathrm{a}} \times \mathrm{c}(\mathrm{HA})}
$$

$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=5.90 \times 10^{-7} \mathrm{~mol} \mathrm{~L}^{-1}$

$$
\mathrm{pH}=-\log 5.90 \times 10^{-7}=6.23
$$

$$
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
$$

## NCEA 2016 pH calculations

Question: 2b: Calculate the pH of a $0.109 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of ethanamine.
$\mathrm{p} \mathrm{K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}\right)=10.6$

$$
\mathrm{K}_{\mathrm{a}}=10^{-\mathrm{Pka}}
$$

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=V\left(\mathrm{~K}_{\mathrm{a}} \times \mathrm{K}_{\mathrm{w}} \div\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}\right]\right)} \\
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=V\left(2.51 \times 10^{-11} \times 1.00 \times 10^{-14} \div 0.109\right)}
\end{aligned}
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{ }\left(K_{\mathrm{a}} \times K_{\mathrm{w}} \div[\mathrm{B}]\right)
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.52 \times 10^{-12} \mathrm{molL}^{-1}
$$

$$
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
$$

## NCEA 2017 pH calculations

Question: 2a: Ammonia, $\mathrm{NH}_{3}$, is a weak base.
$\mathrm{p} K_{\mathrm{a}}\left(\mathrm{NH}_{4}{ }^{+}\right)=9.24 \mathrm{~K}_{\mathrm{a}}\left(\mathrm{NH}_{4}{ }^{+}\right)=5.75 \times 10^{-10}$
(i) Calculate the pH of a $0.105 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{NH}_{3}$ solution.

## $\mathrm{K}_{\mathrm{a}}=10^{-\mathrm{Pka}}$

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=V\left(\mathrm{Ka} \times \mathrm{Kw} \div\left[\mathrm{NH}_{3}\right]\right)} \\
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=V\left(5.75 \times 10^{-10} \times 1.00 \times 10^{-14} \div 0.105\right)}
\end{aligned}
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=7.40 \times 10^{-12} \mathrm{molL}^{-1}
$$

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

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\mathrm{V}\left(K_{\mathrm{a}} \times K_{\mathrm{w}} \div[\mathrm{B}]\right)
$$

## $\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$

Question: 1a: (a) When sodium ethanoate, $\mathrm{CH}_{3} \mathrm{COONa}$, is dissolved in water, the resulting solution has a pH greater than 7 due to the production of hydroxide ions, $\mathrm{OH}^{-}$, as shown in the equation below.
$\mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{OH}^{-}$
$\mathrm{p}_{\mathrm{Ka}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=4.76 \mathrm{~K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=1.74 \times 10^{-5}$
Calculate the pH of a $0.420 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{CH}_{3} \mathrm{COONa}$ solution.
$\mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{OH}^{-}$

$$
\begin{aligned}
\mathrm{H}_{3} \mathrm{O}^{+} & =\sqrt{\frac{K_{\mathrm{a}} \times K_{\mathrm{w}}}{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}} \\
& =\sqrt{\left(\frac{1.74 \times 10^{-5} \times 1 \times 10^{-14}}{0.420}\right)} \\
& =6.44 \times 10^{-10}
\end{aligned}
$$

$$
\mathrm{K}_{\mathrm{a}}=10^{-\mathrm{Pka}}
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\mathrm{V}\left(K_{\mathrm{a}} \times K_{\mathrm{w}} \div[\mathrm{B}]\right)
$$

$$
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
$$

## NCEA 2019 pH calculations

Question: 3a Two solutions of equal concentration were prepared: one of ethanoic acid, $\mathrm{CH}_{3} \mathrm{COOH}$, and one of ammonium chloride, $\mathrm{NH}_{4} \mathrm{Cl}$.
$\mathrm{p} K_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=4.76 \mathrm{p} K_{\mathrm{a}}\left(\mathrm{NH}_{4}{ }^{+}\right)=9.24$
(i) Explain which solution would have the lower pH .

Your answer should refer to the concentration of relevant ion(s) in each solution.
No calculations are necessary.
$\mathrm{CH}_{3} \mathrm{COOH}$ has the smaller $\mathrm{p} K_{\mathrm{a}} / \operatorname{larger} K_{\mathrm{a}}$, so it will be a stronger acid than $\mathrm{NH}_{4}{ }^{+}$.

This means $\mathrm{CH}_{3} \mathrm{COOH}$ will dissociate to a greater extent to produce a higher $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$than $\mathrm{NH}_{4}{ }^{+}$, so $\mathrm{CH}_{3} \mathrm{COOH}$ will have a lower pH .


Question: 3 a (iii) The ethanoic acid solution has a $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$of $1.78 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}$.
Calculate the concentration of the ethanoic acid solution.

$$
\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

$$
\begin{aligned}
& K_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]} \\
& 10^{-4.76}=\frac{\left(1.78 \times 10^{-3}\right)^{2}}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}
\end{aligned}
$$

$$
\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=0.182 \mathrm{~mol} \mathrm{~L}^{-1}
$$

Question: 1c (ii) If the $\mathrm{NH}_{4} \mathrm{Cl}$ solution has a pH of 4.70, calculate its concentration.

$$
K_{\mathrm{a}}\left(\mathrm{NH}_{4}^{+}\right)=5.75 \times 10^{-10} \quad \mathrm{p} K_{\mathrm{a}}\left(\mathrm{NH}_{4}^{+}\right)=9.24
$$

$$
\begin{gathered}
\mathrm{NH}_{4}^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+} \\
K_{\mathrm{a}}=\frac{\left[\mathrm{NH}_{3}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{NH}_{4}^{+}\right]} \\
5.75 \times 10^{-10}=\frac{\left(10^{-4.70}\right)^{2}}{\left[\mathrm{NH}_{4}^{+}\right]} \\
{\left[\mathrm{NH}_{4}^{+}\right]=0.692 \mathrm{~mol} \mathrm{~L}^{-1}}
\end{gathered}
$$


a-basf
Ammonium chiordo AF
家 5030078 - 2164304760 1
115106005110

Ammonium Chloride


## Comparing weak acids - pH, pKa and ions - Q6

## Strong acid

## Weak acid

## pKa value

## stronger acid

## weaker acid

## Link to level of acid dissociation

More dissociation of acid to produce more $\mathrm{H}_{3} \mathrm{O}^{+}$ions and conjugate base
less dissociation of acid to produce more $\mathrm{H}_{3} \mathrm{O}^{+}$ions and conjugate base Link to pKa and pH and acid strength
pKa is a smaller value, as is the pH , therefore this is a stronger acid
pKa is a larger value, as is the pH , therefore this is a weaker acid

## Species in solution

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

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

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

A small amount of $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{OH}^{-}$will always be present in water due to $\mathrm{Kw}=\left[\mathrm{OH}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1 \times 10^{-14}$

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 $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{OH}^{-}$will also be present, according to the $\mathrm{K}_{\mathrm{w}}=$ $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1 \times 10^{-14}$
> 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
$\left[\mathrm{Cl}^{-}\right]=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]>\left[\mathrm{OH}^{-}\right]$
Strong acids will provide good conductivity and $\mathrm{pH} 1-2$ due to the high presence of $\mathrm{H}_{3} \mathrm{O}^{+}$ions


No strong acid will be left in the final mixture.
$\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{Cl}^{-}$are produced in equal concentrations - in the same concentration as the original strong acid.

A small amount of $\mathrm{OH}^{-}$is present as water dissociates into $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{OH}^{-}$

## Concentration of ions in solution - Weak Acid

Weak Acid i.e. $\mathrm{CH}_{3} \mathrm{COOH}$ reacting with water
$\left[\mathrm{CH}_{3} \mathrm{COOH}\right]>\quad\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
$>\quad\left[\mathrm{OH}^{-}\right]$
weak acids will provide poor conductivity and $\mathrm{pH} 3-6$ due to the low presence of $\mathrm{H}_{3} \mathrm{O}^{+}$ions (but still higher than $\mathrm{OH}^{-}$ions)

## $\mathrm{CH}_{3} \mathrm{COOH}$



Most weak acid will be left in the final mixture.
$\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{CH}_{3} \mathrm{COO}^{-}$are produced in equal concentrations - a small amount of the weak acid had dissociated.

A small amount of $\mathrm{OH}^{-}$is present as water dissociates into $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{OH}^{-}$

## Concentration of ions in solution - Strong Base

Strong Base i.e. NaOH reacting with water
$\left[\mathrm{OH}^{-}\right] \quad>=\quad\left[\mathrm{Na}^{+}\right] \quad>\quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$

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


No strong base will be left in the final mixture.
$\mathrm{OH}^{-}$and $\mathrm{Na}^{+}$are produced in equal concentrations - in the same concentration as the original strong base.

A small amount of $\mathrm{H}_{3} \mathrm{O}^{+}$ is present as water dissociates into $\mathrm{H}_{3} \mathrm{O}^{+}$ and $\mathrm{OH}^{-}$

## Concentration of ions in solution - Weak Base

$$
\begin{array}{llllll}
\text { Weak Base i.e. } \mathrm{NH}_{3} \\
{\left[\mathrm{NH}_{3}\right]} & > & {[\mathrm{OH}-]} & > & {\left[\mathrm{NH}_{4}^{+}\right]} & >
\end{array}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
$$

weak bases will provide poor conductivity and $\mathrm{pH} 8-11$ due to the low presence of $\mathrm{OH}^{-}$ions (but still higher than $\mathrm{H}_{3} \mathrm{O}^{+}$ions)


Most weak base will be left in the final mixture.
$\mathrm{OH}^{-}$and $\mathrm{NH}_{4}^{+}$are produced in equal concentrations - a small amount of the weak base had dissociated.

A small amount of $\mathrm{H}_{3} \mathrm{O}^{+}$ is present as water dissociates into $\mathrm{H}_{3} \mathrm{O}^{+}$ and $\mathrm{OH}^{-}$

## Concentration of ions in solution - acid salt

Acid Salt i.e. $\mathrm{NH}_{4} \mathrm{Cl}$
$\left[\mathrm{Cl}^{-}\right]>\left[\mathrm{NH}_{4}{ }^{+}\right]>\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \quad=\left[\mathrm{NH}_{3}\right] \gg\left[\mathrm{OH}^{-}\right]$
Acid salts will provide good conductivity and $\mathrm{pH}<7$ due to the high presence of ions from dissolving and to a lesser extent $\mathrm{H}_{3} \mathrm{O}^{+}$ions


The spectator ion will be left in the highest concentration followed by the weak acid.
$\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{NH}_{3}$ are produced in equal concentrations - a small amount of the weak acid had dissociated.

A small amount of $\mathrm{OH}^{-}$is present as water dissociates into $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{OH}^{-}$

## Concentration of ions in solution - base salt

Base Salt i.e. $\mathrm{CH}_{3} \mathrm{COONa}$
$\left[\mathrm{Na}^{+}\right] \approx\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]>\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=\left[\mathrm{OH}^{-}\right] \geqslant\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
base salts will provide good conductivity and $\mathrm{pH}>7$ due to the high presence of ions from dissolving and to a lesser extent $\mathrm{OH}^{-}$ions


The spectator ion will be left in the highest concentration followed by the weak base.
$\mathrm{OH}^{-}$and $\mathrm{CH}_{3} \mathrm{COOH}$ are produced in equal concentrations - a small amount of the weak base had dissociated.

A small amount of $\mathrm{H}_{3} \mathrm{O}^{+}$is present as water dissociates into $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{OH}^{-}$

## 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, $\mathrm{NH}_{4} \mathrm{Cl}$, contains the cation $\mathrm{NH}_{4}^{+}$and the anion $\mathrm{Cl}^{-}$. The $\mathrm{Cl}^{-}$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 $\mathrm{NH}_{4}{ }^{+}$ion is the conjugate acid of the weak base $\mathrm{NH}_{3}$ 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.

$$
\mathrm{NH}_{4} \mathrm{Cl}_{(s)} \leftrightharpoons \mathrm{NH}_{4}^{+}{ }_{(a q)}+\mathrm{Cl}_{(a q)}^{-}
$$

$\mathrm{NH}_{4}^{+}{ }_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \leftrightharpoons \mathrm{NH}_{3(a q)}+\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)}$

## 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


## 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

ethanoic acid

glucose conduct charge.

## Summary of Species/conductivity in Solution - Acid -Q7



Complete dissociation No strong acid remains
High conductivity


## Summary of Species / conductivity in Solution - Base - Q7

Strong Bases


Complete dissociation No strong base remains

High conductivity


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)

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.
$\mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl} \quad \mathrm{CH}_{3} \mathrm{NH}_{2} \mathrm{HCl}$

## $\mathrm{HCl}<\mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl}<\mathrm{CH}_{3} \mathrm{NH}_{2}$

- HCl , a strong acid, reacts completely with water to form $1 \mathrm{~mol} \mathrm{~L}^{-1}$ $\mathrm{H}_{3} \mathrm{O}^{+}$and hence a low $\mathrm{pH} . \quad \mathrm{HCl}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{Cl}^{-}$
- $\mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl}$ dissociates completely in water to form $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}$and $\mathrm{Cl}^{-}$. $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}$, a weak acid, partially reacts with water to form less than 1 $\mathrm{mol} \mathrm{L}^{-1} \mathrm{H}_{3} \mathrm{O}^{+}$and hence a higher pH than HCl .
$\mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}^{+}+\mathrm{Cl}^{-}$

$$
\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

- $\mathrm{CH}_{3} \mathrm{NH}_{2}$, a weak base, partially reacts with water to form $\mathrm{OH}^{-}$ions. So there are more $\mathrm{OH}^{-}$ions than $\mathrm{H}_{3} \mathrm{O}^{+}$ions and the pH is thus high.

$$
\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{NH}_{3}^{+}+\mathrm{OH}^{-}
$$

Question: 1a: When chlorine gas is added to water, the equation for the reaction is: $\quad \mathrm{Cl}_{2(g)}+\mathrm{H}_{2} \mathrm{O}_{(1)} \rightleftharpoons \mathrm{HCl}_{(a q)}+\mathrm{HOCl}_{(a q)}$
(ii) List all the species present when HOCl reacts with water, in order of decreasing concentration. Justify your order.

## $\mathrm{HOCl}>\mathrm{H}_{3} \mathrm{O}^{+}>\mathrm{OCl}^{-}>\mathrm{OH}^{-}$or $\mathrm{HOCl}>\mathrm{H}_{3} \mathrm{O}^{+}=\mathrm{OCl}^{-}>\mathrm{OH}^{-}$

HOCl partially dissociates, and so the equilibrium lies to the LHS/favours the reactants; therefore HOCl is present in the greatest amounts.
$\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{OCl}^{-}$are produced in equal amounts / there is a small contribution to $\mathrm{H}_{3} \mathrm{O}^{+}$from water therefore $\mathrm{H}_{3} \mathrm{O}^{+}>\mathrm{OCl}^{-}$

Because there is a relatively high $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$, the $\left[\mathrm{OH}^{-}\right]$is very low (or links to $K_{w}$ ).

Question: 2c: Ethyl ammonium chloride, $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{3} \mathrm{Cl}$, is a weak acid that will also react with water. List all the species present in a solution of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{3} \mathrm{Cl}$, in order of decreasing concentration.

Do not include water. Justify the order you have given.

Include equations, where necessary.
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{3} \mathrm{Cl} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}+\mathrm{Cl}^{-}$
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{3} \mathrm{Cl}$ 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.
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}+\mathrm{H}_{3} \mathrm{O}^{+}$
For every mole of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}$that reacts with water, 1 mole of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}$ and $\mathrm{H}_{3} \mathrm{O}^{+}$are formed.
(However, $\mathrm{H}_{3} \mathrm{O}^{+}$is slightly more concentrated than $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}$, as there is a small contribution from water).
$\mathrm{OH}^{-}$is present in the lowest concentration as this comes from the dissociation of water only.
$\mathrm{Cl}^{-}>\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{3}^{+}>\mathrm{H}_{3} \mathrm{O}^{+} \geq \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}>\mathrm{OH}^{-}$

## NCEA 2019 Species in Solution

Question: 2a A titration was carried out by adding $0.140 \mathrm{~mol}^{-1}$ sodium hydroxide, NaOH , to 20.0 mL of $0.175 \mathrm{~mol}^{-1}$ methanoic acid, HCOOH .

The equation for the reaction is:
$\mathrm{HCOOH}+\mathrm{NaOH} \rightarrow \mathrm{HCOONa}+\mathrm{H}_{2} \mathrm{O}$
$\mathrm{p} K_{\mathrm{a}}(\mathrm{HCOOH})=3.74 \quad K_{\mathrm{a}}(\mathrm{HCOOH})=1.82 \times 10^{-4}$
(i) List ALL the species in solution after 12.5 mL of NaOH solution has been added.

Do not include water.
$\mathrm{Na}^{+}, \mathrm{HCOO}^{-}, \mathrm{HCOOH}, \mathrm{OH}^{-}, \mathrm{H}_{3} \mathrm{O}^{+}$


## NCEA 2020 Species in Solution

Question: 1c (i) Solutions of equal concentration were prepared for each of the following: $\mathrm{HBr} \quad \mathrm{CH}_{3} \mathrm{NH}_{2} \quad \mathrm{NH}_{4} \mathrm{Cl}$
Rank the solutions in order of decreasing pH in the box below:
Order of decreasing pH: $\mathrm{CH}_{3} \mathrm{NH}_{2}, \mathrm{NH}_{4} \mathrm{Cl}, \mathrm{HBr}$.
Question: 1c (i) Justify the order. Your answer should include: •relative concentrations of hydronium ions • relevant equation(s).
$\mathrm{CH}_{3} \mathrm{NH}_{2}$ is a weak base, and therefore partially dissociates to produce $\mathrm{OH}^{-}$.
$\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{OH}^{-}$
$\mathrm{NH}_{4} \mathrm{Cl}$ is an acidic salt. The $\mathrm{NH}_{4}{ }^{+}$is a weak acid, and therefore partially dissociates to produce $\mathrm{H}_{3} \mathrm{O}^{+}$. $\mathrm{NH}_{4}^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+}$
HBr is a strong acid, and therefore completely dissociates to produce a higher $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$than $\mathrm{NH}_{4}{ }^{+}$.

$$
\mathrm{HBr}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{Br}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

Since $\mathrm{CH}_{3} \mathrm{NH}_{2}$ is the only base, it has the lowest $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and therefore the highest pH . Since HBr is a strong acid, it has the highest $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and therefore the lowest pH .

Question: 1b: The conductivity of the $1 \mathrm{~mol} \mathrm{~L}-1$ solutions formed in (a) can be measured. $\mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl}$ $\mathrm{CH}_{3} \mathrm{NH}_{2}$ HCl

Rank these solutions in order of decreasing conductivity. Compare and contrast the conductivity of each of the $1 \mathrm{~mol} \mathrm{~L}-1$ solutions, with reference to species in solution.

$$
\mathrm{HCl}=\mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl}>\mathrm{CH}_{3} \mathrm{NH}_{2}
$$

$\mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl}$ and HCl will dissociate completely in water to produce 2 mol $\mathrm{L}^{-1}$ ions.
$\mathrm{CH}_{3} \mathrm{NH}_{2}$ will only partially react with water to produce less than $1 \mathrm{~mol}^{-1}$ of ions.

## NCEA 2015 Conductivity

Question: 1 b : 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 | $\mathbf{N a O H}$ | $\mathbf{C H}_{\mathbf{3}} \mathbf{N H}_{\mathbf{2}}$ | $\mathbf{C H}_{\mathbf{3}} \mathbf{C O O N a}$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{p H}$ | 13.2 | 11.9 | 8.98 |
| Electrical conductivity | good | poor | good |

The pH of a solution is calculated from its $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$.
NaOH is an ionic solid that is a strong base and dissociates completely to produce a high $\mathrm{OH}^{-}$concentration (low $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$). Since $\left[\mathrm{OH}^{-}\right]$is high / $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$is low, the pH is high.
$\mathrm{NaOH} \rightarrow \mathrm{Na}^{+}+\mathrm{OH}^{-}$

## NCEA 2015 Conductivity

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 | $\mathbf{N a O H}$ | $\mathbf{C H}_{\mathbf{3}} \mathbf{N H}_{\mathbf{2}}$ | $\mathbf{C H}_{\mathbf{3}} \mathbf{C O O N a}$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{p H}$ | 13.2 | 11.9 | 8.98 |
| Electrical conductivity | good | poor | good |

- $\mathrm{CH}_{3} \mathrm{NH}_{2}$ is a weak base that partially reacts / dissociates / ionises with $\mathrm{H}_{2} \mathrm{O}$ producing a lower concentration of $\mathrm{OH}^{-}$, Therefore it has a lower pH than NaOH :
$\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{OH}^{-}$
The $\mathrm{CH}_{3} \mathrm{COONa}$ is an ionic solid that dissociates completely in $\mathrm{H}_{2} \mathrm{O}$. The $\mathrm{CH}_{3} \mathrm{COO}^{-}$ion is a weak base that partially reacts / dissociates / ionises with $\mathrm{H}_{2} \mathrm{O}$ producing a lower concentration of $\mathrm{OH}^{-}$.
$\mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{OH}^{-}$
The pH is closer to 7 , showing it is the weakest base. Therefore it has a lowest pH


## NCEA 2015 Conductivity

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 | $\mathbf{N a O H}$ | $\mathbf{C H}_{\mathbf{3}} \mathbf{N H}_{\mathbf{2}}$ | $\mathbf{C H}_{\mathbf{3}} \mathbf{C O O N a}$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{p H}$ | 13.2 | 11.9 | 8.98 |
| Electrical conductivity | good | poor | good |

## Electrical conductivity:

Electrical conductivity is determined by the concentration of ions.
$\square \mathrm{NaOH}$ completely dissolves to produce a high concentration of $\mathrm{Na}^{+}$and $\mathrm{OH}^{-}$ions in solution.
$\mathrm{NaOH} \rightarrow \mathrm{Na}^{+}+\mathrm{OH}^{-}$Therefore it is a good conductor.

## NCEA 2015 Conductivity

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 | $\mathbf{N a O H}$ | $\mathbf{C H}_{3} \mathbf{N H}_{\mathbf{2}}$ | $\mathbf{C H}_{\mathbf{3}} \mathbf{C O O N a}$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{p H}$ | 13.2 | 11.9 | 8.98 |
| Electrical conductivity | good | poor | good |

## Electrical conductivity:

- Since $\mathrm{CH}_{3} \mathrm{NH}_{2}$ 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.
$\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{OH}^{-}$
- $\mathrm{CH}_{3} \mathrm{COONa}$ is also an ionic solid. It dissolves completely to produce a high concentration of $\mathrm{Na}^{+}$and $\mathrm{CH}_{3} \mathrm{COO}^{-}$ions:
$\mathrm{CH}_{3} \mathrm{COONa} \rightarrow \mathrm{Na}^{+}+\mathrm{CH}_{3} \mathrm{COO}^{-}$
Therefore it is a good conductor.

Question: 1a (ii) : Compare and contrast the electrical conductivity of 0.150 mol $\mathrm{L}^{-1}$ 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 $\left[\mathrm{Br}^{-}\right]$and $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$. In contrast, HF is a weak acid and therefore only partially dissociates to produce a lower [ions], i.e. $\mathrm{F}^{-}$and $\mathrm{H}_{3} \mathrm{O}^{+}$.
So, HF is a poorer electrical conductor / weaker electrolyte.

## NCEA 2018 Conductivity

Question: 2. A titration was carried out by adding $0.210 \mathrm{~mol} \mathrm{~L}^{-1}$ hydrochloric acid, HCl , to 25.0 mL of $0.168 \mathrm{~mol} \mathrm{~L}^{-1}$ methanamine, $\mathrm{CH}_{3} \mathrm{NH}_{2}$.

The equation for the reaction is: $\mathrm{HCl}+\mathrm{CH}_{3} \mathrm{NH}_{2} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{Cl}^{-}$
$\mathrm{p}_{\mathrm{Ka}}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=10.6 \quad K_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=2.51 \times 10^{-11}$
(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. $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}$and $\mathrm{OH}^{-}$ions. This means there is mainly $\mathrm{CH}_{3} \mathrm{NH}_{2}$ present, which has no charge. The solution is therefore a poor conductor of electricity compared to the solution at the equivalence point.
$\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{CH}_{3} \mathrm{NH}_{3}^{+}+\mathrm{OH}^{-}$
The solution at the equivalence point is made up of the products from the titration / $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}$and $\mathrm{Cl}^{-}$. As there are more ions in solution / higher [ions] the solution at the equivalence point is a better conductor.

## NCEA 2019 Conductivity

Question: 3 a (ii) Evaluate the electrical conductivity of the $\mathrm{CH}_{3} \mathrm{COOH}$ and $\mathrm{NH}_{4} \mathrm{Cl}$ solutions.

Include relevant equation(s) in your answer.
The electrical conductivity of a solution depends upon [ions]. $\mathrm{NH}_{4} \mathrm{Cl}$ is an acidic salt, so it completely dissociates / dissolves to produce a relatively high $\left[\mathrm{NH}_{4}^{+}\right]$and $[\mathrm{Cl}-]$. This makes $\mathrm{NH}_{4} \mathrm{Cl}$ a good electrical conductor.
$\mathrm{NH}_{4} \mathrm{Cl} \rightarrow \mathrm{NH}_{4}^{+}+\mathrm{Cl}^{-}$
However, $\mathrm{CH}_{3} \mathrm{COOH}$ is a weak acid and only partially dissociates to produce a relatively low $\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]$ and $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$. This makes $\mathrm{CH}_{3} \mathrm{COOH}$ a poorer electrical conductor than $\mathrm{NH}_{4} \mathrm{Cl}$.

Electrical current, I

$\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$

## NCEA 2020 Conductivity

Question: 3b Why are hydrochloric acid and sodium ethanoate solutions both goou electrical conductors?

Justify your answer, including any relevant equation(s).

The electrical conductivity of a solution depends upon its concentration of mobile ions.

HCl is a strong acid and therefore completely dissociates (evidence from equation) to produce a high concentration of $\mathrm{Cl}^{-}$ions and $\mathrm{H}_{3} \mathrm{O}^{+}$ions in solution.
$\mathrm{HCl}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{Cl}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
Sodium ethanoate is a basic salt. It completely dissociates (evidence from equation) to produce a high concentration of $\mathrm{Na}^{+}$ions and $\mathrm{CH}_{3} \mathrm{COO}^{-}$ions in solution.
$\mathrm{CH}_{3} \mathrm{COONa} \rightarrow \mathrm{Na}^{+}+\mathrm{CH}_{3} \mathrm{COO}^{-}$
Since both solutions produce a high concentration of ions, they are both good electrical conductors

## Buffer solutions

The pH of aqueous solutions is controlled by the transfer of protons between ions and water molecules. The pH of blôod, 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.


## 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 $\left(\mathrm{OH}^{-}\right)$ions are added they will react with the ethanoic acid.

$$
\mathrm{CH}_{3} \mathrm{COOH}_{(a q)}+\mathrm{OH}^{-}(a q) \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}_{(a q)}^{-}+\mathrm{H}_{2} \mathrm{O}_{()}
$$

If acid $\left(\mathrm{H}_{3} \mathrm{O}^{+}\right)$ions are added they will react with the ethanoate ions.

$$
\mathrm{CH}_{3} \mathrm{COO}_{(a q)}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COOH}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(0)}
$$

These reactions show that any added acid $\left(\mathrm{H}_{3} \mathrm{O}^{+}\right)$or base $\left(\mathrm{OH}^{-}\right)$are largely consumed and the pH of the solution therefore hardly changes.

Buffers are effective 1 pH either side of buffer mid point - which when $\mathrm{pH}=\mathrm{pKa}$

The pH of a solution falls within a buffer zone when it is 1 pH either side of the pKa ), and therefore it will function as a buffer.

When the pH < pKa , this means [weak acid] > [conjugate], so the buffer will be more effective against added strong base.
$\mathrm{COOH}_{(a q)}+\mathrm{OH}_{(a q)}^{-} \leftrightharpoons \mathrm{COO}_{(a q)}^{-}+\mathrm{H}_{2} \mathrm{O}_{(l)}$


Volume of NaOH added ( mL )

Both reactions still take place in the buffer zone, however.

## Effectiveness of Buffer solutions - weak acid buffer

The pH of a solution falls within a buffer zone when it is 1 pH either side of the pKa ), and therefore it will function as a buffer.

When the $\mathrm{pH}>\mathrm{pKa}$, this means [weak base] > [conjugate], so the buffer will be more effective against added strong acid.
$\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{3} \mathrm{O}^{+} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}^{+}+\mathrm{H}_{2} \mathrm{O}$
When the $\mathrm{pH}<\mathrm{pKa}$, this means [conjugate] > [weak base], so the buffer will be more effective against added strong base.
$\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{OH}^{-} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O}$


Both reactions still take place in the buffer zone, however.

## Effectiveness of Buffer solutions - Summary

## Weak Acids and conjugates

## Weak Bases and conjugates

The pH of a solution falls within a buffer zone when it is 1 pH either side of the pKa ), and therefore it will function as a buffer.

When the $\mathrm{pH}<\mathrm{pKa}$, this means [weak acid] > [conjugate], so the buffer will be more effective against added strong base.
$\mathrm{COOH}_{(a q)}+\mathrm{OH}_{(a q)} \leftrightharpoons \mathrm{COO}_{(a q)}^{-}+\mathrm{H}_{2} \mathrm{O}_{(0)}$
When the $\mathrm{pH}>\mathrm{pKa}$, this means [conjugate] > [weak acid], so the buffer will be more effective against added strong acid.
$\mathrm{COO}_{(a q)}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)} \leftrightharpoons \mathrm{COOH}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(p)}$

The pH of a solution falls within a buffer zone when it is 1 pH either side of the pKa ), and therefore it will function as a buffer.
When the $\mathrm{pH}>\mathrm{pKa}$, this means [weak base] > [conjugate], so the buffer will be more effective against added strong acid.
$\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{3} \mathrm{O}^{+} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}++\mathrm{H}_{2} \mathrm{O}$
When the $\mathrm{pH}<\mathrm{pKa}$, this means [conjugate] > [weak base], so the buffer will be more effective against added strong base.
$\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{OH}^{-} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O}$



Volume of NaOH added (mL)

| Weak acid | Conjugate base |
| :---: | :---: |
| $\mathrm{CH}_{3} \mathrm{COOH}$ | $\mathrm{CH}_{3} \mathrm{COO}^{-}$ |
| $\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$ |  |
| $\mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{OH}^{-}$ |  |
| HF | F- |
| $\mathrm{HF}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{F}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$ |  |
| $\mathrm{F-}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{HF}^{-}+\mathrm{OH}^{-}$ |  |
| $\mathrm{NH}_{4}{ }^{+}$ | $\mathrm{NH}_{3}$ |
| $\mathrm{NH}_{4}^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+}$ |  |
| $\mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{NH}_{4}^{+}+\mathrm{OH}^{-}$ |  |
| $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}$ | $\mathrm{CH}_{3} \mathrm{NH}_{2}$ |
| $\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{3} \mathrm{O}^{+}$ |  |
| $\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{NH}_{3}^{+}+\mathrm{OH}^{-}$ |  |

## Calculating moles given mass

## $\mathrm{n}=\mathrm{m} / \mathbb{M}$

We use the formula above to calculate the number of moles present of a substance when given the mass of the substance and the molar mass (atomic mass) from the Periodic Table.
m - Mass is measured in grams ( g )
$\boldsymbol{\mu}_{\text {- Molar Mass is measured in } \mathrm{gmol}^{-1}}$
$n$ - Moles are measures in mols


## Calculating concentration of solutions (molL-1 $)$

## $\mathrm{c}=\mathrm{n} / \mathrm{V}$

We use the formula above to calculate the concentration of a unknown substance when given the concentration of a known solution when a titration has reached end point.

The moles of each substance is found in a balanced equation.

C - concentration is measured in $\mathrm{molL}^{-1}$
$v$ - volume is measured in $L$
$n$ - moles are measures in mols



## Weak Acids (or conjugates) - buffer pairs

| Weak acid | Conjugate base |
| :---: | :---: |
| $\mathrm{CH}_{3} \mathrm{COOH}$ | $\mathrm{CH}_{3} \mathrm{COO}^{-}$ |
| $\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$ |  |
| $\mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{OH}^{-}$ |  |
| HF | $\mathrm{F}^{-}$ |
| $\mathrm{HF}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{F}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$ |  |
| $\mathrm{F}-+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{HF}^{-}+\mathrm{OH}^{-}$ |  |
| $\mathrm{NH}_{4}^{+}$ | $\mathrm{NH}_{3}$ |
| $\mathrm{NH}_{4}^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+}$ |  |
| $\mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{NH}_{4}^{+}+\mathrm{OH}^{-}$ |  |
| $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}$ | $\mathrm{CH}_{3} \mathrm{NH}_{2}$ |
| $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+} \mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{3} \mathrm{O}^{+}$ |  |
| $\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{NH}_{3}^{+}+\mathrm{OH}^{-}$ |  |

## pH Buffer calculations

Calculate pH of buffer given: $\mathrm{k}_{\mathrm{a}}$ or $\mathrm{Pk}_{\mathrm{a}}+$ conc of [HA] and [A-]

1. Write dissociation equation, and $K$ expression of weak acid (weak acid conjugate)


## Mass Buffer calculations

Calculate Mass of buffer salt given: $\mathrm{pH}+$ conc/volume of $[H A]$ OR $\left[\AA^{\circ}\right]+$ Molar Mass

1. Write dissociation equation, and $K$ expression of weak acid (weak acid conjugate)

| $\mathrm{HA}+\mathrm{H}_{2} \mathrm{O}$ | $\leftrightharpoons$ | $\mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{A}^{-}$ | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10-\mathrm{pH}$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$ | OR | $\left[\mathrm{A}^{-}\right]=\frac{\mathrm{K}_{\mathrm{a}}-\mathrm{X}[\mathrm{HA}]}{10^{-\mathrm{pH}}}$ |  |

2. Calculate Mass - the $\left[A^{-}\right]$is the same as the concentration of the salt (c)
$\mathrm{n}($ salt $)=\mathrm{cv}$ then $\quad \mathrm{m}($ salt $)=\mathrm{n} \times \mathrm{M}$

Reminder that answer in g and to 3 sgf.

## Buffer calculations for monoprotic acids

## Buffer calculations

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{\mathrm{Kax}[\text { weak acid }]}{[\text { conjugate base }]} \quad \mathrm{OR} \quad \mathrm{pH}=\mathrm{pKa}+\log \frac{[\mathrm{A}-]}{[\mathrm{HA}]}
$$

[Weak acid or conjugate base] = original concentration $\times$ original volume 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 $\mathrm{pH}=\mathrm{pKa}$.

## Example

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

$$
\begin{aligned}
\mathrm{pH}=\mathrm{pK}_{\mathrm{a}} & +\log ^{10} \frac{[\text { benzoate ion }]}{[\text { benzoic acid }]} \\
& =4.19+\log ^{10} \quad \frac{0.050}{0.050} \\
& =4.19+\log _{10} 1.0=4.19
\end{aligned}
$$

## Buffer Key Questions - Q8

What is the pH of the buffer solution?

What pH would a buffer be if we added c(acid) with c(base) and $K_{a}$ given? buffer zone?

What type of acid base titration has a

Effectiveness of buffer. What happens when an acid or base is added?

What is the significance of the half equivalence point?
 curve and show buffer zone



## NCEA 2013 Buffers

Question: 1c: (i) The following two solutions from part (a) are mixed to form a buffer solution:
20.0 mL of $1 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl}$ and 30.0 mL of $1 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{CH}_{3} \mathrm{NH}_{2}$

Calculate the pH of the resultant buffer solution. $\mathrm{pKa}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=10.64$
$K_{\mathrm{a}}=\frac{\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right]}$

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\left[\mathrm{A}^{-}\right]\right.}{[\mathrm{HA}]} \text { to }\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{\mathrm{K}_{\mathrm{a}} \times\left[\mathrm{HA}^{2}\right]}{\left[\mathrm{A}^{-}\right]}
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{K_{\mathrm{a}}\left[\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]}
$$

$\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]=\frac{30 \quad 10^{3} 1}{50 \quad 10^{3}}=0.600 \mathrm{~mol} \mathrm{~L}^{1}$

## Calculating dilutions

$\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]=$ original volume $\times$ conc. total volume
$\left[\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}\right]=\frac{20 \quad 10^{3} 1}{50 \quad 10^{3}}=0.400 \mathrm{~mol} \mathrm{~L}^{1}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.52705 \quad 10^{11} \mathrm{~mol} \mathrm{~L}^{1}$
$\mathrm{pH}=10.8$

## NCEA 2013 Buffers

Question: 1c: The following two solutions from part (a) are mixed to form a buffer solution:
20.0 mL of $1 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl}$ and 30.0 mL of $1 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{CH}_{3} \mathrm{NH}_{2}$
(ii) Explain the effect on the solution formed in (i) when a small amount of acid is added.

When a small amount of acid $\left(\mathrm{H}_{3} \mathrm{O}^{+}\right)$ions are added, they will react with the $\mathrm{CH}_{3} \mathrm{NH}_{2(a q)}$ molecules to form $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}{ }_{(a q)}$ ions.
$\mathrm{CH}_{3} \mathrm{NH}_{2(a q)}+\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)} \leftrightharpoons \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}{ }_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(\ell)}$
The added acid $\left(\mathrm{H}_{3} \mathrm{O}^{+}\right)$, is mostly consumed, and the pH of the solution changes very little.

## NCEA 2014 Buffers

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 $\mathrm{L}^{-1} \mathrm{HF}$ to give a buffer solution with a pH of 4.02 .

Assume there is no change in volume.

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

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10-\mathrm{pH}
$$

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

As question is

$$
[\mathrm{F}]=0.354 \mathrm{~mol} \mathrm{~L}^{1}
$$ asking for mass,

$$
\mathrm{n}(\mathrm{NaF})=0.354 \mathrm{~mol} \mathrm{~L}^{1} \quad 0.150 \mathrm{~L}=0.0531 \mathrm{~mol}
$$ use:

$$
n=c \times V
$$

$\mathrm{n}=\mathrm{c} \times V$
$\mathrm{m}(\mathrm{NaF})=0.0531 \mathrm{~mol}$

$$
42.0 \mathrm{~g} \mathrm{~mol}^{1}=2.23 \mathrm{~g} \quad \begin{aligned}
& \mathrm{g} \\
& \mathrm{~m}=n \times \mathrm{M}
\end{aligned}
$$

$$
K_{\mathrm{a}}=\frac{[\mathrm{F}]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{[\mathrm{HF}]}
$$

## NCEA 2017 Buffers

Question 2a (ii) : Dilute hydrochloric acid, HCl , is added to the $\mathrm{NH}_{3}$ solution until the ratio of $\mathrm{NH}_{3}$ to $\mathrm{NH}_{4}{ }^{+}$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.


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 $\left[\mathrm{NH}_{3}\right]>\left[\mathrm{NH}_{4}{ }^{+}\right] /$ $\mathrm{pH}>\mathrm{pKa}$, the buffer will be more effective at neutralising added strong acid.

## NCEA 2018 Buffers

Question: 2. A titration was carried out by adding $0.210 \mathrm{~mol} \mathrm{~L}^{-1}$ hydrochloric a HCl , to 25.0 mL of $0.168 \mathrm{~mol} \mathrm{~L}^{-1}$ methanamine, $\mathrm{CH}_{3} \mathrm{NH}_{2}$.

The equation for the reaction is: $\mathrm{HCl}+\mathrm{CH}_{3} \mathrm{NH}_{2} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{Cl}^{-}$
$\mathrm{p}_{\kappa \mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=10.6 \quad K_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=2.51 \times 10^{-11}$
(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 $\mathrm{CH}_{3} \mathrm{NH}_{2}$ solution above to make a buffer solution of pH 10.0 .


## NCEA 2018 Buffers

Question: 2. A titration was carried out by adding $0.210 \mathrm{~mol} \mathrm{~L}^{-1}$ hydrochloric a HCl , to 25.0 mL of $0.168 \mathrm{~mol} \mathrm{~L}^{-1}$ methanamine, $\mathrm{CH}_{3} \mathrm{NH}_{2}$.

The equation for the reaction is: $\mathrm{HCl}+\mathrm{CH}_{3} \mathrm{NH}_{2} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{Cl}^{-}$
$\mathrm{p} K_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=10.6 \quad \mathrm{~K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=2.51 \times 10^{-11}$
(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 $\mathrm{H}_{3} \mathrm{O}^{+}$ions are neutralised by the basic component of the buffer, $\mathrm{CH}_{3} \mathrm{NH}_{2}$, according to the equation below:
$\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{3} \mathrm{O}^{+} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}^{+}+\mathrm{H}_{2} \mathrm{O}$
OR

$$
\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{HCl} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}^{+}+\mathrm{Cl}^{-}
$$

Since the $\mathrm{H}_{3} \mathrm{O}^{+}$are removed from the solution, the pH of the solution does not significantly change.

## NCEA 2018 Buffers

Question: 3b. 5.11 g of sodium methanoate, HCOONa , was added to 125 mL of $0.105 \mathrm{~mol} \mathrm{~L}^{-1}$ methanoic acid, HCOOH , to make a buffer solution. Assume there is no change in the total volume.
$\mathrm{p} K_{\mathrm{a}}(\mathrm{HCOOH})=3.74 \quad K_{\mathrm{a}}(\mathrm{HCOOH})=1.82 \times 10^{-4}$
(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 .
$M(\mathrm{HCOONa})=68.0 \mathrm{~g} \mathrm{~mol}^{-1}$
The solution will function as a buffer over a pH range $2.74-4.74\left(\mathrm{p} K_{\mathrm{a}}+/-1\right)$.

$$
\begin{aligned}
& n(\mathrm{HCOONa})=\frac{m}{M}=\frac{5.11}{68}=0.0751 \mathrm{~mol} \\
& c\left(\mathrm{HCOO}^{-}\right)=\frac{n}{V}=\frac{0.0751}{0.125}=0.601 \mathrm{~mol} \mathrm{~L}^{-1} \\
& K_{\mathrm{a}}=1.82 \times 10^{-4}=\frac{\left[\mathrm{HCOO}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{[\mathrm{HCOOH}]} \\
& \quad=\frac{0.601 \times\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{0.105}
\end{aligned}
$$

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=3.18 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1}} \\
& \mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=4.50
\end{aligned}
$$

Since the pH of the solution falls within the buffer zone (2.74-4.74), it will function as a buffer. However, as the $\mathrm{pH}>\mathrm{pKa}$, this means $\left[\mathrm{HCOO}^{-}\right]>[\mathrm{HCOOH}]$, so the buffer will be more effective against added strong acid.

## NCEA 2019 Buffers

Question: 3b (i) Dilute hydrochloric acid, HCl , is added to a solution of sodium ethanoate, $\mathrm{CH}_{3} \mathrm{COONa}$, until the ratio of $\mathrm{CH}_{3} \mathrm{COONa}$ to ethanoic acid, $\mathrm{CH}_{3} \mathrm{COOH}$, in the solution is two to five (2:5).

Calculate the pH of this buffer solution. $\quad \mathrm{p} \mathrm{K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=4.76$

$$
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} \\
& K_{\mathrm{a}}=\frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]} \\
& 10^{-4.76}=2 \times \frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{5} \\
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=4.34 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1}} \\
& \mathrm{pH}=-\log 4.34 \times 10^{-5}=4.36
\end{aligned}
$$



## NCEA 2019 Buffers

Question: 3b (ii) Explain why this buffer solution would be more effective at resisting a change in pH when a small volume of strong base is added, rather than strong acid. Dilute hydrochloric acid, HCl , is added to a solution of sodium ethanoate, $\mathrm{CH}_{3} \mathrm{COONa}$

Your answer should include an equation to show how the buffer neutralises added strong base.
$\left[\mathrm{CH}_{3} \mathrm{COOH}\right]>\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right] / \mathrm{pH}<\mathrm{pK}_{\mathrm{a}}$
Therefore the buffer solution is more effective at neutralising strong base:
$\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{OH}^{-} \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{2} \mathrm{O}$
(iii) How would the pH of this buffer solution be affected when it is diluted with water? Explain your answer.

When water is added, the ratio of $\mathrm{CH}_{3} \mathrm{COOH}$ to $\mathrm{CH}_{3} \mathrm{COO}^{-}$is unchanged, so the pH of the buffer solution is unaffected.

## NCEA 2020 Buffers

Question: 1a An aqueous solution containing a mixture of ammonium chloride, $\mathrm{NH}_{4} \mathrm{Cl}$, and ammonia, $\mathrm{NH}_{3}$, can act as a buffer solution.
$\mathrm{K}_{\mathrm{a}}\left(\mathrm{NH}_{4}{ }^{+}\right)=5.75 \times 10^{-10} \quad \mathrm{pK}_{\mathrm{a}}\left(\mathrm{NH}_{4}{ }^{+}\right)=9.24$
(i) Give the pH range over which the solution will function as a buffer.
$8.24-10.24$
(ii) Explain why the addition of a small volume of nitric acid, $\mathrm{HNO}_{3}$, to this buffer solution will not result in a significant change in pH .

Y our answer should include relevant equation(s).
The $\mathrm{H}_{3} \mathrm{O}^{+}$ions from the $\mathrm{HNO}_{3}$ solution are neutralised/removed from the solution by the basic component of the buffer, $\mathrm{NH}_{3}$, according to the equation below:
$\mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+} \rightarrow \mathrm{NH}_{4}^{+}+\mathrm{H}_{2} \mathrm{O}$
$\left(\mathrm{HNO}_{3}+\mathrm{NH}_{3} \rightarrow \mathrm{NH}_{4}^{+}+\mathrm{NO}_{3}^{-}\right)$
The pH of the solution does not significantly change since the $\mathrm{H}_{3} \mathrm{O}^{+}$are removed from the solution / $\mathrm{NH}_{4}{ }^{+}$produced is a much weaker acid than $\mathrm{HNO}_{3}$.

## NCEA 2020 Buffers

Question: 1b (i) Calculate the mass of $\mathrm{NH}_{4} \mathrm{Cl}$ that must be added to 200 mL of 0.0500 mol $\mathrm{L}^{-1} \mathrm{NH}_{3}$ to give a buffer solution with a pH of 8.75 .
Assume there is no change in volume when the solid is added.
$\mathrm{M}\left(\mathrm{NH}_{4} \mathrm{Cl}\right)=53.5 \mathrm{~g} \mathrm{~mol}^{-1}$

$$
\begin{aligned}
& \mathrm{NH}_{4}^{+}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+} \\
& K_{\mathrm{a}}=\frac{\left[\mathrm{NH}_{3}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{NH}_{4}^{+}\right]}
\end{aligned}
$$

$$
5.75 \times 10^{-10}=\frac{0.0500 \times 10^{-8.75}}{\left[\mathrm{NH}_{4}^{+}\right]}
$$

$$
\left[\mathrm{NH}_{4}^{+}\right]=0.155 \mathrm{~mol} \mathrm{~L}^{-1}
$$

$$
n\left(\mathrm{NH}_{4} \mathrm{Cl}\right)=c \mathrm{~V}=0.155 \times 0.200=0.0309 \mathrm{~mol}
$$

$$
m\left(\mathrm{NH}_{4} \mathrm{Cl}\right)=n \times M=0.0309 \times 53.5=1.65 \mathrm{~g}
$$

(ii) Explain whether the buffer in part (i) will be more effective at neutralising strong acid or strong base.

Since the pH of the buffer is less than the $\mathrm{p} K_{\mathrm{a}}(8.75<9.24)$, $\left[\mathrm{NH}_{4}{ }^{+}\right]>\left[\mathrm{NH}_{3}\right]$. As a result, the buffer will be more effective at neutralising small volumes of added strong base.

## Acid - base titration curves

A plot of the pH of an acid solution against the volume of added base (or vice-versa) produces what is called a pH titration curve. The example below shows how the pH (measured using a pH meter) changes when a strong acid is added to a strong base. There are characteristic points on the curve that can be identified. One of these is the equivalence point, the midpoint of the section where the pH of the solution rises (or falls) sharply. The equivalence points for titrations between a strong acid and a strong base have a pH of 7 . Both before and after this section the pH only changes slowly.


Because the pH rises so sharply at the equivalence point of a strong acid/strong base titration a range of indicators can be used to determine the end-point of the titration. If the indicator has a pKa value equal to a pH value within the steep rise in the curve then it will change colour at the equivalence point for this titration.

## Acid - base titration curves



Note that the equivalence point has a $\mathrm{pH}>7$ 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 $\mathrm{HCOO}^{-}$formed reacts with water:
$\mathrm{HCOO}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{HCOOH}+\mathrm{OH}^{-}$

## 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

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 $\mathrm{pk}_{\mathrm{a}}$ 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



## 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

Volume of HCl added (mL)

## Characteristics

Start point below pH 12
Equivalence point below 7
End of titration below pH3
Unsymmetrical shape

## Question: <br> 20.0 mL of $0.0896 \mathrm{~mol} \mathrm{~L}^{-1}$ ethanoic acid is titrated with $0.100 \mathrm{~mol} \mathrm{~L}^{-1}$ sodium hydroxide up to a total of 30 mL $\mathrm{pKa}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=4.76$

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 $\mathrm{pH}=\mathrm{pKa}$
4. The pH at equivalence point
5. The pH after all of the base 30 mL
has been added



Calculate the volume of NaOH at the endpoint.
Titration reaction is:
$\mathrm{CH}_{3} \mathrm{COOH}_{(a q)}+\mathrm{NaOH}_{(a q)} \rightarrow \mathrm{CH}_{3} \mathrm{COONa}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{()}$

From the equation 1:1. Every mole of $\mathrm{CH}_{3} \mathrm{COOH}=$ NaOH

$\mathrm{V}(\mathrm{NaOH}) \quad=\mathrm{n} / \mathrm{C}$
$\mathrm{V}(\mathrm{NaOH})$
Rearrange $n=c / v$ to calculate v of NaOH needed to neutralise
$\mathrm{V}(\mathrm{NaOH})=17.9 \mathrm{~mL}$

Neutralisation equation at end point
$=1.79 \times 10^{-3} \mathrm{~mol}$
$=n\left(\mathrm{CH}_{3} \mathrm{COOH}\right)$
$=1.79 \times 10^{-3} \mathrm{~mol}$
Volume of acid in flask at start $\mathrm{CH}_{3} \mathrm{COOH}$ present

## Calculate the volume of NaOH when $\mathrm{pH}=\mathrm{pKa}$

The volume of NaOH at equivalence point is 17.9 mL

When exactly $1 / 2$ way to end point then $1 / 2$ acid has dissociated into conjugate $\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=\left(\mathrm{CH}_{3} \mathrm{COO}^{-}\right)$
The pH = pKa when
The buffer zone will be 1 pH point above and below pH
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


$$
\mathrm{CH}_{3} \mathrm{COO}_{-(\mathrm{aq)}}+\mathrm{H}_{2} \mathrm{O}_{(0)} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq)}}+\mathrm{OH}_{-(\mathrm{aq})}
$$

$\left[\mathrm{H}_{3} \mathrm{O}+\right]=\sqrt{ }\left(K_{\mathrm{a}} \times K_{\mathrm{w}} \div\right.$ [Conj base] $)$

$$
\left[\mathrm{H}_{3} \mathrm{O}+\right]=\sqrt{ }\left(10^{-4.76} \times 10^{-14} \div\left[0.0472 \mathrm{molL}^{-1}\right]\right)
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}+\right]=1.92 \times 10^{-9} \mathrm{molL}^{-1}
$$



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

Assume

Concentration calculated from previous step $\mathrm{c}=\mathrm{n} / \mathrm{v}$

$$
\begin{aligned}
& 1\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]=\left[\mathrm{OH}^{-}\right] \\
& 2\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]=0.0472 \mathrm{molL}^{-1}
\end{aligned}
$$

Calculate the pH after 30 mL of NaOH has been added.
Since the equivalence point is at 17.9 mL of NaOH , this results in an excess of 12.1 mL of NaOH

Calculate concentration of added base or acid. Although the conjugate does react we assume all $\left[\mathrm{OH}^{-}\right]$or $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$comes from excess added


## NaOH is a strong base

## Assume $\left[\mathrm{OH}^{-}\right]=\quad c(\mathrm{NaOH})$

$\left[\mathrm{OH}^{-}\right]=0.0242 \mathrm{molL}^{-1}$
Strong bases or acids fully dissociate


$$
\begin{aligned}
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] } & =\mathrm{K}_{\mathrm{w}} / 0.0242 \mathrm{molL}^{-1} \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] } & ={ }_{1}^{1} \times 10^{-14} / 0.0242 \mathrm{molL}^{-} \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] } & =4.13 \times 10^{-13} \mathrm{molL}^{-1} \\
\mathrm{pH} & =-\log \left(4.13 \times 10^{-13} \mathrm{molL}^{-1}\right)
\end{aligned}
$$

$$
\mathrm{pH}=12.4
$$

## 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 $\mathrm{pH}=\mathrm{pKa}$ :
8.96 mL

The pH at equivalence point:
8.72

The pH after 30 mL of NaOH is added:



## Drawing titration curves (additional Notes)

Step One: Calcullate the start pH (in flask),

$$
\mathrm{K}_{\mathrm{a}}=10^{-\mathrm{pKa}}
$$

Weak acid $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{\mathrm{K}_{\mathrm{a}} \times \mathrm{c}(\mathrm{HA})}$

Weak base $\left[\mathrm{OH}^{-}\right]=\sqrt{\mathrm{K}_{\mathrm{b}} \times \mathrm{C}(\mathrm{B})}$

$$
\mathrm{K}_{\mathrm{b}}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{~K}_{\mathrm{a}}}
$$

> Assumptions: $[\mathrm{HA}]=\mathrm{c}(\mathrm{HA})$ $\mathrm{H}_{2} \mathrm{O}$ concentration is $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=$[conj base $]$
$\mathrm{H}_{2} \mathrm{O}$ concentration is the same before and after

## 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 $\mathrm{U} / \mathrm{K}$

$$
\mathrm{n}=\mathrm{c} \times \mathrm{v}
$$

Example - if concentration given for NaOH and you are calculating the concentration for $\mathrm{H}_{2} \mathrm{SO}_{4}$
$\bigcap_{\substack{\text { MKNOWN } \\ \text { Moles Unknown }=\text { Moles known } \times \mathrm{U} / \mathrm{K}=\text { Mole Known } \times 1 / 2}}^{\mathrm{H}_{2} \mathrm{SO}_{4}}+\underset{\text { Kin }}{2 \mathrm{NaOH}} \rightarrow \mathrm{Na}_{2} \mathrm{SO}_{4}+2 \mathrm{H}_{2} \mathrm{O}$
c) Rearrange equation to calculate volume

$$
v=n / c
$$

$v=$ volume $(\mathrm{L}) \mathrm{c}=$ concentration $\left(\mathrm{molL}^{-1}\right)$

## 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) $=\mathrm{pK}_{\mathrm{a}}$ of the Weak Acid ( or conjugate acid of Weak base)

The buffer zone is 1 pH either side of the mid-point
Why is $\mathrm{pKa}=\mathrm{pH}$ at mid-point of the buffer?
At this point half of the weak acid has reacted with the base to form equal quantities of conjugate. Acid + water $\leftrightharpoons$ conjugate base + $\mathrm{H}_{3} \mathrm{O}^{+}$

So $\mathrm{K}_{\mathrm{a}}=$ [conjugate base $]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
facid]
If they are equal concentration they are cancelled and $\mathrm{K}_{\mathrm{a}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
Therefore $\mathrm{pK}_{\mathrm{a}}=\mathrm{pH}$ as $\mathrm{pK}_{\mathrm{a}}=-\log \mathrm{K}_{\mathrm{a}}$ and $\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$

## Drawing titration curves (additional notes)

Step Four: Calcưlate 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
$\mathrm{HCOOH}_{(\mathrm{aq)}}+\mathrm{NaOH}_{(\mathrm{aq)}} \leftrightharpoons \mathrm{HCOONa}_{(\mathrm{aq)}}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}$
b) Calculate $c$ ( conjugate base) using $c=n / v$
$V=$ initial volume in flask + volume added during titration to reach equivalence
c) Use pH equations

## Drawing titration curves (additional notes)

Step Five: Calculate pH after the equivalence point
$\left[\mathrm{OH}^{-}\right]=$start concentration $\times$volume added after equivalence
total volume acid + base

Plot all of these points on the graph and join with a curved line. If the acid or base is weak the curve will be gentle, if the acid or base is strong the curve will be sharp.

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

for weak acid + strong base identify "limiting" reagent
e.g in $20 \mathrm{~mL} 0.10 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{CH}_{3} \mathrm{COOH}+15 \mathrm{~mL} 0.20 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{NaOH}$ $\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{NaOH} \rightarrow \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{Na}^{+}+\mathrm{H}_{2} \mathrm{O}$

| $n$ | $\left[\mathrm{CH}_{3} \mathrm{COOH}\right]$ | $[\mathrm{NaOH}]$ | $\left[\mathrm{CH}_{3} \mathrm{COO}-\right]$ |
| :---: | :---: | :---: | :---: |
| Initial | $\mathrm{n}=0.1 \times 0.02$ | $\mathrm{n}=0.2 \times 0.015$ <br> $=0.003 \mathrm{~mol}$ <br> $=0.002 \mathrm{~mol}$ | O <br> $=0 \mathrm{~mol}$ |
| Change | -0.002 mol | -0.002 mol | +0.002 mol |
| Equilibrium | $\approx 0$ | $=0.001 \mathrm{~mol}$ | 0.002 mol |

Strong base determines pH i.e. $\left[\mathrm{OH}^{-}\right]=0.001 \mathrm{~mol} / 0.035 \mathrm{~L}$
Then $\mathrm{pH}=-\log \left(1 \times 10^{-14}\right) /\left[\mathrm{OH}^{-}\right]=12.5$

## Making use of $\mathrm{K}_{\mathrm{a}}$ expressions

The equilibrium expressions are generated from an acid dissociation reaction - remember that is a weak acid dissociating in water
$\mathrm{HA}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{A}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$

$$
\left.\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{A}^{-}\right]\left[\mathrm{H}_{3}\right.}{[\mathrm{O}} \mathrm{O}^{+}\right]
$$

If your solution is a weak base then use the conjugate acid to write a dissociation equation and write the expression from this.

The $K_{a}$ in the question will indicate the acid used i.e.
$\mathrm{K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]\left[\mathrm{H}_{3} \underline{\mathrm{O}^{+}}\right.$ $\left[\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right]$
The acid is the denominator

The expression can be rearranged in any way to calculate any of the values.

The relationship of $\quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\mathrm{K}_{\mathrm{w}} /\left[\mathrm{OH}^{-}\right]$
$\left[\mathrm{A}^{-}\right]=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right],[\mathrm{HA}]=\mathrm{C}(\mathrm{HA})$ in acid dissociation
or $\mathrm{pK}_{\mathrm{a}}=-\log \mathrm{K}_{\mathrm{a}}$ and $\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
can also be substituted into the expression as a short cut.
so
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{ } \mathrm{K}_{\mathrm{a}} \times \mathrm{c}(\mathrm{HA})$ for pH of acid
or $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\downarrow \mathrm{K}_{\mathrm{a}} \times \mathrm{K}_{\mathrm{w}} \div \mathrm{c}(\mathrm{B})$ for pH of base
or $\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log \quad[\mathrm{A}-]$ for a buffer pH [HA]

## Which Equation to Use?

When calculating the pH or start concentration you need to use the acid dissociation equation. But what if the solution is a base? and which acid to we use?

This is where the $\mathrm{pK}_{\mathrm{a}} / \mathrm{K}_{\mathrm{a}}$ and mole ratio of equations can help.
Take the reaction: $\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{HBr} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{Br} \quad \mathrm{K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=2.29 \times 10^{-11}$
This is the acid-base reaction (and mol ratio) at equivalence point, when all the moles of base are neutralised by acid. But at the start, no acid ( HBr ) has been added yet. So the only reaction is $\mathrm{CH}_{3} \mathrm{NH}_{2}$ in water:
$\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{OH}^{-}$
$\mathrm{CH}_{3} \mathrm{NH}_{2}$ is the base, therefore $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}$is the conjugate acid.
Also note that the concentration of $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}$and $\mathrm{OH}^{-}$will be the same.
The $\mathrm{K}_{\mathrm{a}}$ indicates that $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}$is the acid used in the $\mathrm{K}_{\mathrm{a}}$ expression, so

$$
\begin{gathered}
\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{3} \mathrm{O}^{+} \\
\mathrm{K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}\right)=\frac{\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}\right]}
\end{gathered}
$$

pH can be used to calculate $\mathrm{H}_{3} \mathrm{O}^{+}$
As per the equation above, the concentration of $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}=\mathrm{OH}^{-}$and if you know $\mathrm{H}_{3} \mathrm{O}^{+}$ then you also know $\mathrm{OH}^{-}$

## Calculating the start concentration

Sample question: A titration was carried out by adding hydrobromic acid, HBr , to 20.0 mL of aqueous methylamine, $\mathrm{CH}_{3} \mathrm{NH}_{2}$, solution.
The equation for the reaction is: $\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{HBr} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}^{+}+\mathrm{Br}^{-} \quad \mathrm{K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=2.29 \times 10^{-11}$ The aqueous methylamine, $\mathrm{CH}_{3} \mathrm{NH}_{2}$, solution has a pH of 11.8 before any HBr is added. Show by calculation that the concentration of this solution is $0.0912 \mathrm{~mol} \mathrm{~L}^{-1}$.
$\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+} \mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{3} \mathrm{O}^{+}$

Remember that pH is determined by $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and the conjugate produced will react
with water to produce the $\mathrm{H}_{3} \mathrm{O}^{+}$. Therefore this is the equation used in $\mathrm{K}_{\mathrm{a}}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-11.8}=1.58 \times 10^{-12}$
calculate $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-\mathrm{pH}}$
${\underset{\mathrm{K}}{\mathrm{a}}}=\frac{\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}\right]}$
$=\underline{\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}$
[ OH ]
$2.29 \times 10^{-11}=$
$\frac{\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right] \times\left(10^{-11.8}\right)^{2}}{1 \times 10^{-14}}$
$\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]=\frac{\left(2.29 \times 10^{-11}\right) \times\left(1 \times 10^{-14}\right)}{\left(10^{-11.8}\right)^{2}}$


Rearrange so
$[$ weak base $]=\mathrm{K}_{\mathrm{a}} \times \mathrm{K}_{\mathrm{w}} \div\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}$


$$
\begin{aligned}
& \text { write out } \mathrm{K}_{\mathrm{a}} \text { expression } \\
& {[\text { [Conj }]=\left[\mathrm{OH}^{-}\right]}
\end{aligned}
$$

Add in values $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10-\mathrm{pH}$
substitute $\quad\left[\mathrm{OH}^{-}\right]=\mathrm{k}_{\mathrm{w}} /\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
$=0.0912 \mathrm{~mol} \mathrm{~L}^{-1}$
Calculate to 3 sgf with units

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

Sample question: 20.0 mL of $0.0896 \mathrm{~mol} \mathrm{~L}^{-1}$ ethanoic acid is titrated with $0.100 \mathrm{~mol} \mathrm{~L}^{-1}$ sodium hydroxide. $\mathrm{pKa}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=4.76$

Calculate the pH of the titration mixture after 5.00 mL of NaOH has been added.
$\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}-+\mathrm{H}_{3} \mathrm{O}^{+}$

This is the equation that the $\mathrm{K}_{\mathrm{a}}$ is derived from - but as most of the $\mathrm{CH}_{3} \mathrm{OO}^{-}$is produced from the NaOH reacting, this is the concentration we use to calculate pH
$\mathrm{NaOH}(a q)+\mathrm{CH}_{3} \mathrm{COOH}_{(a q)} \leftrightharpoons \mathrm{NaCH}_{3} \mathrm{COO}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(1)}$ Calculate the number of moles of 20 ml acid $n=c x v$
$n\left(\mathrm{CH}_{3} \mathrm{COOH}\right.$ at start $)=0.0896 \times\left(20 \times 10^{-3}\right)=1.79 \times 10^{-3} \mathrm{~mol}$ $n(\mathrm{NaOH}$ added $)=0.1 \times\left(5 \times 10^{-3}\right)=5 \times 10^{-4} \mathrm{~mol}$

After 5 mL NaOH added: (total 25 mL )

Calculate the number of moles of 5 ml base
$n\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=129 \times 10^{-3} \mathrm{Subtract}$ moles of base from acid - neutralised $\left(\mathrm{n}\left(\mathrm{CH}_{3} \mathrm{COOH}-\mathrm{n}(\mathrm{NaOH})\right.\right.$ after 5 mL
Remember $1 \mathrm{~mol} \mathrm{CH}_{3} \mathrm{COO}^{-}$produced for each mol NaOH reacting.

Also produced from $\mathrm{CH}_{3} \mathrm{COOH}$ reacting with water but $\mathrm{K}_{\mathrm{a}}$ is small so can disregard
$n\left(\mathrm{CH}_{3} \mathrm{COO}^{-}\right)=5 \times 10^{-4} \mathrm{~mol}$
$c=n / v$
Volume is 25 ml total
$\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=0.0516 \mathrm{~mol} \mathrm{~L}^{-1}$

$\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]=0.0200 \mathrm{~mol} \mathrm{~L}^{-1}$


$$
\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\mathrm{log}
$$

pH
$=4.35$

## Summary of steps - After amount base/acid added - Q9

## Weak base vs Strong Acid

1. Calculate n weak base n (weak base (start)) = cv
2. Calculate n strong acid $\mathrm{n}($ strong acid $(\mathrm{start}))=\mathrm{cv}$ $\square$
After acid added
3. $n($ weak base $)=n($ weak base(start $))-n($ acid $)$
4. $c($ weak base $)=n($ weak base $) /$ total volume

NOTE: n (conj. acid) $=\mathrm{n}$ (strong acid)
3. $c($ conj. acid $)=n($ conj. acid $) /$ total volume
$\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log$

$$
\frac{[\text { weak base] }}{[\text { conj. acid] }}
$$

Concentration and volume given for both acid and base

## Weak acid vs Strong Base

1. Calculate $n$ weak acid n(weak acid (start)) = cv
$\square$
2. Calculate n strong base $\mathrm{n}($ strong base $(\mathrm{start}))=\mathrm{cv}$

After base added

3. $n($ weak acid $)=n($ weak acid (start $))-n($ base $)$
4. $c($ weak acid $)=n($ weak acid $) /$ total volume

NOTE: n (conj. base) $=\mathrm{n}$ (strong base)
3. $c($ conj. base $)=n($ conj. Base $) /$ total volume
$\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log$

$$
\frac{\text { [conj. base] }}{\text { [weak acid] }}
$$

## Equivalence point pH

Sample question: 20.00 mL of $0.320 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{ammonia}, \mathrm{NH}_{3}$, is titrated with $0.640 \mathrm{~mol} \mathrm{~L}^{-1}$ hydrochloric acid, $\mathrm{HCl} . \quad \mathrm{pK}_{\mathrm{a}}\left(\mathrm{NH}_{4}{ }^{+}\right)=9.24 \quad \mathrm{NH}_{3}+\mathrm{HCl} \leftrightharpoons \mathrm{NH}_{4}{ }^{+}+\mathrm{Cl}^{-}$ Show, by calculation, that the pH at the equivalence point (point C ) is 4.96 .
$n\left(\mathrm{NH}_{3}\right)=\mathrm{cv}$
$\mathrm{n}\left(\mathrm{NH}_{3}\right)=0.320 \mathrm{~mol} \mathrm{~L}^{-1} \times 0.0200 \mathrm{~L}$
$\mathrm{n}\left(\mathrm{NH}_{3}\right)=6.40 \times 10^{-3} \mathrm{~mol}$
$\mathrm{v}(\mathrm{HCl})=\mathrm{n} / \mathrm{c}$
$v(\mathrm{HCl})=6.40 \times 10^{-3} \mathrm{~mol} / 0.640 \mathrm{~mol} \mathrm{~L}^{-1}$
$v(\mathrm{HCl})=0.0100 \mathrm{~L}(10.0 \mathrm{~mL})$
$\mathrm{c}\left(\mathrm{NH}_{4}{ }^{+}\right)=\mathrm{n} /$ total V
$\mathrm{c}\left(\mathrm{NH}_{4}{ }^{+}\right)=6.40 \times 10^{-3} \mathrm{~mol} / 0.0300 \mathrm{~L}$
$\mathrm{c}\left(\mathrm{NH}_{4}{ }^{+}\right)=0.213 \mathrm{molL}^{-1}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{\mathrm{K}} \times \mathrm{C}\left(\mathrm{NH}_{4}{ }^{+}\right)$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{ } 10^{-9.24} \times 0.213 \mathrm{molL}^{-1}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.11 \times 10^{-5} \mathrm{molL}^{-1}$

Plus starting volume

also assume $n(B)=n\left(B^{+}\right)$see step 1 .
$\mathrm{B}=\mathrm{NH}_{3} \quad \mathrm{~B}^{+}=\mathrm{NH}_{4}{ }^{+}$
total $\mathrm{v}=$ start volume base +v acid added
calculate $[B+] \quad C=n /$ total $v$
$\left(\mathrm{n}\left(\mathrm{NH}_{3}\right)=\mathrm{n}(\mathrm{HCl})\right.$ from $1: 1$ equation $)$
$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
$\mathrm{pH}=-\log \left[1.11 \times 10^{-5} \mathrm{molL}^{-1}\right]$
$\mathrm{pH}=4.96$
calculate $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \quad \mathrm{K}_{\mathrm{a}}=10^{-\mathrm{pKa}}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{ } \mathrm{K}_{\mathrm{a}} \times \mathrm{C}\left(\mathrm{B}^{+}\right)$
Calculate $\mathrm{pH} \quad \mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \quad 3 \mathrm{sgf}$
Check pH against estimate on curve

## Summary of steps - Equivalence point pH - Q10

## From neutralisation equation <br> $n($ acid $)=n($ weak base $)=n($ conjugate acid $)$ <br> Weak base vs Strong Acid

1. Calculate n weak base n (weak base) $=\mathrm{cv}$ (info from question)
2. Calculate $v$ strong acid v (strong acid) $=\mathrm{n} / \mathrm{c}$
3. Calculate c conjugate acid $c$ (conjugate acid) $=n$ /total $v$
4. $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\vee \mathrm{K}_{\mathrm{a}} \times \mathrm{C}($ conjugate acid $)$
5. $\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$

## Alternative

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}}{(\mathrm{c}(\text { acid }) \times \quad \text { original } \mathrm{v} / \text { total } \mathrm{v})}
$$

If given $v$ in the question (from graph)

## From neutralisation equation

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

## Weak acid vs Strong Base

1. Calculate n weak acid
n (weak acid) $=\mathrm{cv}$ (info from question)
2. Calculate v strong base $\mathrm{v}($ strong base) $=\mathrm{n} / \mathrm{c}$
3. Calculate c conjugate base
c (conjugate base) $=\mathrm{n} /$ total v
4. $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{\mathrm{K}_{\mathrm{a}} \times \mathrm{K}_{\mathrm{w}}}$
c(conjugate base)
5. $\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$

## Summary of steps - Equivalence point pH - Q10

Finish here

$$
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
$$

Need to find pH
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{ } \mathrm{K}_{\mathrm{a}} \times \mathrm{c}$ (conj acid)

You can work also backwards to find out what calculations you need to do

Need to find $\mathrm{H}_{3} \mathrm{O}^{+}$

$$
c(\text { conj acid) }=n \text { /total } v
$$

n(base) $=$ n(conj acid)

Need to find n(conj acid)

Start v(base) + v(Acid)
Need to find $v$ (conj acid)

$$
n(\text { base })=c . v \quad n(\text { base })=n \text { (acid) } \quad v \text { (acid) }=n / c
$$

Given conc of acid + base and volume start base

## NCEA 2013 Titrations- (PART ONE)

Question: 3a: 20.0 mL of $0.0896 \mathrm{~mol} \mathrm{~L}^{-1}$ ethanoic acid is titrated with 0.100 Question $\mathrm{L}^{-1}$ sodium hydroxide. $\mathrm{pKa}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=4.76$
(a) Calculate the pH of the ethanoic acid before any NaOH is added.

```
CH3}\textrm{COOH}+\mp@subsup{\textrm{H}}{2}{}\textrm{O}\leftrightharpoons\mp@subsup{\textrm{CH}}{3}{}\textrm{COO}-+\mp@subsup{\textrm{H}}{3}{}\mp@subsup{\textrm{O}}{}{+
```

This is the equation that the $\mathrm{K}_{\mathrm{a}}$ is derived from
As no base is added yet - the $\mathrm{H}_{3} \mathrm{O}^{+}$produced just comes from reaction with water

Using usual method of pH calculation Remember $\mathrm{K}_{\mathrm{a}}=10^{-\mathrm{pKa}}$ and $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]$

$$
\begin{aligned}
& K_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{COO}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]} \\
& {\left[\begin{array}{c}
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}
\end{array}\right]=\sqrt{1.74} 10^{5} \quad 0.0896} \\
& \mathrm{pol} \mathrm{~L} \\
& \\
& =1.25 \quad 10^{3} \mathrm{~mol} \mathrm{~L}^{1}
\end{aligned}
$$

$$
\text { - } \mathrm{pH}=\mathrm{p} K_{\mathrm{a}}+\log \frac{[\text { base }]}{[\text { acid }]}
$$

$$
\mathrm{pH}=\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=2.90
$$

## NCEA 2013 Titrations - (PART TWO)

Question: 3b: Halfway to the equivalence point of the titration, the $\mathrm{pH}=\mathrm{pKa}$ 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 $\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]$
then $\mathrm{K}_{\mathrm{a}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
So $\mathrm{pK}_{\mathrm{a}}=\mathrm{pH}$


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.
$\mathrm{NaOH}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \rightarrow \mathrm{NaCH}_{3} \mathrm{COO}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
[ $\left.\mathrm{CH}_{3} \mathrm{COO}^{-}\right]$increases as it is formed in reaction
[ $\mathrm{Na}^{+}$] increases as NaOH is added
[ $\left[\mathrm{CH}_{3} \mathrm{COOH}\right]$ decreases as it reacts with NaOH
[ $\mathrm{H}_{3} \mathrm{O}^{+}$] decreases because $\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right] /\left[\mathrm{CH}_{3} \mathrm{COOH}\right]$ increases and $K_{\mathrm{a}}$ is a constant.
[ $\mathrm{OH}^{-}$] increases because $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$decreases and $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]$is constant.

Question: 3c: 20.0 mL of $0.0896 \mathrm{~mol} \mathrm{~L}^{-1}$ ethanoic acid is titrated with 0.100 mol $\mathrm{L}^{-1}$ sodium hydroxide. $\mathrm{pKa}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=4.76$
(ii) Calculate the pH of the titration mixture after 5.00 mL of NaOH has been added.

$$
\begin{aligned}
& \mathrm{NaOH}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COOH}_{(a q)} \rightarrow \\
& \mathrm{NaCH}_{3} \mathrm{COO}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l}} \\
& n\left(\mathrm{CH}_{3} \mathrm{COOH} \text { at start }\right) \quad=0.0896 \times\left(20 \times 10^{-3}\right)=1.79 \times 10^{-3} \mathrm{~mol} \quad \mathrm{n}=\mathrm{c} \times \mathrm{v} \\
& n(\mathrm{NaOH} \text { added })=0.1 \times\left(5 \times 10^{-3}\right)=5 \times 10^{-4} \mathrm{~mol} \quad \mathrm{n}=\mathrm{cx} \mathrm{v}
\end{aligned}
$$

After 5 mL NaOH added: (total 25 mL )

$$
n\left(\mathrm{CH}_{3} \mathrm{COOH}\right) \quad=1.29 \times 10^{-3} \mathrm{~mol}
$$

$\left(\mathrm{n}\left(\mathrm{CH}_{3} \mathrm{COOH}-\mathrm{n}(\mathrm{NaOH})\right.\right.$ after 5 mL$)$
$n\left(\mathrm{CH}_{3} \mathrm{COO}^{-}\right)=5 \times 10^{-4} \mathrm{~mol}$
$\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=0.0516 \mathrm{~mol} \mathrm{~L}^{-1} \quad \mathrm{c}=\mathrm{n} / \mathrm{v}$
$\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]=0.0200 \mathrm{~mol} \mathrm{~L}^{-1}$
$\mathrm{c}=\mathrm{n} / \mathrm{v}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=4.48 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1}$
$\mathrm{pH} \quad=4.35$

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
$\mathrm{HCOOH}_{(a q)}+\mathrm{NaOH}_{(\mathrm{aq)}} \leftrightarrow \mathrm{HCOONa}_{(\mathrm{aq)}}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}$

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

V = initial volume in flask + volume added during titration to reach equivalence
c) Use pH equations

## NCEA 2014 Titrations - (PART ONE)

Question: 3a: A titration was carried out by adding hydrobromic acid, HBr , to 20.0 mL of aqueous methylamine, $\mathrm{CH}_{3} \mathrm{NH}_{2}$, solution.

The equation for the reaction is:
$\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{HBr} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}++\mathrm{Br}$
$K_{a}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=2.29 \times 10^{-11}$
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 $\mathrm{A},\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right] \approx\left[\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right]$. So the solution has buffering properties in the proximity of point A . When HBr is added, the $\mathrm{H}_{3} \mathrm{O}^{+}$is consumed:
$\mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{CH}_{3} \mathrm{NH}_{2} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{H}_{2} \mathrm{O}$
Since the $\mathrm{H}_{3} \mathrm{O}^{+}$is removed from the solution (neutralised), the pH does not change significantly.


## NCEA 2014 Titrations - (PART TWO)

Question: 3b: A titration was carried out by adding hydrobromic acid HBr Question to 20.0 mL of aqueous methylamine, $\mathrm{CH}_{3} \mathrm{NH}_{2}$, solution.

The equation for the reaction is: $\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{HBr} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}++\mathrm{Br}$
$K_{a}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=2.29 \times 10^{-11}$
The aqueous methylamine, $\mathrm{CH}_{3} \mathrm{NH}_{2}$, 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 $L^{-1}$.

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-11.8}=1.58 \times 10^{-12}} \\
& \underbrace{}_{3}=\frac{\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}\right]} \\
& \quad=\frac{\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{[\mathrm{OH}]} \\
& 2.29 \times 10^{-11}=\frac{\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right] \times\left(10^{-1.8}\right)^{2}}{1 \times 10^{-14}} \\
& {\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]=\frac{\left(2.29 \times 10^{-11}\right) \times\left(1 \times 10^{-14}\right)}{\left(10^{-11.8}\right)^{2}}} \\
& =0.0912 \mathrm{~mol}^{\mathrm{L}-1}
\end{aligned}
$$



## NCEA 2014 Titrations - (PART THREE)

Question: 3c: Write the formulae of the four chemical species, apart from water and $\mathrm{OH}^{-}$, that are present at the point marked B on the curve.
(ii) Compare and contrast the solution at point $\mathbf{B}$ 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.
$\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}, \mathrm{Br}, \mathrm{CH}_{3} \mathrm{NH}_{2}, \mathrm{H}_{3} \mathrm{O}^{+}$



## NCEA 2014 Titrations - (PART FOUR)

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 $\left(\mathrm{CH}_{3} \mathrm{NH}_{2}\right)$ which only partially reacts with water to produce a relatively low concentration of ions.

As a result, the initial $\mathrm{CH}_{3} \mathrm{NH}_{2}$ solution will be a poor electrical conductor.
$\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{CH}_{3} \mathrm{NH}_{3}^{+}+\mathrm{OH}^{-}$
Therefore species present are $\mathrm{CH}_{3} \mathrm{NH}_{2}>\mathrm{OH}^{-} \geq \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}>\mathrm{H}_{3} \mathrm{O}^{+}$
At point B , there is a solution of the salt $\mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Br}$ present which is dissociated completely into ions. Therefore there is a relatively high concentration of ions $\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right.$and Br$)$ present in the solution, so it will be a good electrical conductor / electrolyte.
$\mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Br} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{Br}$
$\mathrm{CH}_{3} \mathrm{NH}_{3}+$ reacts with water according to the equation
$\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{3} \mathrm{O}^{+}$
Species present are $\mathrm{Br}^{-}>\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}>\mathrm{H}_{3} \mathrm{O}^{+} \geq \mathrm{CH}_{3} \mathrm{NH}_{2}>\left(\mathrm{OH}^{-}\right)$

Question: 3a: 20.0 mL of $0.258 \mathrm{~mol}^{-1}$ hydrofluoric acid, HF, solution is titrated with a sodium hydroxide, NaOH , solution.
The equation for the reaction is:
$\mathrm{HF}+\mathrm{NaOH} \rightarrow \mathrm{NaF}+\mathrm{H}_{2} \mathrm{O}$

$$
\mathrm{pKa}(\mathrm{HF})=3.17
$$

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

$\mathrm{Na}^{+}, \mathrm{F}_{\mathrm{H}} \mathrm{H}_{2} \mathrm{HF}_{2}$
$\mathrm{OH}^{-}, \mathrm{H}_{3} \mathrm{O}^{2}$

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


## NCEA 2015 Titrations - (PART THREE)

Question: 3a: 20.0 mL of $0.258 \mathrm{~mol} \mathrm{~L}^{-1}$ hydrofluoric acid, HF , solution is titrated with a sodium hydroxide, NaOH , solution.

$$
\mathrm{HF}+\mathrm{NaOH} \rightarrow \mathrm{NaF}+\mathrm{H}_{2} \mathrm{O} \quad \mathrm{pKa}(\mathrm{HF})=3.17
$$

(iii) After a certain volume of NaOH solution has been added, the concentration of HF in the solution will be twice that of the $\mathrm{F}^{-}$.

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

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=2 \times 10^{-3.17}=1.35 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}} \\
& \mathrm{pH}=-\log \left(1.35 \times 10^{-3}\right)=2.87 .
\end{aligned}
$$

$$
\begin{aligned}
\mathrm{pH} & =\mathrm{p} K_{\mathrm{a}}+\log \left[\mathrm{F}^{-}\right] /[\mathrm{HF}] \\
& =3.17+\log 0.5 \\
& =2.87
\end{aligned}
$$

Since there are significant concentrations of the weak acid

Alternative method and its conjugate base the solution can resist added acid or base.

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

Question: 3a: 20.0 mL of $0.258 \mathrm{~mol}^{-1}$ hydrofluoric acid, HF , solution is titrated with a sodium hydroxide, NaOH , solution.

$$
\mathrm{HF}+\mathrm{NaOH} \rightarrow \mathrm{NaF}+\mathrm{H}_{2} \mathrm{O} \quad \mathrm{p} K_{a}(\mathrm{HF})=3.17
$$

(iv) Determine by calculation, the pH of the solution after 24.0 mL of $0.258 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{NaOH}$ solution has been added. .

Remember after neutralization pH from all additional strong base added can be calculated as per usual


$$
\begin{array}{r}
n(\mathrm{NaOH})=c v=0.258 \quad \frac{24 \quad 20}{1000}=1.032 \quad 10^{3} \mathrm{~mol} \\
c(\mathrm{NaOH})=\frac{n}{v}=\frac{1.032 \quad 10^{3}}{44 / 1000}=0.0235 \mathrm{~mol} \mathrm{~L}^{1} \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{K_{\mathrm{w}}}{[\mathrm{OH}]}=\frac{10^{14}}{0.0235}=4.26 \quad 10^{13} \mathrm{~mol} \mathrm{~L}^{1}} \\
\substack{\text { Total volume } \\
\text { added Nor }} \\
\mathrm{pH}=\log 4.26 \quad 10^{13}=12.4 \\
\mathrm{pH} \text { must be higher than equivalence point after base added }
\end{array}
$$

## NCEA 2015 Titrations - (PART FIVE)

Question: 3b: In a second titration, a $0.258 \mathrm{~mol} \mathrm{~L}^{-1}$ ethanoic acid, $\mathrm{CH}_{3} \mathrm{COOH}$, solution was titrated with the NaOH solution.
Contrast the expected pH at the equivalence point with the HF titration.
$\mathrm{p} K_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=4.76 \quad \mathrm{p} K_{\mathrm{a}}(\mathrm{HF})=3.17 \quad$ No calculations are necessary.
$\rightarrow$ larger $\mathrm{pK}_{\mathrm{a}} \rightarrow$ less dissociation $\rightarrow$ weaker acid
Since $\mathrm{CH}_{3} \mathrm{COOH}$ has a higher $\mathrm{p} \mathrm{a}_{\mathrm{a}^{\prime}}$ it is a weaker acid than HF. Therefore its conjugate base, $\mathrm{CH}_{3} \mathrm{COO}^{-}$, will be a stronger base than $\mathrm{F}^{-}$.

This means $\left[\mathrm{OH}^{-}\right]$will be higher at the equivalence point for the $\mathrm{CH}_{3} \mathrm{COOH}$ vs NaOH titration, so the equivalence point pH will be higher.

Question: 3a: 20.00 mL of $0.320 \mathrm{~mol} \mathrm{~L}^{-1}$ ammonia, $\mathrm{NH}_{3}$, is titrated with $0.640 \mathrm{~mol} \mathrm{~L}^{-1}$ hydrochloric acid, HCl .
The equation for this reaction is:
$\mathrm{NH}_{3}+\mathrm{HCl} \rightarrow \mathrm{NH}_{4}^{+}+\mathrm{Cl}^{-} \quad \mathrm{pK}_{\mathrm{a}}\left(\mathrm{NH}_{4}^{+}\right)=9.24$
The curve for this titration is given below.
Explain why the pH at the equivalence point (point C ) is not 7 .
pH

(Ammonium chloride) is acidic

$$
\mathrm{NH}_{4}^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{NH}_{3}
$$

So therefore

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]>\left[\mathrm{OH}^{-}\right]
$$

When considering pH think about which ion, $\mathrm{H}_{3} \mathrm{O}^{+}$or $\mathrm{OH}^{-}$, will be at the higher concentration

## NCEA 2016 Titrations - (PART TWO)

Question 3b: 20.00 mL of $0.320 \mathrm{~mol} \mathrm{~L}^{-1}$ ammonia, $\mathrm{NH}_{3}$, is titrated with 0.640 mol $\mathrm{L}^{-1}$ hydrochloric acid, $\mathrm{HCl} . \mathrm{pK}_{\mathrm{a}}\left(\mathrm{NH}_{4}{ }^{+}\right)=9.24$

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

Since $B$ is half way to the equivalence point, $\left[\mathrm{NH}_{4}{ }^{+}\right]=\left[\mathrm{NH}_{3}\right]$.

OR
$\mathrm{pK}_{\mathrm{a}}=\mathrm{pH}+\log$ [acid] $\div[$ c.base]

$$
\text { so } \mathrm{K}_{\mathrm{a}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
$$

therefore $\mathrm{pK}_{\mathrm{a}}=\mathrm{pH}$.

## NCEA 2016 Titrations - (PART THREE)

Question 3c: 20.00 mL of $0.320 \mathrm{~mol} \mathrm{~L}^{-1}$ ammonia, $\mathrm{NH}_{3}$, is titrated with 0.640 mol $\mathrm{L}^{-1}$ hydrochloric acid, $\mathrm{HCl} . \mathrm{p} K_{\mathrm{a}}\left(\mathrm{NH}_{4}{ }^{+}\right)=9.24$

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

> As HCl is twice as concentrated as $\mathrm{NH}_{3}$, only need $1 / 2$ volume - so $20 \mathrm{~mL}+10 \mathrm{~mL}=$ total volume. Each mol of NH 3 produces a mol of conjugate at equivalence point. Then need to calculate concentration after dilution
$\left[\mathrm{NH}_{4}^{+}\right]=0.320 \times 20 / 30=0.213 \mathrm{molL}^{-1}$
$\left(K_{a}=10^{-9.24}=5.75 \times 10^{-10}\right)$
pH


$$
\begin{aligned}
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=} & \sqrt{ }\left(5.75 \times 10^{-10} \times 0.213\right) \\
& =1.11 \times 10^{-5} \mathrm{molL}^{-1}
\end{aligned}
$$

$$
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
$$

$$
\mathrm{pH}=4.96
$$

## NCEA 2016 Titrations - (PART THREE)

Question 3c: 20.00 mL of $0.320 \mathrm{~mol} \mathrm{~L}^{-1}$ ammonia, $\mathrm{NH}_{3}$, is titrated with 0.640 mol $\mathrm{L}^{-1}$ hydrochloric acid, $\mathrm{HCl} . \mathrm{p} K_{\mathrm{a}}\left(\mathrm{NH}_{4}{ }^{+}\right)=9.24$

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

> As HCl is twice as concentrated as $\mathrm{NH}_{3}$, only need $1 / 2$ volume - so $20 \mathrm{~mL}+10 \mathrm{~mL}=$ total volume. Each mol of NH 3 produces a mol of conjugate at equivalence point. Then need to calculate concentration after dilution
$\left[\mathrm{NH}_{4}^{+}\right]=0.320 \times 20 / 30=0.213 \mathrm{molL}^{-1}$
$\left(K_{a}=10^{-9.24}=5.75 \times 10^{-10}\right)$
pH


$$
\begin{aligned}
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=} & \sqrt{ }\left(5.75 \times 10^{-10} \times 0.213\right) \\
& =1.11 \times 10^{-5} \mathrm{molL}^{-1}
\end{aligned}
$$

$$
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
$$

$$
\mathrm{pH}=4.96
$$

Question 3d: 20.00 mL of $0.320 \mathrm{~mol} \mathrm{~L}{ }^{-1}$ ammonia, $\mathrm{NH}_{3}$, is titrated with 0.640 mol $\mathrm{L}^{-1}$ hydrochloric acid, $\mathrm{HCl} . \mathrm{p} K_{\mathrm{a}}\left(\mathrm{NH}_{4}{ }^{+}\right)=9.24$

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 $\mathrm{NH}_{4} \mathrm{Cl}$.
$\mathrm{NH}_{4}{ }^{+}$solution is acidic since, $\mathrm{NH}_{4}{ }^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+}$

## NCEA 2017 Titrations - (PART ONE)

Question 3a: A titration was carried out by adding $0.112 \mathrm{~mol} \mathrm{~L}^{-1}$ sodium hydroxide solution, $\mathrm{NaOH}_{(\text {aq) }}$, to 20.0 mL of ethanoic acid solution, $\mathrm{CH}_{3} \mathrm{COOH}_{(a q)}$.
The equation for the reaction is:
$\mathrm{CH}_{3} \mathrm{COOH}_{(a q)}+\mathrm{NaOH}_{(a q)} \rightarrow \mathrm{CH}_{3} \mathrm{COONa}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \quad K_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=1.74 \times 10^{-5}$

Titration curve for $\mathrm{CH}_{3} \mathbf{C O O H}$ 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 | $\mathbf{p} \boldsymbol{K}_{\mathbf{a}}$ | Tick ONE box below |
| :--- | :---: | :---: |
| Methyl yellow | 3.1 |  |
| Bromocresol purple | 6.3 |  |
| Phenolphthalein | 9.6 |  |

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

Show by calculation that the concentration of the $\mathrm{CH}_{3} \mathrm{COOH}$ solution is 0.166 mol $\mathrm{L}^{-1}$.
$\mathrm{CH}_{3} \mathrm{COOH}_{(a q)}+\mathrm{NaOH}_{(a q)} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COONa}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \quad K_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=1.74 \times 10^{-5}$
$\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
$K_{\mathrm{a}}=\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
[ $\left.\mathrm{CH}_{3} \mathrm{COOH}\right]$
Use standard weak acid pH method and re-arrange to find [acid]
$1.74 \times 10^{-5}=\quad \underline{\left(10^{-2.77}\right)^{2}}$
[ $\mathrm{CH}_{3} \mathrm{COOH}$ ]
$\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=0.166 \mathrm{~mol} \mathrm{~L}^{-1}$

## NCEA 2017 Titrations - (PART THREE)

Question 3b (ii) :
Calculate the pH of the solution in the flask after 10.0 mL of $0.112 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{NaOH}$ has been added to 20.0 mL of ethanoic acid solution, $\mathrm{CH}_{3} \mathrm{COOH}_{(a q)}$.
$\mathrm{CH}_{3} \mathrm{COOH}_{(a q)}+\mathrm{NaOH}_{(a q)} \rightarrow \mathrm{CH}_{3} \mathrm{COONa}_{(q q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \quad \mathrm{K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=1.74 \times 10^{-5}$
$n(\mathrm{NaOH})$ added $=0.112 \mathrm{~mol} \mathrm{~L}^{-1} \times 0.01 \mathrm{~L}$
$=1.12 \times 10^{-3} \mathrm{~mol}$
$K_{\mathrm{a}}=\frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]_{\mid}}$
$n\left(\mathrm{CH}_{3} \mathrm{COO}^{-}\right)$in $30 \mathrm{~mL}=1.12 \times 10^{-3} \mathrm{~mol}$
As $n\left(\mathrm{CH}_{3} \mathrm{COO}^{-}\right)=n(\mathrm{NaOH})$
Initial $n\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=0.166 \mathrm{~mol} \mathrm{~L}^{-1} \times 0.02 \mathrm{~L}$
$=3.32 \times 10^{-3} \mathrm{~mol}$
$n\left(\mathrm{CH}_{3} \mathrm{COOH}\right)$ remaining in 30 mL
$=3.32 \times 10^{-3} \mathrm{~mol}-1.12 \times 10^{-3} \mathrm{~mol}$
$=2.2 \times 10^{-3} \mathrm{~mol}$


## NCEA 2017 Titrations - (PART FOUR)

## 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 $0.166 \mathrm{~mol} \mathrm{~L}^{-1}$ methanoic acid solution, $\mathrm{HCOOH}_{(a q)}$ is titrated with the NaOH solution. The equivalence point pH for this titration is 8.28 .
The equivalence point pH for the $\mathrm{CH}_{3} \mathrm{COOH}$ titration is 8.79.
Compare and contrast the pH values at the equivalence point for both titrations. $K_{\mathrm{a}}(\mathrm{HCOOH})=1.82 \times 10^{-4} K_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=1.74 \times 10^{-5}$
No calculations are necessary.

## $\mathrm{CH}_{3} \mathrm{COO}^{-}, \mathrm{Na}^{+}, \mathrm{CH}_{3} \mathrm{COOH}^{-}, \mathrm{OH}^{-}, \mathrm{H}_{3} \mathrm{O}^{+}$

## NCEA 2017 Titrations - (PART FOUR)

Question 3c: (ii)
Compare and contrast the pH values at the equivalence point for both titrations.
$K_{\mathrm{a}}(\mathrm{HCOOH})=1.82 \times 10^{-4} \quad K_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=1.74 \times 10^{-5}$
No calculations are necessary.
Both titrations produce a basic salt at the equivalence point because $\left[\mathrm{OH}^{-}\right]$ $>\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] / \mathrm{pH}>7$ / 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 $\mathrm{OH}^{-}$ions than ethanoate ions

OR HCOOH has a larger $K_{\mathrm{a}}$ than $\mathrm{CH}_{3} \mathrm{COOH}$, as it is a stronger acid. As a result, its conjugate base, $\mathrm{HCOO}^{-}$, is weaker than $\mathrm{CH}_{3} \mathrm{COO}^{-}$, so the pH will be lower at the equivalence point.

## NCEA 2018 Titrations (Part ONE)

Question: 2. A titration was carried out by adding $0.210 \mathrm{~mol} \mathrm{~L}^{-1}$ hydrochloric a HCl , to 25.0 mL of $0.168 \mathrm{~mol} \mathrm{~L}^{-1}$ methanamine, $\mathrm{CH}_{3} \mathrm{NH}_{2}$.

The equation for the reaction is: $\mathrm{HCl}+\mathrm{CH}_{3} \mathrm{NH}_{2} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{Cl}^{-}$
$\mathrm{p}_{K \mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=10.6 \quad K_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=2.51 \times 10^{-11}$
(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 $\mathbf{C H}_{3} \mathbf{N H}_{2}$ versus $\mathbf{~} \mathbf{H C l}$


$$
\mathrm{Cl}^{-}>\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}>\mathrm{CH}_{3} \mathrm{NH}_{2}=\mathrm{H}_{3} \mathrm{O}^{+}>\mathrm{OH}^{-}
$$

## NCEA 2018 Titrations (Part TWO)

Question: 2. A titration was carried out by adding $0.210 \mathrm{~mol} \mathrm{~L}^{-1}$ hydrochloric acid, HCl , to 25.0 mL of $0.168 \mathrm{~mol} \mathrm{~L}^{-1}$ methanamine, $\mathrm{CH}_{3} \mathrm{NH}_{2}$.

The equation for the reaction is: $\mathrm{HCl}+\mathrm{CH}_{3} \mathrm{NH}_{2} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{Cl}^{-}$
$\mathrm{p} K_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=10.6 \quad \mathrm{~K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=2.51 \times 10^{-11}$
(ii) Calculate the pH at the equivalence point.

Remember - at equivalence point the source of $\mathrm{H}_{3} \mathrm{O}^{+}$ions is the conjugate acid reacting with water

Titration Curve for $\mathbf{C H}_{3} \mathbf{N H}_{2}$ versus $\mathbf{H C l}$


$$
\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.53 \times 10^{-6} \mathrm{~mol} \mathrm{~L}^{-1}} \\
& \mathrm{pH}=-\log 1.53 \times 10^{-6}=5.82
\end{aligned}
$$

## NCEA 2019 Titrations

Question: 2a A titration was carried out by adding $0.140 \mathrm{~mol} \mathrm{~L}^{-1}$ sodium hydroxide, NaOH , to 20.0 mL of $0.175 \mathrm{~mol} \mathrm{~L}^{-1}$ methanoic acid, HCOOH .

The equation for the reaction is:
$\mathrm{HCOOH}+\mathrm{NaOH} \rightarrow \mathrm{HCOONa}+\mathrm{H}_{2} \mathrm{O}$
$\mathrm{p} K_{\mathrm{a}}(\mathrm{HCOOH})=3.74 \quad K_{\mathrm{a}}(\mathrm{HCOOH})=1.82 \times 10^{-4}$
(ii) After 12.5 mL of NaOH has been added, the solution has a pH of 3.74.

Explain the significance of this pH with reference to the relative concentrations of the species present.

No calculations are necessary.
After 12.5 mL NaOH has been added, it is halfway to the equivalence point.

This means that $[\mathrm{HCOOH}]=\left[\mathrm{HCOO}^{-}\right]$.
Therefore pH equals $\mathrm{p} K_{\mathrm{a}}$.


## NCEA 2019 Titrations

Question: 2 b (i) A titration was carried out by adding $0.140 \mathrm{~mol} \mathrm{~L}^{-1}$ sodium hydroxide, NaOA , to 20.0 mL of $0.175 \mathrm{~mol} \mathrm{~L}^{-1}$ methanoic acid, HCOOH .
$\mathrm{p} K_{\mathrm{a}}(\mathrm{HCOOH})=3.74 \quad K_{\mathrm{a}}(\mathrm{HCOOH})=1.82 \times 10^{-4}$
With reference to the titration curve, put a tick next to the indicator most suited to identify the equivalence point.

Explain your choice, including the consequences of choosing the other indicators.

| Indicator | $\mathbf{p} K_{\mathrm{a}}$ | Tick <br> ONE box <br> below |
| :--- | :---: | :---: |
| Thymol blue | 1.70 |  |
| Bromocresol green | 4.70 |  |
| Cresol red | 8.30 |  |



Indicators change colour at a $\mathrm{pH} \pm 1$ of the $\mathrm{pK}_{\mathrm{a}}$ / near the $\mathrm{pK}_{\mathrm{a}}$. Therefore, cresol red should be used as it will change near the equivalence point/steepest part of the curve, whereas thymol blue and bromocresol green will change before the equivalence point/steepest part of the curve.

Question: 2 b A titration was carried out by adding $0.140 \mathrm{~mol} \mathrm{~L}^{-1}$ sodium hydroxide, NaOH , to 20.0 mL of $0.175 \mathrm{~mol} \mathrm{~L}^{-1}$ methanoic acid, $\mathrm{HCOOH} . \mathrm{p} K_{\mathrm{a}}(\mathrm{HCOOH})=3.74$ $K_{\mathrm{a}}(\mathrm{HCOOH})=1.82 \times 10^{-4}$ (ii) Calculate the pH at the equivalence point. $\mathrm{V}(\mathrm{NaOH})=25 \mathrm{~mL}$ from graph


## NCEA 2019 Titrations

Question: 2c A titration was carried out by adding $0.140 \mathrm{~mol} \mathrm{~L}^{-1}$ sodium hydroxide, NaOH , to 20.0 mL of $0.175 \mathrm{~mol} \mathrm{~L}^{-1}$ methanoic acid, HCOOH .
$\mathrm{p} K_{\mathrm{a}}(\mathrm{HCOOH})=3.74 \quad K_{\mathrm{a}}(\mathrm{HCOOH})=1.82 \times 10^{-4}$
Calculate the pH of the solution after 28.0 mL of $0.140 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{NaOH}$ has been added.

$$
\begin{aligned}
& \text { After } 28 \mathrm{~mL} \mathrm{NaOH} \text { added: } \\
& n(\text { unreacted } \mathrm{NaOH})=c V=0.140 \times 0.003=4.2 \times 10^{-4} \mathrm{~mol} \\
& c(\mathrm{NaOH})=\frac{n}{V}=\frac{4.2 \times 10^{-4}}{0.048}=8.75 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1} \\
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{1 \times 10^{-14}}{8.75 \times 10^{-3}}=1.14 \times 10^{-12} \mathrm{~mol} \mathrm{~L}^{-1}} \\
& \mathrm{pH}=-\log 1.14 \times 10^{-12}=11.9
\end{aligned}
$$



Remember equivalence at 25 mL from graph

## NCEA 2020 Titrations - (PART ONE)

Question 3a: A titration was carried out by adding $0.280 \mathrm{~mol} \mathrm{~L}^{-1}$ hydrochloric acia, HCl , to 25.0 mL of $0.224 \mathrm{~mol} \mathrm{~L}^{-1}$ sodium ethanoate solution, $\mathrm{CH}_{3} \mathrm{COONa}$.

The equation for the reaction is:

$$
\begin{array}{ll}
\mathrm{CH}_{3} \mathrm{COONa}+\mathrm{HCl} \rightarrow \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{NaCl} & \mathrm{pK}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=4.76 \\
\mathrm{~K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=1.74 \times 10^{-5} & \\
\hline
\end{array}
$$

Titration curve for $\mathrm{CH}_{3} \mathrm{COONa}$ versus HCl

(i) List all the species present in a solution of sodium ethanoate.

Do not include water

$$
\mathrm{Na}^{+}, \mathrm{CH}_{3} \mathrm{COO}^{-}, \mathrm{CH}_{3} \mathrm{COOH}, \mathrm{OH}^{-}, \mathrm{H}_{3} \mathrm{O}^{+}
$$

## NCEA 2020 Titrations - (PART TWO)

Question 3a: A titration was carried out by adding $0.280 \mathrm{~mol} \mathrm{~L}^{-1}$ hydrochloric acia, HCl , to 25.0 mL of $0.224 \mathrm{~mol} \mathrm{~L}^{-1}$ sodium ethanoate solution, $\mathrm{CH}_{3} \mathrm{COONa}$.

The equation for the reaction is: $\mathrm{CH}_{3} \mathrm{COONa}+\mathrm{HCl} \rightarrow \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{NaCl}$ $\mathrm{pK}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=4.76 \quad \mathrm{~K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=1.74 \times 10^{-5}$
(ii) Calculate the pH of the $0.224 \mathrm{~mol} \mathrm{~L}-1$ sodium ethanoate solution before any hydrochloric acid is added.

For this solution: $\quad \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{OH}^{-}$
$\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]=0.224 \mathrm{~mol} \mathrm{~L}^{-1}$
$\mathrm{K}_{\mathrm{a}}=\left[\mathrm{H}_{3} \underline{\mathrm{O}}^{+}\right]\left[\mathrm{CH}_{3} \underline{\left.\mathrm{COO}^{-}\right]}\right.$
$\left[\mathrm{CH}_{3} \mathrm{COOH}\right]$
$1.74 \times 10^{-5}=\underline{0.224\left[\mathrm{H}_{3} \underline{\left.\mathrm{O}^{+}\right]^{2}}\right.}$

$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=8.81 \times 10^{-10} \mathrm{molL}^{-1}$
$\mathrm{pH}=9.05$

## NCEA 2020 Titrations - (PART THREE)

Question 3c: A titration was carried out by adding $0.280 \mathrm{~mol} \mathrm{~L}^{-1}$ hydrochloric acia, HCl , to 25.0 mL of $0.224 \mathrm{~mol} \mathrm{~L}{ }^{-1}$ sodium ethanoate solution, $\mathrm{CH}_{3} \mathrm{COONa}$.

The equation for the reaction is: $\mathrm{CH}_{3} \mathrm{COONa}+\mathrm{HCl} \rightarrow \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{NaCl}$
$\mathrm{pK}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=4.76 \quad \mathrm{~K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=1.74 \times 10^{-5}$
(i) Calculate the pH at the equivalence point.

For this solution: $\quad \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
$\mathrm{K}_{\mathrm{a}}=\left[\mathrm{H}_{3} \underline{\mathrm{O}}^{+}\right]\left[\mathrm{CH}_{3} \underline{\left.\mathrm{COO}^{-}\right]}\right.$
$\left[\mathrm{CH}_{3} \mathrm{COOH}\right]$
$1.74 \times 10^{-5}=\left[\underline{H}_{3} \underline{\left.\mathrm{O}^{+}\right]^{2}}\right.$
( $0.224 \times 25 / 45$ )
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.47 \times 10^{-3} \mathrm{molL}^{-1}$
$\mathrm{pH}=2.83$

Remember to factor in dilution. Titration curve shows equivalence point at 20 mL HCl added

Titration curve for $\mathrm{CH}_{3} \mathrm{COONa}$ versus $\mathbf{H C l}$


## NCEA 2020 Titrations - (PART FOUR)

Question 3c: (ii) In a second titration, 25.0 mL of $0.224 \mathrm{~mol} \mathrm{~L}^{-1}$ methanamine, $\mathrm{CH}_{3} \mathrm{NH}_{2}$, is titrated with the same $0.280 \mathrm{~mol} \mathrm{~L}^{-1}$ hydrochloric acid.
$\mathrm{K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right)=2.29 \times 10^{-11}$
$\mathrm{K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=1.74 \times 10^{-5}$

For this second titration, circle how the pH at the equivalence point will compare to the pH at the equivalence point in the titration of sodium ethanoate.
Lower pH Same pH Higher pH

Explain your answer. No calculations are necessary.

At the equivalence point, the weak acid is present, i.e. either $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}$or $\mathrm{CH}_{3} \mathrm{COOH}$. Since $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}$has a smaller $K_{\mathrm{a}}$ (larger $\mathrm{p} K_{\mathrm{a}}$ ), it is a weaker acid than $\mathrm{CH}_{3} \mathrm{COOH}$ and will therefore dissociate to a lesser extent to produce a lower $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$. As a result, the pH at the equivalence point will be higher for $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}$.

