

# Chemistry AS 91392 C3.6 Aqueous Systems

### Achievement Criteria - Solubility

Demonstrate understanding of equilibrium principles in aqueous systems Aqueous systems are limited to those involving sparingly soluble ionic solids Equilibrium principles in aqueous systems are limited to qualitative descriptions and/or calculations involving:

- relative concentrations of dissolved species
- □ sparingly soluble ionic solids
  - relating solubility to  $K_{\rm s}$
  - 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

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predicting precipitation or dissolution

Sparingly soluble ionic solids are limited to AB, A<sub>2</sub>B and AB<sub>2</sub> types where neither of the ions A nor B reacts further with water.

Candidates are expected to recognise common strong acids (HCl, HBr, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>); strong bases (KOH, NaOH); weak acids (HF, CH<sub>3</sub>COOH, and NH<sub>4</sub><sup>+</sup>); weak bases (NH<sub>3</sub>, CH<sub>3</sub>NH<sub>2</sub>, and CH<sub>3</sub>COO<sup>-</sup>). Less familiar weak acids and bases may be included in the context of appropriate resource information. Values of  $K_b$  or  $pK_b$  will not be provided, but may be derived and used in calculations. Knowledge of specific complex ions covered in <u>Chemistry Level 2 AS91162</u> will be assumed. Less familiar complex ions may be included in the context of appropriate resource information.

### Achievement Criteria – Acids and Bases

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Demonstrate understanding of equilibrium principles in aqueous systems

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

- acidic and basic solutions (includes buffers)
  - acid/base strength,  $K_a$  (p $K_a$ )
  - concentration of species present in weak acidic and/or basic solutions (includes buffers)
  - relating concentration of species to pH and conductivity
  - titration curves to represent an acid-base system including selection of indicators (titrations of weak acids with weak bases are excluded).

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



#### Equilibrium 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.

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The proportion of reactants to products depends upon the reaction and the environmental conditions of a reaction such as temperature, pressure and concentration. On the left hand side the proportion of products will be higher than the reactants and on the right hand side the proportion of reactants will be higher than products.



#### Equilibrium – Evaporation case study

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

The example below shows a system where liquid water is 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.





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### Changes in Equilibrium

<u>A system stays in equilibrium unless a change is made</u> 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

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### Solubility

The solubility of a substance is the **amount** of that substance that will dissolve in a given amount of solvent. Solubility is a <u>quantitative</u> 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.



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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.







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)



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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.

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The solubility of a salt is often measured in grams per litre, g L<sup>-1</sup>, or **moles per litre, mol L**<sup>-1</sup>. 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.

 $\leftrightarrow$  2Ag<sup>+</sup><sub>(aq)</sub>  $CrO_4^{2-}$  (aq  $Ag_2CrO_{4(s)}$ 

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

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### Solubility [s] and Concentration

At room temperature the solubility of silver chromate,  $Ag_2CrO_4$ , is 6.5 x 10<sup>-5</sup> mol L<sup>-1</sup>.

What is the concentration of Ag<sup>+</sup> and CrO<sub>4</sub><sup>2-</sup> ions [s] in 500 mL of a saturated solution?

Start with the equation for the dissolving process.

$$Ag_2CrO_{4(s)} \rightleftharpoons 2Ag_{(aq)}^+ CrO_4^{2-}(aq)$$

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

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

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

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



[] indicates

concentration



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

Example question: What is the solubility [s] of  $Ag_2CrO_4$  in g L<sup>-1</sup>?

To convert from moles per litre to grams per litre it is necessary to use the molar mass  $M(Ag_2CrO_4) = 332$  g mol<sup>-1</sup> and the relationship  $\mathbf{M} = \mathbf{n} \times \mathbf{M}$ . s= 6.5 x 10<sup>-5</sup> mol L<sup>-1</sup>.

Since there is 6.5 x 10<sup>-5</sup> 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  $0.0216 \text{ g L}^{-1}$ .



### Equilibrium Constant: K<sub>C</sub>

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

#### Large K value eg K=10000

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

r products

#### Small K value eg K=0.0001

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



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

### Equilibrium Constant: K<sub>c</sub>

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.

Given 
$$aA + bB \longrightarrow cC + d$$
  
e.g.  $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ 

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.

$$K_{c} = [C]^{C} \times [D]^{d} \qquad [] = \text{concentration in molL}^{-1}$$
  

$$at \text{ equilibrium}$$
e.g.  $K_{c} = \frac{[NH_{3}]^{2}}{[N_{2}] \times [H_{2}]^{3}}$ 

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

### Solubility product K<sub>s</sub>

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

Consider a saturated solution of Ca(OH)<sub>2</sub>. For this equilibrium, we have the solubility product expression:

$$Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^{-}_{(aq)}$$

$$K_s$$
 (Ca(OH)<sub>2</sub>) = [Ca<sup>2+</sup>] [OH<sup>-</sup>]<sup>2</sup>



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

### Solubility product K<sub>s</sub>

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

(a)  $CaCO_{3(s)}$  1.3 x 10<sup>-4</sup>gL<sup>-1</sup> (b)  $Ag_2S_{(s)}$  2.8 x 10<sup>-3</sup> gL<sup>-1</sup>

(c)  $PbI_{2(s)}$  4.2 x 10<sup>-5</sup> gL<sup>-1</sup> (d)  $Fe(OH)_{3(s)}$  6.4 x 10<sup>-2</sup>gL<sup>-1</sup>

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A \Rightarrow cC + dD
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K_{s} = [C]^{c} \times [D]^{d}
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Remember: The **solid salt is not included** in the expression only the ions in aqueous state.

] = concentration in molL<sup>-1</sup>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 K<sub>s</sub>: 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. <u>AB type of salt</u> (ratio of cation to anion = 1:1)

The solubility of BaSO<sub>4</sub> is given as  $1.05 \times 10^{-5}$  mol L<sup>-1</sup> at 25°C. Calculate the value of  $K_s$ .

 $BaSO_4(s) \Rightarrow Ba^{2+}(aq) + SO_4^{2-}(aq)$ 

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

$$K_s$$
 (BaSO<sub>4</sub>) = [Ba<sup>2+</sup>] x [SO<sub>4</sub><sup>2-</sup>] = s<sup>2</sup> = (1.05 x 10<sup>-5</sup>)<sup>2</sup>

$K_s = s^2$	
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 $= 1.10 \times 10^{-10}$ 

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

### **Determining K\_s:** ratio of cation to anion 2:1 or 1:2

<u>AB<sub>2</sub> (or A<sub>2</sub>B) type of salt</u> (ratio cation to anion = 1:2 OR 2:1) Calculate the solubility product for PbI<sub>2</sub> at 25 °C, given the solubility at 25 °C is  $1.52 \times 10^{-3}$  mol L<sup>-1</sup>.

Pbl<sub>2</sub>(s)  $\rightleftharpoons$  Pb<sup>2+</sup>(aq) + 2I<sup>-</sup> (aq) This tells us that [Pb<sup>2+</sup>] = solubility, s = 1.52 x 10<sup>-3</sup> mol L<sup>-1</sup> and [I<sup>-</sup>] = 2 x solubility = 2s = 2 x 1.52 x 10<sup>-3</sup> = 3.04 x 10<sup>-3</sup> mol L<sup>-1</sup>

The expression for  $K_s$  is  $K_s$  (PbI<sub>2</sub>) = [Pb<sup>2+</sup>] x [I<sup>-</sup>]<sup>2</sup>

and substituting for solubility we get

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

 $K_{s} = 4s^{3}$ 

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



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

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

 $S = \gamma$ 

#### Example

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

FeS(s)  $\rightleftharpoons$  Fe<sup>2+</sup>(aq) + S<sup>2-</sup>(aq)

 $K_{\rm s}$  (FeS) = [Fe<sup>2+</sup>] x [S<sup>2-</sup>] = 6.3 x 10<sup>-18</sup>

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

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

:.  $K_s$  (FeS) = s<sup>2</sup> and s = = 2.51 x 10<sup>-9</sup> mol L<sup>-1</sup>

Calculate the solubility of zinc hydroxide at 25 °C given  $K_s$  (Zn(OH)<sub>2</sub>) = 2.0 x 10<sup>-17</sup>

The dissolving equation is  $Zn(OH)_{2(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2OH^{-}_{(aq)}$ This means that  $[Zn^{2+}] =$  solubility = s and  $[OH^{-}] = 2 \times$  solubility = 2s The expression for  $K_s$  is  $K_s (Zn(OH)_2) = [Zn^{2+}] \times [OH^{-}]^2$ 

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

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

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

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

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

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

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

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

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

Silver carbonate,  $Ag_2CO_3$ , is a sparingly soluble salt.  $K_s(Ag_2CO_3) = 8.10 \times 10^{-12} \text{ at } 25^{\circ}C$  $M(Ag_2CO_3) = 276 \text{ g mol}^{-1}$ 

Calculate the mass of  $Ag_2CO_3$  that will dissolve in 50 mL of water to make a saturated solution at 25°C.

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



#### Adding or removing products





Increasing solubility

Neutralisation

Forming complex ions

decreasing solubility Adding more product

#### Analysing the K<sub>s</sub> value

The  $K_s$  value is an indication of position of the equilibrium. A small  $K_s$  indicates more reactants (solid salt) therefore less solubility. A larger  $K_s$  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.  $Ag_2CO_3$  which is sparingly soluble, it will dissociate into its ions – one ion being a cation and the other the anion carbonate.

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

#### **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**

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

Base "locks up" many cations into complex ions

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

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

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

### Effects of adding hydroxide on Solubility

#### Decrease SOLUBILITY

If a sparingly soluble salt contains hydroxide i.e. Zn(OH)<sub>2</sub>, 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** 

#### Increase SOLUBILITY

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

## $[Ag(CN)_{2}]^{-}$ $[AI(OH)_{4}]^{-}$ $[Pb(OH)_{4}]^{2-}$ $[Zn(NH_{3})_{4}]^{2+}$ $[Ni(CN)_{4}]^{2-}$

 $[Ag(NH_3)_4]^{2+}$  $[Cu(NH_3)_4]^{2+}$  $[Zn(OH)_4]^{2-}$  $[Ni(NH_3)_6]^{2+}$ 

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

#### Possible Complex Ions





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



Remove product – solubility increases.

Add to product – solubility decreases

#### NCEA 2013 solubility

Question: 2a: In an experiment, a saturated solution was made by dissolving 1.44 ×  $10^{-3}$  g of Ag<sub>2</sub>CrO<sub>4</sub> in water, and making it up to a volume of 50.0 mL.

 $M (Ag_2CrO_4) = 332 \text{ g mol}^{-1}$ 

(a) Write the  $K_s$  expression for Ag<sub>2</sub>CrO<sub>4(s)</sub>.

 $K_{\rm s} = [{\rm Ag}^+]^2 [{\rm CrO}_4^{2-}]$ 

Achieved

Question

#### NCEA 2013 solubility

**Question: 2b:** In an experiment, a saturated solution was made by dissolving  $1.44 \times 10^{-3}$  g of Ag<sub>2</sub>CrO<sub>4</sub> in water, and making it up to a volume of 50.0 mL.  $M(Ag_2CrO_4) = 332$  g mol<sup>-1</sup>

(i) Calculate the solubility of  $Ag_2CrO_{4(s)}$ , and hence give the [Ag<sup>+</sup>] and [CrO<sub>4</sub><sup>2–</sup>] in the solution.

$$K_{\rm s} = [{\rm Ag}^+]^2 [{\rm CrO_4}^{2-}]$$

$$n(\text{Ag}_{2}\text{CrO}_{4}) = \frac{1.44 \cdot 10^{-3}}{332}$$
  
= 4.33 \cdot 10^{-6} mol in 50 mL  
$$[\text{Ag}_{2}\text{CrO}_{4}] = \frac{4.33 \cdot 10^{-6}}{50 \cdot 10^{-3}}$$
  
= 8.67 \cdot 10^{-5} mol L<sup>-1</sup>  
$$[\text{Ag}^{+}] = 8.67 \cdot 10^{-5} \cdot 2 = 1.73 \cdot 10^{-4} mol L^{-1}$$
  
$$[\text{CrO}_{4}^{2^{-}}] = 8.67 \cdot 10^{-5} mol L^{-1}$$

(ii) Determine the  $Ks(Ag_2CrO_4)$ .

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Excellence

Question

$$K_{\rm s} = (1.73 \ 10^{-4})^2 \ (8.67 \ 10^{-5})$$
  
= 2.61 \ 10^{-12}

**Ouestion: 2a:** A flask contains a saturated solution of PbCl<sub>2</sub> in the presence of undissolved PbCl<sub>2</sub>. (i) Write the equation for the dissolving equilibrium in a saturated solution of PbCl<sub>2</sub>.

 $PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$ 



Question: 2a: (ii) Write the expression for  $K_s$ (PbCl<sub>2</sub>).

$$K_{\rm s} = [{\rm Pb}^{2+}][{\rm Cl}^{-}]^2$$
### NCEA 2014 solubility

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

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

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

$$2x \quad K_{s} = 4x^{3}$$
  

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

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

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

 $[Pb^{2+}] = 1.62 \times 10^{-2} \text{ mol } L^{-1}$  $[Cl^{-}] = 3.24 \times 10^{-1} \text{ mol } L^{-1}$ 

$$s = \sqrt[3]{K_{s}}$$

Merit

Achieved Question

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

❑ Write the equation for the equilibrium occurring in a saturated solution of CaCO<sub>3</sub>.

 $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$ 

Question: 2a: (ii) Write the expression for Ks(CaCO<sub>3</sub>).

 $K_{\rm s} = [{\rm Ca}^{2+}][{\rm CO}_3^{2-}]$ 

Merit

Question

Question: 2a: (iii) Calculate the solubility product of  $CaCO_3$ ,  $K_s(CaCO_3)$ .

The solubility of CaCO<sub>3</sub> is  $5.74 \times 10^{-5}$  mol L<sup>-1</sup>.

# $K_{\rm s}({\rm CaCO}_3) = (5.74 \times 10^{-5})^2 = 3.29 \times 10^{-9}$

200 10

150





$$K_{\rm s} = [{\rm Ag}^+]^2 [{\rm CO}_3^{2-}]$$



Let <i>s</i> = solubility	OR
$[Ag^{+}] = 2s$	$g L^{-1} = c \times M = 0.0349 \text{ g L}^{-1}$
$[CO_3^{2-}] = s$ $K = Ac^3$	so mass in 50 mL = $0.0349 \pm 50$
$K_s = 4s^3$ $s = 1.27 \times 10^{-4} \text{ mol } \text{L}^{-1}$ $n = c \times v = 6.33 \times 10^{-6} \text{ mol}$ $m = n \times M = 1.75 \times 10^{-3} \text{ g}$	$= 1.75 \times 1^{-3} \text{ g}$

## NCEA 2017 Solubility

Question 1b:

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

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(ii) Write the expression for K_s(Cu(OH)_2).
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(iii) Calculate the solubility of Cu(OH)<sub>2</sub> in water at 25°C.

 $K_{\rm s}({\rm Cu(OH)}_2) = 4.80 \times 10^{-20}$ 

Let s = solubility  $[Cu^{2+}] = s$   $[OH-]2 = (2s)^2$   $Ks = 4s^3$   $4s^3 = 4.80 \times 10^{-20}$ So;  $s = 2.29 \times 10^{-7} \text{ mol L}^{-1}$  Merit Question

#### NCEA 2018 Solubility

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

Question: 1b (ii). Calculate the solubility of Ca F<sub>2</sub> in water at 25°C.

 $K_{\rm s}({\rm Ca}~{\rm F_2}) = 3.20 \times 10^{-11}$ 

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

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



Merit Question

#### NCEA 2019 Solubility

Merit Question

**Question:** 1a (i). Write the equation for the equilibrium occurring in a saturated solution of zinc hydroxide,  $Zn(OH)_2$ .

 $\Theta$ 

```
(ii) Write the expression for K_s(Zn(OH)_2).
```

(iii) Calculate the solubility of  $Zn(OH)_2$  in water at 25°C, and give the  $[Zn^{2+}]$  and  $[OH^-]$  in the solution.

 $K_{\rm s}({\rm Zn}({\rm OH})_2) = 3.80 \times 10^{-17}$ 

```
Zn(OH)<sub>2</sub> \rightleftharpoons Zn<sup>2+</sup> + 2OH<sup>-</sup>

Let solubility be 's':

[Zn<sup>2+</sup>] = s [OH<sup>-</sup>] = 2s

K_s = 4s^3

4s^3 = 3.80 \times 10^{-17}

s = 2.12 \times 10^{-6} \text{ mol } L^{-1}

[Zn<sup>2+</sup>] = 2.12 x 10<sup>-6</sup> mol L<sup>-1</sup>

[OH<sup>-</sup>] = 4.24 x 10<sup>-6</sup> mol L<sup>-1</sup>
```

#### NCEA 2020 Solubility

**Question: 2a (i).** Write the equation for the equilibrium occurring in a saturated solution of lead bromide, PbBr<sub>2</sub>.

```
(ii) Write the expression for K_s(PbBr_2).
```

(iii) Calculate the solubility of PbBr<sub>2</sub> in water at 25 °C.  $K_s(PbBr_2) = 2.10 \times 10^{-6}$ 

$$PbBr_2 \rightleftharpoons Pb^{2+} + 2Br^{-}$$
  $K_s = [Pb^{2+}] [Br^{-}]^2$ 

Let solubility be 's':

$$[Pb^{2+}] = s$$
  $[Br^{-}] = 2s$ 

$$K_{\rm s} = 4s^3$$

 $4s^3 = 2.10 \times 10^{-6}$ 

 $s = 8.07 \times 10^{-3} \text{ mol } \text{L}^{-1}$ 



Merit Question



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

$$[OH^{-}] = K_w / [H_3O^+] = 1 \times 10^{-14} / 10^{-8.25} = 1.78 \times 10^{-6} \text{ mol } L^{-1}$$
  
 $K_s = [Ni^{2+}] [OH^{-}]^2$   
 $6.00 \times 10^{-16} = [Ni^{2+}] \times (1.78 \times 10^{-6})^2$ 

 $[Ni^{2+}] = 1.90 \times 10^{-4} \text{ mol } L^{-1}$ 



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

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

The Ag<sub>2</sub>CrO<sub>4</sub> will dissociate completely and form an equilibrium.

 $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$ 

 $\mathsf{Ag^{+}}+\mathsf{2NH}_{\mathsf{3}}\rightarrow[\mathsf{Ag}(\mathsf{NH}_{\mathsf{3}})_{\mathsf{2}}]^{+}$ 

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

#### NCEA 2014 solubility and equilibrium

Excellence

Question

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

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

 $Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^{-}(aq)$  When pH is less than 4 / low, [OH<sup>-</sup>] is decreased due to the reaction with  $H_3O^+$  to form water,

 $H_3O^+ + OH^- \rightarrow H_2O$  so equilibrium shifts to the right to produce more [OH<sup>-</sup>], therefore more Zn(OH)<sub>2</sub> will dissolve.

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

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

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

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

Explain why the solubility of  $CaCO_3$  is higher in an acidic solution.

Use an equation to support your explanation.

The H<sub>3</sub>O<sup>+</sup> from the acidic solution reacts with the CO<sub>3</sub><sup>2–</sup>. This reduces [CO<sub>3</sub><sup>2–</sup>], causing the equilibrium to shift towards the products / RHS to replace some of the lost  $CO_3^{2-}$ . Therefore more solid CaCO<sub>3</sub> will dissolve.

 $2H_3O^+ + CO_3^{2-} \rightarrow 3H_2O + CO_2$ 

Merit Ouestion



$$Ag_2CO_{3(s)} \rightarrow 2Ag_{(aq)}^+ + CO_3^{2-}(aq)$$

$$Ag_{(aq)}^{+} + 2NH_{3(aq)} \Leftrightarrow [Ag(NH_3)_2]_{(aq)}$$

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

Excellence

Question

Question 1b:

(i) 40.0 mL of 0.150 mol L–1 HBr solution was added to 25.0 mL of a saturated silver bromide, AgBr, solution.

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

 $AgBr \Leftrightarrow Ag^+ + Br^-$ 

Br is a common ion / added to solution

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

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



When copper(II) hydroxide is dissolved in an acidic solution, the  $H_3O^+$  ions neutralise

the OH<sup>-</sup> ions /  $H_3O^+$  + OH<sup>-</sup>  $\rightarrow$  2 $H_2O$ 

A decrease in [OH<sup>-</sup>] will result in the forward reaction being favoured, to restore equilibrium / minimise the change.

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

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

Excellence Question

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

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

(i) pH lowered below 4

In a saturated solution:

 $Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$ 

As the pH is lowered,  $[H_3O^+]$  increases. The  $H_3O^+$  will remove and neutralise  $OH^-$  /

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

A decrease in [OH<sup>-</sup>] will result in the forward reaction being favoured, to restore equilibrium / minimise the change.

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

NCEA 2018 Solubility and Equilibrium

#### Excellence Question

Question: 1c. Explain the effect of the following on the solubility of iron(III) hydroxide, Fe(OH)<sub>3</sub>, in water.

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

(ii) Potassium thiocyanate, KSCN, solution added

The SCN– ions can form a complex ion with Fe<sup>3+</sup> ions:

 $Fe^{3+} + SCN^{-} \rightarrow [FeSCN]^{2+}$ 

Since the Fe<sup>3+</sup> are removed from the equilibrium, more Fe(OH)<sub>3</sub> dissolves to

replace some of the Fe<sup>3+</sup>, i.e. equilibrium will shift towards the products / speed up the forward reaction. As a result, the solubility of Fe(OH)<sub>3</sub> increases.



NCEA 2018 Solubility and Equilibrium

Question: (a) (i) Write the solubility product expression, Ks, for silver chloride, AgCl.

(ii) Why does the solubility of AgCl decrease when a small volume of silver nitrate, AgNO<sub>3</sub>, solution is added to a saturated solution of AgCl?

Explain your answer.

 $Ks = [Ag^+][CI^-]$ 

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



Merit

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

NCEA 2019 Solubility and Equilibrium

Excellence Question

Question: 1b Use equilibrium principles to explain why the solubility of Zn(OH)<sub>2</sub> increases when an excess of dilute sodium hydroxide, NaOH, is added.

Include relevant equation(s) in your answer.

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

When the  $OH^-$  ions are in excess, the  $Zn^{2+}$  ions can form a complex ion:

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

A decrease in [Zn<sup>2+</sup>] will result in the forward reaction being favoured, to restore equilibrium / minimise the change.

This causes more solid  $Zn(OH)_2$  to dissolve / the solubility of  $Zn(OH)_2$ increases / so that  $[Zn^{2+}][OH^{-}]$  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, Ni(OH)<sub>2</sub>, in water.

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

• Ammonia solution,  $NH_{3(aq)}$ , is added:

 $Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$ 

When ammonia solution is added, the Ni<sup>2+</sup>ions ar removed from the saturated solution to form a complex ion, as shown below:

 $\mathsf{Ni}^{2+} + \mathsf{6NH}_3 \rightarrow [\mathsf{Ni}(\mathsf{NH}_3)_6]^{2+}$ 

To restore the equilibrium, more solid Ni(OH)<sub>2</sub> dissolves to replace some of the Ni<sup>2+</sup> / increase [Ni<sup>2+</sup>]. Therefore the solubility of Ni(OH)<sub>2</sub> increase<sub>3</sub>.



Excellence

Question (i) And (ii)

### NCEA 2020 Solubility and Equilibrium

Question: 2c (i) Explain the effect of the following on the solubility of nickel hydroxide, Ni(OH)<sub>2</sub>, in water.

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

• The pH is decreased below 4:

 $Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$ 

When the pH is decreased below pH 4,  $[H_3O^+]$ increases. The  $H_3O^+$  remove the OH<sup>-</sup> from the equilibrium according to the neutralisation

equation below:

 $H_3O^+ + OH^- \rightarrow 2H_2O$ 

To restore the equilibrium, more solid  $Ni(OH)_2$ dissolves to replace some of the  $OH^-$  / increase [ $OH^-$ ]. Therefore the solubility of  $Ni(OH)_2$  increases.



Excellence

Question

i) And (ii)

# Ionic product

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

maximum

hold (at a given

temperature)

In any solution, whether it is saturated or not, such as AgCI the product formed [Ag<sup>+</sup>][Cl<sup>-</sup>] is called the **ionic product** and can not exceed the K<sub>s</sub>. If either Ag<sup>+</sup> ions or Cl<sup>-</sup> ions are added from another source, such as by adding NaCl, and the new concentrations of ions exceed the K<sub>s</sub> then a precipitate will form. Ks is the

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#### Example

concentration What is the minimum concentration of Cl<sup>-</sup> ions to give a precipitate of ions the of AgCl?  $c(AgNO_3) = 0.01 molL^{-1}$   $K_s = 2 x 10^{-10}$ solution can

If IP > Ks then precipitate will form

- 1.  $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$
- 2.  $K_s = [Ag^+] [CI^-] = K_s = [0.01] [CI^-]$
- 3. Rearrange  $K_s = [Ag^+] [CI^-]$

[Cl⁻] = K<sub>s</sub>  $= 2 \times 10^{-8}$  $= 2 \times 10^{-10}$ [0.01] 0.01

A precipitate will form if the concentration of Cl<sup>-</sup> ions exceeds 2 x 10<sup>-8</sup> molL<sup>-1</sup>



# 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

 $AgCI(s) \rightleftharpoons Ag^{+}(aq) + CI^{-}(aq)$ 

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

Ag Cr  $4g^+$  + Cr 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 mol L<sup>-1</sup> solution of NaCl?

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

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

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

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

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

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

0.0025

= 6.4 x 10<sup>-8</sup> mol L<sup>-1</sup>.

GZ Science

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



Excellence

Question

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

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

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

$$n(Pb(NO_3)_2) = \frac{2.00 \text{ g}}{331 \text{ g mol}^{-1}}$$
  
= 6.04 × 10<sup>-3</sup> mol  
 $\therefore [Pb^{2+}] = 6.04 \times 10^{-3} \text{ mol } / 0.500$   
= 1.21 × 10<sup>-2</sup> mol L<sup>-1</sup>  
 $Q = (1.21 \times 10^{-2}) \times (0.440)^2$   
= 2.34 × 10<sup>-3</sup>  
As  $Q > K_{s'}$  a precipitate will form.

#### NCEA 2015 Common Ion effect

Question: 2c: Show, by calculation, that a precipitate of lead(II) hydroxide, Pb(OH)<sub>2</sub>, 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 mol L<sup>-1</sup> lead(II) nitrate,  $Pb(NO_3)_2$ , solution.

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

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

Sp

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Excellence

$$\begin{array}{l} \mathsf{Pb}(\mathsf{OH})_2 \rightleftharpoons \mathsf{Pb}^{2+} + 2\mathsf{OH}^-\\ Q = [\mathsf{Pb}^{2+}][\mathsf{OH}^-]^2\\ [\mathsf{Pb}^{2+}] = 0.5 \times 0.00421 = 2.105 \times 10^{-3}\\ [\mathsf{OH}^-] = 0.5 \times 0.0398 = 1.99 \times 10^{-2}\\ Q = (2.105 \times 10^{-3}) \times (1.99 \times 10^{-2})^2\\ Q = 8.34 \times 10^{-7}\\ \mathsf{Since}\ Q > K_{cl} \text{ a precipitate of }\mathsf{Pb}(\mathsf{OH})_2 \text{ will form.} \end{array} \right| \begin{array}{l} \mathsf{PH} = 12.6\\ \mathsf{pOH} = 1.4\\ [\mathsf{OH}^-] = 0.0398\\ \mathsf{OH}^-] = 0.0398\\ \mathsf{PH} = 1.4\\ \mathsf{OH}^-] = 0.0398\\ \mathsf{PH} = 1.4\\ \mathsf{PH} = 1$$

#### NCEA 2016 Common Ion effect

**Excellence** 

Question

**Question:** 1d: Show by calculation whether a precipitate of  $Ag_2CO_3$  will form when 20.0 mL of 0.105 mol L<sup>-1</sup> silver nitrate, AgNO<sub>3</sub>, solution is added to 35.0 mL of a 0.221 mol L<sup>-1</sup> sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>, solution.

 $K_{\rm s}({\rm Ag}_{2}{\rm CO}_{3}) = 8.10 \times 10^{-12} \text{ at } 25^{\circ}{\rm C}$ 

$AaNO_{2}$ dilution:	$\frac{20}{55}$ $(0.105) = 0$	).0382	
5	55	The ratio of the	
$Na_2CO_3$ dilution:	$\frac{35}{55}$ $\sim 0.221 = 0$	<sup>0.141</sup> concentrations of products and reactants called O	is
Q / I.P. = [0.03818]	<sup>12</sup> [0.1406] = 2.06 x 10 <sup>-</sup>	-4 Called Q.	2.6
As $Q / I.P. > K_{sr} a \mu$	precipitate will form.	$K_{\rm s} = [Ag^+]^2[CO_3^{2-}]$	

#### NCEA 2017 Common Ion effect

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

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

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

Assume the concentration of Br<sup>-</sup> in the original saturated solution of AgBr is insignificant.

AgBr  $\Rightarrow$  Ag<sup>+</sup> + Br<sup>-</sup> Ks(AgBr) = [Ag<sup>+</sup>] [Br<sup>-</sup>] 5 ×10<sup>-13</sup> = [Ag<sup>+</sup>] × <u>0.150 × 40</u> 65 [Ag<sup>+</sup>] = 5.42 ×10<sup>-12</sup> mol L<sup>-1</sup> The ratio of the concentrations of products and reactants is called Q.

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Excellence

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 mol L<sup>-1</sup> AgNO<sub>3</sub> is added to 50.0 mL of 0.0550 mol L<sup>-1</sup> sodium chloride, NaCl.

 $K_{\rm s}({\rm AgCl}) = 1.80 \times 10^{-10}$ 

Dilution: volume / total volume of solutions

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



Excellence

NCEA 2019 Common Ion Effect

Question: 1a (iv). The presence of a common ion decreases the solubility of a sparingly soluble solid, such as Zn(OH)<sub>2</sub>.

63

Calculate the concentration of the hydroxide ions, OH<sup>-</sup>, in solution after 25.0 mL of 0.210 mol L<sup>-1</sup> zinc chloride, ZnCl<sub>2</sub>, solution was added to 25.0 mL of a saturated  $Zn(OH)_2$  solution.

 $K_{\rm s}({\rm Zn}({\rm OH})_2) = 3.80 \times 10^{-17}$ 

(0.210/2) due to dilution factor from adding two solutions together.

 $K_{\rm s} = [{\rm Zn}^{2+}][{\rm OH}^{-}]^2$ 

3.80 x 10<sup>-17</sup> = (0.210/2) x [OH<sup>-</sup>]<sup>2</sup>

[OH<sup>-</sup>] = 1.90 x 10<sup>-8</sup> mol L<sup>-1</sup>

n solutio 25.0 mL	n after 25.0 mL of of a saturated	f
-		
CHEMSOLU both face. ALSO III face. W. 2011 ME 1920 ME	Art.: 110.1000 1 kg Zinkchlorid, wasserfrei reinst Zinckhlorid, wafr nea zinkklorid, vattenfri mycket ren zinkklorid, vattenfri mycket ren Chlorure de zin, enhydee exiru pyr 98.0 - 100.5 % ZnCl2 For laboratory use, DAB, Ph. Eur., Bi, Ph. Fran., USP	
RD)	UN 2331 ADR 8. III	

Merit



#### NCEA 2020 Common Ion Effect

Excellence Question

**Question: 2b** Determine whether a precipitate of lead bromide,  $PbBr_2$ , will form when 125 mL of 0.0365 mol L<sup>-1</sup> lead nitrate,  $Pb(NO_3)_2$ , is added to 175 mL of 0.00262 mol L<sup>-1</sup> magnesium bromide, MgBr<sub>2</sub>.

$$K_{s}(PbBr_{2}) = 2.10 \times 10^{-6}$$



# Solubility Key concepts



## Equilibrium effects

GZ Science Resources

Acids increase solubility if the salt contains a carbonate Bases increase solubility if the salt contains a cation that forms a complex ion When pH is above 10 Bases decrease solubility if the salt contains a hydroxide ion This occurs when pH is above 4 but below 10

# Common ion effect

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

- If IP > 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**.



Bockononegoe
### Acids – their characteristics

GZ Science

An Acid donates its Hydrogen ion (H<sup>+</sup>), which is really just a proton - the electron remains behind. Common acids (that you need to know) include: Strong acids: HNO<sub>3</sub> - nitric acid, HCl - hydrochloric acid, H<sub>2</sub>SO<sub>4</sub> – sulfuric acid, HBr - Hydrobromic acid Weak acids: CH<sub>3</sub>COOH – ethanoic acid, HF - Hydrofluoric acid, and NH<sub>4</sub><sup>+</sup> - ammonium



### Bases – their characteristics

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

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

Bockononio



### Bases – their characteristics

A Base accepts a Hydrogen ion that have been donated from an Acid. Common bases (that you need to know) include: Strong bases: NaOH – sodium hydroxide, KOH – potassium hydroxide Weak bases: NH<sub>3</sub> – ammonia, CH<sub>3</sub>NH<sub>2</sub> - methylamine and CH<sub>3</sub>COO<sup>-</sup> - ethanoate ion Some substances such as water are **amphiprotic** and can act as both an acid and a base depending on what other substance the water is with.



GZ Science Resources

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

Acids are substances that donate protons (H <sup>+</sup> ) in solution	Bases are substances that accept protons (H <sup>+</sup> ) in solution	
$HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^{(aq)}$	$NH_{3(g)} + H_2O_{(l)} \rightarrow NH_4^+_{(aq)} + OH_{(aq)}^-$	
HCl gas dissolved in water	$NH_3$ gas dissolved in water	
HCI has donated a H <sup>+</sup> so is acting as an acid	NH <sub>3</sub> has accepted a H <sup>+</sup> so it is acting as a base	
$H_2O$ has accepted a $H^+$ so it is acting as a base	H <sub>2</sub> O has donated a H <sup>+</sup> so is acting as an acid	
Solution becomes acidic since $H_3O^+$ ions form	Solution becomes basic since OH <sup>-</sup> ions form.	





An **amphiprotic substance** is a substance that can **donate** or **accept** a proton, H<sup>+</sup>

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,  $\rm H_2O,\, HCO_3^-$  ,  $\rm HSO_4^-$  ,  $\rm HPO_4^{2-}$  and  $\rm H_2PO_4^{--}$ 

Name of amphiprotic species	Chemical formula	Able to donate a proton, H <sup>+</sup>	Able to accept a proton, H⁺
Water	H <sub>2</sub> O	$H_2O(I) \rightarrow H^+(aq) + OH^-(aq)$	$H_2O(I) + H^+(aq) \rightarrow H_3O^+(aq)$
Hydrogen carbonate ion	HCO <sub>3</sub> -	$HCO_3^{-1}(aq) \rightarrow H^+(aq) + CO_3^{-2}(aq)$	$HCO_3^{-}(aq) + H^{+}(aq) \rightarrow H_2CO_3(aq)$
Hydrogen sulfate ion	HSO <sub>4</sub> -	HSO <sub>4</sub> -(aq) → H⁺(aq) + SO <sub>4</sub> ²-(aq)	$HSO_4^-(aq) + H^+(aq) \rightarrow H_2SO_4(aq)$
Dihydrogen phosphate ion	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	$H_2PO_4^-(aq) \rightarrow H^+(aq) + HPO_4^{-2}^-(aq)$	$H_2PO_4^{-}(aq) + H^+(aq) \rightarrow H_3PO_4(aq)$



### Strong and weak acids

You can define acids and bases as being "strong" or "weak". Strong acids are compounds that completely dissociate (break up) in water. All of the 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 H<sup>+</sup> ion. A weak base is a compound where only some of the molecules will accept a H<sup>+</sup> ion. Most weak base molecules remain un reacted.

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





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### Strong and Weak Acids

The strength of an acid is determined by how readily it will donate its H<sup>+</sup> ions. Strong acids will have a low pH (0-3) and include  $HNO_3$ , HCl, H<sub>2</sub>SO<sub>4</sub>, and HBr

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

#### Strong acids

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

$$HCl_{(g)} + H_2O_{(I)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

HCl gas dissolved in water

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

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

Solution contains <u>virtually no</u> intact HCI molecules after reaction.

#### Weak acids

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

 $CH_3COOH_{(I)} + H_2O_{(I)} \Leftrightarrow CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$ 

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

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

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

Solution contains mostly intact  $CH_3COOH$  molecules.

#### Strong and Weak Acids

In reality the strong acid molecules would be almost completely dissociated in an aqueous solution. The Cl<sup>-</sup> would remain in solution and free H<sup>+</sup> ions would join with available water to form hydronium ions



#### GZ Science Resources

#### Strong and Weak Bases

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

#### **Strong Bases**

Completely accept protons (H<sup>+</sup>) in aqueous solution

 $NaOH_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + OH^-_{(aq)}$ 

NaOH completely dissociates

The OH- ions will readily accept H<sup>+</sup> ions.

Solution contains very <u>few</u> intact NaOH molecules after reaction.

#### Weak Bases

Partially accept protons (H<sup>+</sup>) in aqueous solution

 $NH_{3(g)} + H_2O \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$ 

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

Because ammonium is a reasonably strong acid (conjugate pairs) it will readily donate H<sup>+</sup> and become ammonia. Solution contains <u>mostly</u> intact NH<sub>3</sub> molecules.



80

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

Examples of acid-base pairs are  $H_2SO_4/HSO_4^-$  and  $NH_4^+/NH_3$ .

The acid is always the species with the additional proton.

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

	Base	Conjugate Acid
H <sub>2</sub> O	water	H <sub>3</sub> O+
SO <sub>4</sub> <sup>2-</sup>	sulfate ion	HSO <sub>4</sub> -
NH <sub>3</sub>	ammonia	NH <sub>4</sub> +
OH-	hydroxide ion	H <sub>2</sub> O
HCO <sub>3</sub> <sup>−</sup>	hydrogen carbonate ion	H <sub>2</sub> CO <sub>3</sub>
CO <sub>3</sub> <sup>2-</sup>	carbonate ion	HCO <sub>3</sub> -

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#### Transfer of hydrogen ions in conjugate pairs



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

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

In other words: When an acid gives up its proton, what remains is called the **conjugate base** of that acid. When a base accepts a proton, the resulting substance is called the **conjugate acid** of that original base.



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

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





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



#### Conjugate Acid and Base pairs (Base)

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





Relative base strength increasing

### Conjugate Acid and Base pairs

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

A strong acid like HCl donates its proton so readily that there is essentially no tendency for the conjugate base Cl<sup>-</sup> to reaccept a proton. Consequently, Cl<sup>-</sup> is a very weak base. A strong base like the H<sup>-</sup> ion accepts a proton and holds it so firmly that there is no tendency for the conjugate acid H<sub>2</sub> to donate a proton. Hence, H<sub>2</sub> is a very weak acid.







strong acids HCl, HBr, HNO<sub>3</sub>,  $H_2SO_4$ 

strong bases KOH, NaOH

2015 dissociation equations - NCEA Case Study

Achieved

Question

Question: 1a: (i) Methylammonium chloride,  $CH_3NH_3CI$ , dissolves in water to form a weakly acidic solution.

 $Ka(CH_3NH_3^+) = 2.29 \times 10^{-11}$ 

(a) (i) Write an equation to show  $CH_3NH_3CI$  dissolving in water.

 $CH_{3}NH_{3}CI(s) \rightarrow CH_{3}NH_{3}^{+}(aq) + CI^{-}(aq) \quad CH_{3}NH_{3}^{+} + H_{2}O \rightleftharpoons CH_{3}NH_{2} + H_{3}O^{+}$ 

2014 dissociation equations - NCEA Case Study

**Question: 1a:** When chlorine gas is added to water, the equation for the reaction is:  $Cl_{2(g)} + H_2O_{(I)} \rightleftharpoons HCl_{(aq)} + HOCl_{(aq)}$ 

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

## $HOCI + H_2O \rightleftharpoons OCI^- + H_3O^+$

#### NCEA 2016 dissociation equations

Achieved

Question

Question: 2a: (i) Ethanamine,  $CH_3CH_2NH_2$ , is a weak base.  $pK_a(CH_3CH_2NH_3^+) = 10.6 K_a(CH_3CH_2NH_3^+) = 2.51 \times 10^{-11}$ 

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

### $CH_3CH_2NH_2 + H_2O \Leftrightarrow CH_3CH_2NH_3^+ + OH^-$

#### NCEA 2017 dissociation equations

Achieved

Question

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

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

Hydrogen fluoride, HF, with water:

Hydrogen bromide, HBr, with water:

 $HF + H_2O \iff F^- + H_3O^+$  $HBr + H_2O \rightarrow Br^- + H_3O^+$ 

### Kw – the ionic product for water

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

$$K_{c} = [\underline{H_{3}O^{+}}][OH^{-}] \text{ from } 2H_{2}O_{(I)} \rightleftharpoons H_{3}O^{+}_{(aq)} + OH^{-}_{(aq)}$$
$$[H_{2}O]^{2} \qquad (\Delta_{r}H = +ve)$$

Or  $K_c \ge [H_2O]^2 = [H_3O^+] [OH^-]$ Because the concentration of water is so large it does not change  $\rightarrow$  considered constant So  $K_c \ge [H_2O]^2$  is also constant – called  $K_w$ 

As  $[H_3O^+] \times [OH^-]$  always equals 1 x 10<sup>-14</sup> then so does  $K_w$ 

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

## Using $K_w$ to Calculate [OH<sup>-</sup>] or [H<sub>3</sub>O<sup>+</sup>]

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

IONIC PRODUCT  $K_W = [OH^-] \times [H_3O^+] = 1 \times 10^{-14}$ 

e.g. If solution A has  $[OH-] = 1 \times 10^{-1} \text{ molL}^{-1}$  find  $[H_3O^+]$ 

$$[H_3O^+] = \frac{1 \times 10^{-14}}{1 \times 10^{-1}} = 1 \times 10^{-13} \text{ molL}^{-1}$$

 $[OH^{-}] = 1 \times 10^{-14}$  or  $[H_3O^{+}] = 1 \times 10^{-14}$  $[H_3O^{+}]$   $[OH^{-}]$ 



Bockononinge



8.10

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

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

The equilibrium can be written symbolically as:

5.0 3.0

1



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

Resources

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

#### Small Intermediate Large $(K < 10^{-3})$ $(10^{-3} \le K \le 10^3)$ $(K > 10^3)$ 000000 000000 0000 000000 0000 000000 0000 000000 000000 Products Products Products Reactants Reactants Reactants Significant amounts Mostly products Mostly reactants of reactants and products

### Magnitude of K increasing $\rightarrow$

**Composition of equilibrium mixture** 



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

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

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

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

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

### Analysing the K<sub>a</sub> value

The K<sub>a</sub> value is an indication of position of the equilibrium. A small K<sub>a</sub> indicates more reactants, so less dissociation of the acid, and therefore a weaker acid. A larger K<sub>a</sub> indicates more products ( $H_3O^+$  ions and conjugate base), so more dissociation of acid, and therefore a stronger acid



Some questions will ask you, when comparing two acids, to discuss the link between Ka, level of dissociation, the relative amount of  $H_3O^+$  ions produced and therefore the pH and strength of the acids



Acidity constant =  $K_a$ [H<sub>3</sub>O<sup>+</sup>] = [A<sup>-</sup>] hydronium concentration = conjugate base concentration

 $K_a = [H_3O^+]^2$ [HA]

→ if  $K_a$  small then [H<sub>3</sub>O<sup>+</sup>] much smaller than [HA] – <u>very little dissociation</u> [HA] can then be assumed to be equal to c(HA)

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

### 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(HA). ie [HA] =  $c(HA) - [H_3O^+]$  and this should be corrected for by solving a quadratic equation or by method of first approximation.

For example: determine the pH of a solution made from 0.01 mole of HNO<sub>2</sub> in 1.0 L of water.

 $HNO_2 + H_2O_{(I)} \Leftrightarrow H^+_{(aq)} + NO_2^-_{(aq)}$ 

extro

Initial concentration0.01Equilibrium concentration(0.01-x)xx

 $K_a = 10^{-3.29} = [H^+][NO_2^-] = x^2$ [HNO\_2] (0.01-x)

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### $\mathbf{pK}_{a} = -\log K_{a}$

## → larger pKa more reactants

- $\rightarrow$  negative for strong acids (HX)
- $\rightarrow$  gets larger (3 13) as acids get weaker less dissociation



The pK<sub>a</sub> 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 converted to Ka to use in calculations. pK<sub>a</sub> have no units attached.

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

### pH calculations – Weak acid

1.4

Convert pK<sub>a</sub> to K<sub>a</sub>
(if required)

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

2. Calculate  $[H_3O^+]$ 

$$[H_30^+] = \sqrt{K_a \times c(HA)}$$

3. Calculate pH

(start here if strong acid)

$$pH = -log[H_30^+]$$

### pH calculations – Weak acid



# $K_{a} = \frac{[H_{3}O^{+}] [A^{-}]}{[HA]}$ 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

 $HA + H_20 \iff A^- + H_30^+$ 

Use this equation to compare number of mols.

As weak acids are diluted they become "stronger" as degree of dissociation (a =  $[H^+]/c_{HA}$ ) increases. (At infinite dilution a weak acid is 100% dissociated) This is because in the equilibrium  $HA + H_2O \rightleftharpoons H_3O^+ + A^-$ , adding water dilutes all concentrations equally in the expression  $K_a =$  $[H_3O^+] \times [A^-]/HA$  so to keep K constant, the equilibrium i position needs to shift to the right. extra

into



Strong base – completely dissociates (accepts all H<sup>+</sup> ions)

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

Strong bases will have a conjugate weak acid

Weak base – partly dissociates (accepts few H<sup>+</sup> ions)

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



 $K_b = 1 \times 10^{-14} / K_a$  $[OH^-] = \sqrt{K_b \times c(B)}$   $K_b = 1 \times 10^{-14} / K_a$   $K_b = 1 \times 10^{-14} / K_a$   $K_b = 1 \times 10^{-14} / K_a$   $K_b = 1 \times 10^{-14} / K_a$ 



 $pH = -log[H_30^+]$ 

4. Calculate pH


#### pH Calculations – Q5



strong acids HCl, HBr, HNO<sub>3</sub>,  $H_2SO_4$ 

strong bases KOH, NaOH

#### NCEA 2014 pH calculations

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

A 0.100 mol L–1 solution of each acid was prepared by dissolving it in water.

Compare the pHs of these two solutions.

No calculations are necessary.

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

So HF will therefore have a higher  $[H_3O^+]$ . As  $[H_3O^+]$  increases, the pH decreases, so HF will have a lower pH than HOCI.

(pH HF = 2.09, HOCI = 4.27)

→ larger pKa more reactants, the weaker the acid Merit

Question

Question: 1a: (iv) Calculate the pH of 0.0152 mol L<sup>-1</sup> CH<sub>3</sub>NH<sub>3</sub>Cl solution.  $Ka(CH_3NH_3^+) = 2.29 \times 10^{-11}$ 

 $\begin{bmatrix} H_3O^+ \end{bmatrix} = \sqrt{K_a} \times HA$  $= 5.90 \times 10^{-7}$ pH = 6.23

 $[H_3O^+] = 5.90 \times 10^{-7} \text{ mol } \text{L}^{-1}$ pH = -log 5.90 × 10<sup>-7</sup> = 6.23  $K_a = 10^{-Pka}$ 

Merit

Question

 $[H_30^+] = \sqrt{K_a \times c(HA)}$ 

 $pH = -log[H_30^+]$ 

Description: Description: 2b: Calculate the pH of a 0.109 mol L<sup>-1</sup> solution of  
ethanamine.  
$$pK_a(CH_3CH_2NH_3^+) = 10.6$$
 $K_a = 10^{-Pka}$  $[H_3O^+] = \sqrt{(K_a \times K_w \div [CH_3CH_2NH_2])}$  $[H_3O^+] = \sqrt{(2.51 \times 10^{-11} \times 1.00 \times 10^{-14} \div 0.109)}$ 

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

$$[\Pi_3 \bigcirc ] = \vee (\Lambda_a \land \Lambda_w \div [D])$$

 $pH = -log[H_30^+]$ 

 $[H_3O^+] = 1.52 \times 10^{-12} \text{ molL}^{-1}$ pH = -log  $[H_3O^+] = 11.8$ 

NCEA 2017 pH calculationsExcellence  
QuestionQuestion: 2a: Ammonia, NH3, is a weak base.
$$pK_a(NH_4^+) = 9.24 K_a(NH_4^+) = 5.75 \times 10^{-10}$$
(i) Calculate the pH of a 0.105 mol L<sup>-1</sup> NH3 solution.

$$[H_{3}O^{+}] = \sqrt{(Ka \times Kw \div [NH_{3}])}$$
  

$$[H_{3}O^{+}] = \sqrt{(5.75 \times 10^{-10} \times 1.00 \times 10^{-14} \div 0.105)}$$
  

$$[H_{3}O^{+}] = 7.40 \times 10^{-12} \text{ molL}^{-1}$$
  

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

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

$$[\mathsf{H}_3\mathsf{O}^+] = \sqrt{(K_\mathsf{a} \times K_\mathsf{w} \div [\mathsf{B}])}$$

$$pH = -log[H_30^+]$$

NCEA 2018 pH calculations

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

 $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ 

 $p_{Ka}(CH_3COOH) = 4.76 K_a(CH_3COOH) = 1.74 \times 10^{-5}$ 

Calculate the pH of a 0.420 mol  $L^{-1}$  CH<sub>3</sub>COONa solution.

$$CH_{3}COO^{-} + H_{2}O \rightleftharpoons CH_{3}COOH + OH^{-}$$
$$H_{3}O^{+} = \sqrt{\frac{K_{a} \times K_{w}}{[CH_{3}COO^{-}]}}$$
$$= \sqrt{\frac{1.74 \times 10^{-5} \times 1 \times 10^{-14}}{0.420}}$$

 $= 6.44 \times 10^{-10}$ 

$$\mathsf{D}^+] = \sqrt{(K_\mathsf{a} \times K_\mathsf{w} \div [\mathsf{B}])}$$

 $[H_3($ 

 $K_a = 10^{-Pka}$ 

Merit

Question

$$pH = -log[H_30^+]$$

#### NCEA 2019 pH calculations

Question: 3a Two solutions of equal concentration were prepared: one of ethanoic acid, CH<sub>3</sub>COOH, and one of ammonium chloride, NH<sub>4</sub>Cl.

 $pK_a(CH_3COOH) = 4.76 pK_a(NH_4^+) = 9.24$ 

(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.

CH<sub>3</sub>COOH has the smaller  $pK_a$  / larger  $K_{a}$ , so it will be a stronger acid than NH<sub>4</sub><sup>+</sup>.

This means  $CH_3COOH$  will dissociate to a greater extent to produce a higher  $[H_3O^+]$  than  $NH_4^+$ , so  $CH_3COOH$  will have a lower pH.



Merit Questior



$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$K_{a} = \frac{\left[H_{3}O^{+}\right]\left[CH_{3}COO^{-}\right]}{\left[CH_{3}COOH\right]}$$
$$10^{-4.76} = \frac{\left(1.78 \times 10^{-3}\right)^{2}}{\left[CH_{3}COOH\right]}$$
$$\left[CH_{3}COOH\right] = 0.182 \text{ mol } L^{-1}$$





$$NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$$

$$K_{a} = \frac{\left[NH_{3}\right]\left[H_{3}O^{+}\right]}{\left[NH_{4}^{+}\right]}$$
$$5.75 \times 10^{-10} = \frac{\left(10^{-4.70}\right)^{2}}{\left[NH_{4}^{+}\right]}$$
$$\left[NH_{4}^{+}\right] = 0.692 \text{ mol } \text{L}^{-2}$$



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



Weak acids CH<sub>3</sub>COOH, HF



## Species in solution

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

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

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

A small amount of  $H_3O^+$  and  $OH^-$  will always be present in water due to  $Kw = [OH^-] [H_3O^+] = 1 \times 10^{-14}$ 

Water will always be present in large concentrations.



## Concentration of species in solution



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

- In aqueous solutions water will almost always be present in the highest concentration.
- Small quantities of  $H_3O^+$  and OH<sup>-</sup> will also be present, according to the K<sub>w</sub> = [H<sub>3</sub>O<sup>+</sup>] [OH<sup>-</sup>] = 1 x 10<sup>-14</sup>
- 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 acids will provide **good conductivity** and **pH 1-2** due to the high presence of  $H_3O^+$  ions



No strong acid will be left in the final mixture.

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

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



# Concentration of ions in solution – Weak Acid





Most weak acid will be left in the final mixture.

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

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



# Concentration of ions in solution – Strong Base



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



GZ Science Resources	Concer	ntration c	of ions i	n solution	– Wea	ak Base	
Weak Base [NH <sub>3</sub> ]	e i.e. NH <sub>3</sub> >	[OH-]	>	[NH <sub>4</sub> +]	>	[H <sub>3</sub> O+]	

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





[Cl-]

Acid Salt i.e. NH<sub>4</sub>Cl

>

 $[NH_{4}^{+}] >$ 

## Concentration of ions in solution – acid salt

 $[H_3O^+] = [NH_3]$ 

[OH-]

>

Acid salts will provide **good conductivity** and pH < 7 due to the high presence of ions from dissolving and to a lesser extent H<sub>3</sub>O<sup>+</sup> ions





# Concentration of ions in solution – base salt

Base Salt i.e.  $CH_3COONa$ [Na<sup>+</sup>]  $\approx$  [CH<sub>3</sub>COO<sup>-</sup>] > [CH<sub>3</sub>COOH] = [OH<sup>-</sup>] > [H<sub>3</sub>O<sup>+</sup>]

base salts will provide **good conductivity** and pH > 7 due to the high presence of ions from dissolving and to a lesser extent OH<sup>-</sup> ions



## pH of salt solutions

All cations that are the conjugate acids of weak bases act as weak acids and lower the pH of the solution. This means that a salt solution containing this cation could be acidic. For example, a solution of ammonium chloride, NH<sub>4</sub>Cl, contains the cation NH<sub>4</sub><sup>+</sup> and the anion Cl<sup>-</sup>. The Cl<sup>-</sup> ion acts as a neutral species and does not affect the pH (as it is the conjugate base of a strong acid and is so weakly basic that it effectively has no reaction with water). The NH<sub>4</sub><sup>+</sup> ion is the conjugate acid of the weak base NH<sub>3</sub> and so itself is a weak acid.

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

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

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

$$NH_4Cl_{(s)} \Leftrightarrow NH_4^+{}_{(aq)} + Cl_{(aq)}$$

 $NH_4^+(aq) + H_2O_{(l)} \Leftrightarrow NH_{3(aq)} + H_3O^+(aq)$ 



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

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

### High conductivity

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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 conduct charge.



ethanoic acid



glucose

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

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Water concentration is assumed to remain constant so is left out

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

GZ Science Resources



water concentration is assumed to remain constant so is left out



# $HCI < CH_3NH_3CI < CH_3NH_2$

- □ HCl, a strong acid, reacts completely with water to form 1 mol L<sup>-1</sup> H<sub>3</sub>O<sup>+</sup> and hence a low pH. HCl + H<sub>2</sub>O → H<sub>3</sub>O<sup>+</sup> + Cl<sup>-</sup>
- □ CH<sub>3</sub>NH<sub>3</sub>Cl dissociates completely in water to form CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> and Cl<sup>-</sup>. CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>, a weak acid, partially reacts with water to form less than 1 mol L<sup>-1</sup>H<sub>3</sub>O<sup>+</sup> and hence a higher pH than HCl. CH<sub>3</sub>NH<sub>3</sub>Cl → CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> + Cl<sup>-</sup>

 $CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$ 

□  $CH_3NH_2$ , a weak base, partially reacts with water to form  $OH^-$  ions. So there are more  $OH^-$  ions than  $H_3O^+$  ions and the pH is thus high.

 $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$ 

### NCEA 2014 Species in Solution

Excellence

Question

**Question: 1a:** When chlorine gas is added to water, the equation for the reaction is:  $CI_{2(q)} + H_2O_{(l)} \rightleftharpoons HCI_{(aq)} + HOCI_{(aq)}$ 

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

## $HOCI > H_3O^+ > OCI^- > OH^-$ or $HOCI > H_3O^+ = OCI^- > OH^-$

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

 $H_3O^+$  and OCI<sup>-</sup> are produced in equal amounts / there is a small contribution to  $H_3O^+$  from water therefore  $H_3O^+ > OCI^-$ 

Because there is a relatively high  $[H_3O^+]$ , the  $[OH^-]$  is very low (or links to  $K_w$ ).

Question: 2c: Ethyl ammonium chloride,  $CH_3CH_2NH_3CI$ , is a weak acid that will also react with water.

List all the species present in a solution of  $CH_3CH_2NH_3CI$ , in order of decreasing concentration.

Do not include water.

Justify the order you have given.

Include equations, where necessary.  $\mathsf{CH}_3\mathsf{CH}_2\mathsf{NH}_3\mathsf{CI} \to \mathsf{CH}_3\mathsf{CH}_2\mathsf{NH}_3^+ + \mathsf{CI}^-$ 

CH<sub>3</sub>CH<sub>2</sub>NH<sub>3</sub>Cl completely dissociates.

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

Excellence

Question

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

 $CH_3CH_2NH_3^+ + H_2O \iff CH_3CH_2NH_2 + H_3O^+$ 

For every mole of  $CH_3CH_2NH_3^+$  that reacts with water, 1 mole of  $CH_3CH_2NH_2$  and  $H_3O^+$  are formed.

(However,  $H_3O^+$  is slightly more concentrated than  $CH_3CH_2NH_2$ , as there is a small contribution from water).

OH<sup>-</sup> is present in the lowest concentration as this comes from the dissociation of water only.

 $\mathsf{CI}^{-} > \mathsf{CH}_3\mathsf{CH}_2\mathsf{NH}_3^{+} > \mathsf{H}_3\mathsf{O}^{+} \ge \mathsf{CH}_3\mathsf{CH}_2\mathsf{NH}_2 > \mathsf{OH}^{-}$ 

#### NCEA 2019 Species in Solution

Question: 2a A titration was carried out by adding 0.140 mol L<sup>-1</sup> sodium hydroxide, NaOH, to 20.0 mL of 0.175 mol L<sup>-1</sup> methanoic acid, HCOOH.

The equation for the reaction is:

 $HCOOH + NaOH \rightarrow HCOONa + H_2O$ 

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

(i) List ALL the species in solution after 12.5 mL of NaOH solution has been added. Do not include water.

Na<sup>+</sup>, HCOO<sup>-</sup>, HCOOH, OH<sup>-</sup>, H<sub>3</sub>O<sup>+</sup>



Achieved Question



#### NCEA 2020 Species in Solution

Excellence

Question

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Question: 1c (i) Solutions of equal concentration were prepared for eachof the following:HBr $CH_3NH_2$  $NH_4CI$ 

Rank the solutions in order of decreasing pH in the box below:

Order of decreasing pH: CH<sub>3</sub>NH<sub>2</sub>, NH<sub>4</sub>Cl, HBr.

**Question:** 1c (i) Justify the order. Your answer should include: •relative concentrations of hydronium ions • relevant equation(s).

CH<sub>3</sub>NH<sub>2</sub> is a weak base, and therefore partially dissociates to produce OH<sup>-</sup>.

### $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$

 $NH_4CI$  is an acidic salt. The  $NH_4^+$  is a weak acid, and therefore partially dissociates to produce  $H_3O^+$ .  $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ 

HBr is a strong acid, and therefore completely dissociates to produce a higher  $[H_3O^+]$  than  $NH_4^+$ .  $HBr + H_2O \rightarrow Br^- + H_3O^+$ 

Since  $CH_3NH_2$  is the only base, it has the lowest  $[H_3O^+]$  and therefore the highest pH. Since HBr is a strong acid, it has the highest  $[H_3O^+]$  and therefore the lowest pH.

Excellence

Question

**Question: 1b:** The conductivity of the 1 mol L–1 solutions formed in (a) can be measured.  $CH_3NH_3CI$   $CH_3NH_2$  HCI

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

## $HCI = CH_3NH_3CI > CH_3NH_2$

 $CH_3NH_3CI$  and HCI will dissociate completely in water to produce 2 mol  $L^{-1}$  ions.

 $CH_3NH_2$  will only partially react with water to produce less than 1 mol L<sup>-1</sup> of ions.

Excellence Question

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

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

The pH of a solution is calculated from its  $[H_3O^+]$ .

□ NaOH is an ionic solid that is a strong base and dissociates completely to produce a high OH<sup>-</sup> concentration (low  $[H_3O^+]$ ). Since  $[OH^-]$  is high /  $[H_3O^+]$  is low, the pH is high.

NaOH  $\rightarrow$  Na<sup>+</sup> + OH<sup>-</sup>

Excellence Question

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

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

- □ CH<sub>3</sub>NH<sub>2</sub> is a weak base that partially reacts / dissociates / ionises with H<sub>2</sub>O producing a lower concentration of OH<sup>-</sup>, Therefore it has a lower pH than NaOH:
- $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$
- □ The CH<sub>3</sub>COONa is an ionic solid that dissociates completely in H<sub>2</sub>O. The CH<sub>3</sub>COO<sup>-</sup> ion is a weak base that partially reacts / dissociates / ionises with H<sub>2</sub>O producing a lower concentration of OH<sup>-</sup>.
- $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

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

Excellence Question

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

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

#### Electrical conductivity:

Electrical conductivity is determined by the concentration of ions.

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

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

Excellence Question

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

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

### Electrical conductivity:

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

 $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$ 

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

 $\rm CH_3COONa \rightarrow Na^{\scriptscriptstyle +} + \rm CH_3COO^{\scriptscriptstyle -}$ 

Therefore it is a good conductor.

Excellence

Question

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

In your answer, you should:

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

No calculations are necessary.

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

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

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

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

Excellence Question

Question: 2. A titration was carried out by adding 0.210 mol L<sup>-1</sup> hydrochloric acid, HCl, to 25.0 mL of 0.168 mol L<sup>-1</sup> methanamine,  $CH_3NH_2$ .

The equation for the reaction is:  $HCI + CH_3NH_2 \rightarrow CH_3NH_3^+ + CI^-$ 

 $p_{Ka}(CH_3NH_3^+) = 10.6$   $K_a(CH_3NH_3^+) = 2.51 \times 10^{-11}$ 

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

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

 $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$ 

The solution at the equivalence point is made up of the products from the titration /  $CH_3NH_3^+$  and  $CI^-$ . As there are more ions in solution / higher [ions] the solution at the equivalence point is a better conductor.
#### NCEA 2019 Conductivity

**Question: 3a** (ii) Evaluate the electrical conductivity of the CH<sub>3</sub>COOH and NH<sub>4</sub>Cl solutions.

Include relevant equation(s) in your answer.

The electrical conductivity of a solution depends upon [ions].  $NH_4CI$  is an acidic salt, so it completely dissociates / dissolves to produce a relatively high  $[NH_4^+]$  and  $[CI_-]$ . This makes  $NH_4CI$  a good electrical conductor.

 $NH_4CI \rightarrow NH_4^+ + CI^-$ 

However,  $CH_3COOH$  is a weak acid and only partially dissociates to produce a relatively low  $[CH_3COO^-]$  and  $[H_3O^+]$ . This makes  $CH_3COOH$  a poorer electrical conductor than  $NH_4CI$ .

 $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ 



Excellence Question

#### NCEA 2020 Conductivity

Excellence Question

Question: 3b Why are hydrochloric acid and sodium ethanoate solutions both good 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 Cl<sup>-</sup> ions and  $H_3O^+$  ions in solution.

#### $\mathrm{HCI} + \mathrm{H_2O} \rightarrow \mathrm{CI^-} + \mathrm{H_3O^+}$

Sodium ethanoate is a basic salt. It completely dissociates (evidence from equation) to produce a high concentration of Na<sup>+</sup> ions and  $CH_3COO^-$  ions in solution.

#### $CH_3COONa \rightarrow Na^+ + CH_3COO^-$

Since both solutions produce a high concentration of ions, they are both good electrical conductors



**Buffer solutions** 

Sp

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

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

added.





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

 $CH_3COOH_{(aq)} + OH_{(aq)} \Leftrightarrow CH_3COO_{(aq)} + H_2O_{(l)}$ 

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

$$CH_3COO^-_{(aq)} + H_3O^+_{(aq)} \Leftrightarrow CH_3COOH_{(aq)} + H_2O_{(l)}$$

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

Buffers are effective 1 pH either side of buffer mid point – which when pH=pKa

## Effectiveness of Buffer solutions – weak base 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 pH < pKa, this means [weak acid] > [conjugate], so the buffer will be more effective against added strong base.

$$COOH_{(aq)} + OH^{-}_{(aq)} \iff COO^{-}_{(aq)} + H_2O_{(l)}$$

When the pH > pKa, this means [conjugate] > [weak acid], so the buffer will be more effective against added strong acid.

$$COO^{-}_{(aq)} + H_{3}O^{+}_{(aq)}$$

$$\Rightarrow$$
 COOH<sub>(aa)</sub> + H<sub>2</sub>O<sub>(l)</sub>



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 pH > pKa, this means [weak base] > [conjugate], so the buffer will be more effective against added strong acid.

```
CH_3NH_2 + H_3O^+ \rightarrow CH_3NH_3^+ + H_2O
```

When the pH < pKa, this means [conjugate] > [weak base], so the buffer will be more effective against added strong base.

 $CH_3NH_3^+ + OH^- \rightarrow CH_3NH_2 + H_2O$ 



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



## Effectiveness of Buffer solutions – Summary

## Weak Acids 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 pH < pKa, this means [weak acid] > [conjugate], so the buffer will be more effective against added strong base.

 $COOH_{(aq)} + OH_{(aq)} \iff COO_{(aq)} + H_2O_{(l)}$ 

When the pH > pKa, this means [conjugate] > [weak acid], so the buffer will be more effective against added strong acid.

$$COO^{-}_{(aq)}$$
 +  $H_3O^{+}_{(aq)}$   $\Leftrightarrow$   $COOH_{(aq)}$  +  $H_2O_{(l)}$ 



## 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 pH > pKa, this means [weak base] > [conjugate], so the buffer will be more effective against added strong acid.

 $\mathsf{CH}_3\mathsf{NH}_2 + \mathsf{H}_3\mathsf{O}^+ \to \mathsf{CH}_3\mathsf{NH}_3^+ + \mathsf{H}_2\mathsf{O}$ 

When the pH < pKa, this means [conjugate] > [weak base], so the buffer will be more effective against added strong base.

 $CH_3NH_3^+ + OH^- \rightarrow CH_3NH_2 + H_2O$ 



Volume of NaOH added (mL)	
Weak acid	Conjugate base
CH₃COOH	CH₃COO-
$CH_3COOH + H_2O \iff CH_3COO^- + H_3O^+$	
$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$	
HF	F-
$HF + H_2O \iff F^- + H_3O^+$	
$F- + H_2O \iff HF^- + OH^-$	
$NH_4^+$	NH <sub>3</sub>
$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$	
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	
CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	CH <sub>3</sub> NH <sub>2</sub>
$CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$	
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	

## Calculating moles given mass



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.

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m - Mass is measured in grams (g)

Bockononegoe

- $\mu$  Molar Mass is measured in gmol<sup>-1</sup>
- n Moles are measures in mols



### Calculating concentration of solutions (molL<sup>-1</sup>)

c = n / v

Bockolonegoe 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.

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- c concentration is measured in molL<sup>-1</sup>
- v volume is measured in L
- moles are measures in mols n



## Weak Acids (or conjugates) – buffer pairs

Conjugate base		
CH <sub>3</sub> COO <sup>-</sup>		
$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$		
$CH_3COO^- + H_2O \Leftrightarrow CH_3COOH + OH^-$		
F-		
$HF + H_2O \iff F^- + H_3O^+$		
$F- + H_2O \rightleftharpoons HF^- + OH^-$		
NH <sub>3</sub>		
$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$		
$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$		
CH <sub>3</sub> NH <sub>2</sub>		
$CH_3NH_3^+ + H_2O \iff CH_3NH_2 + H_3O^+$		
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$		



Bockoronyledge



## Weak Acids (or conjugates) – buffer pairs

Weak acid	Conjugate base	
CH <sub>3</sub> COOH	CH <sub>3</sub> COO <sup>-</sup>	
$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$		
$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$		
HF	F-	
$HF + H_2O \iff F^- + H_3O^+$		
$F- + H_2O \iff HF^- + OH^-$		
NH4 <sup>+</sup>	NH <sub>3</sub>	
$NH_4^+ + H_2O \iff NH_3 + H_3O^+$		
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$		
CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	CH <sub>3</sub> NH <sub>2</sub>	
$CH_3NH_3^+ + H_2O \iff CH_3NH_2 + H_3O^+$		
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$		



Sp

## Calculate pH of buffer given: $k_a$ or $Pk_a$ + conc of [HA] and [A<sup>-</sup>]

63

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





### Calculate Mass of buffer salt given: pH + conc/volume of [HA] OR [A<sup>-</sup>] + Molar Mass

63

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



2. Calculate Mass – the [A<sup>-</sup>] is the same as the concentration of the salt (c)

n(salt) = cv then  $m(salt) = n \times M$ 

5.0 3.0

GZ Science Resources

Reminder that **answer in g and** to 3 sgf.

500



## Buffer calculations for monoprotic acids

#### **Buffer calculations**

 $[H_3O^+] = Ka \times [weak acid]$ 

[conjugate base]

OR pH = pKa + log [A-] [HA]

[Weak acid or conjugate base] = original concentration x 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 pH = pKa.

#### Example

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

$$pH = pK_{a} + log^{10} \frac{[benzoic \ acid]}{[benzoic \ acid]} Log^{10} \ 1.0 = 0$$

$$= 4.19 + log^{10} \frac{0.050}{0.050} = 4.19 + log_{10} \ 1.0 = 4.19$$

Sam



### Buffer Key Questions – Q8

definition

54<sup>56</sup> 1

**Buffer solutions** 

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

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

What type of acid base titration has a buffer zone?

What pH would a buffer be if we added c(acid) with c(base) and K<sub>a</sub> given? How could you make this a better buffer?

What is the pH of the buffer solution?

500

given concentration, mass or ratios of weak acid/ conjugate



### Excellence NCEA 2013 Buffers Question Sp Question: 1c: (i) The following two solutions from part (a) are mixed to form a buffer solution: 20.0 mL of 1 mol L<sup>-1</sup> CH<sub>3</sub>NH<sub>3</sub>Cl and 30.0 mL of 1 mol L<sup>-1</sup> CH<sub>3</sub>NH<sub>2</sub> Calculate the pH of the resultant buffer solution. pKa (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>) = 10.64 $K_{a} = \frac{[CH_{3}NH_{2}][H_{3}O^{+}]}{[CH_{3}NH_{3}^{+}]}$ $K_a = [H_3O^+][A^-]$ to $[H_3O^+] = K_a \times [HA]$ [HA] [A<sup>-</sup>] $[H_{3}O^{+}] = \frac{K_{a}[CH_{3}NH_{3}^{+}]}{[CH_{3}NH_{2}]}$ **Calculating dilutions** $[CH_3NH_2] = original volume x conc.$ $[CH_3NH_2] = \frac{30 \cdot 10^{-3} \cdot 1}{50 \cdot 10^{-3}} = 0.600 \text{ mol } \text{L}^{-1}$ total volume $[CH_{3}NH_{3}^{+}] = \frac{20 \cdot 10^{-3} \cdot 1}{50 \cdot 10^{-3}} = 0.400 \text{ mol } \text{L}^{-1}$ $[H_3O^+] = 1.52705 \ 10^{-11} \ \text{mol } L^{-1}$ pH = 10.8

### NCEA 2013 Buffers

Excellence

Question

Question: 1c: The following two solutions from part (a) are mixed to form a buffer solution: 20.0 mL of 1 mol L<sup>-1</sup> CH<sub>3</sub>NH<sub>3</sub>Cl and 30.0 mL of 1 mol L<sup>-1</sup> CH<sub>3</sub>NH<sub>2</sub>

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

When a small amount of acid ( $H_3O^+$ ) ions are added, they will react with the  $CH_3NH_{2(aq)}$  molecules to form  $CH_3NH_3^+_{(aq)}$  ions.

 $CH_{3}NH_{2(aq)} + H_{3}O^{+}_{(aq)} \Leftrightarrow CH_{3}NH_{3}^{+}_{(aq)} + H_{2}O_{(\ell)}$ 

The added acid ( $H_3O^+$ ), is mostly consumed, and the pH of the solution changes very little.

#### Excellence NCEA 2014 Buffers Question Question: 1c: An aqueous solution containing a mixture of HF and sodium fluoride, NaF, can act as a buffer solution. Calculate the mass of NaF that must be added to 150 mL of 0.0500 mol $L^{-1}$ HF to give a buffer solution with a pH of 4.02. Assume there is no change in volume. $M(\text{NaF}) = 42.0 \text{ g mol}^{-1} \text{ p}K_{a}(\text{HF}) = 3.17$ $[H_3O^+] = 10^{-pH}$ $K_{a} = \frac{[F^{-}][H_{3}O^{+}]}{[HF]}$ $n(F^{-}) = n(NaF)$ $10^{-3.17} = \frac{[F^{-}]^{-10^{-4.02}}}{10^{-4.02}}$ n = c x v0.0500 As question is asking for mass, $[F^{-}] = 0.354 \text{ mol } L^{-1}$ use: $n(NaF) = 0.354 \text{ mol } L^{-1} \stackrel{<}{} 0.150 \text{ } L = 0.0531 \text{ mol}$ $n = c \times V$ $m(NaF) = 0.0531 \text{ mol} 42.0 \text{ g mol}^{-1} = 2.23 \text{ g}^{-1}$ $m = n \times M$

#### NCEA 2017 Buffers

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

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



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).

Excellence

Question

Since the  $[NH_3] > [NH_4^+] / pH > pKa$ , the buffer will be more effective at neutralising added strong acid.

#### NCEA 2018 Buffers

Achieved Question

Question: 2. A titration was carried out by adding 0.210 mol L<sup>-1</sup> hydrochloric a HCl, to 25.0 mL of 0.168 mol  $L^{-1}$  methanamine, CH<sub>3</sub>NH<sub>2</sub>.

The equation for the reaction is:  $HCI + CH_3NH_2 \rightarrow CH_3NH_3^+ + CI^-$ 

 $p_{Ka}(CH_3NH_3^+) = 10.6$   $K_a(CH_3NH_3^+) = 2.51 \times 10^{-11}$ 

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

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



Titration Curve for CH<sub>3</sub>NH<sub>2</sub> versus HCl

Volume from curve at pH 10.0 = 15 -16.0 mL

#### NCEA 2018 Buffers

Merit

Question: 2. A titration was carried out by adding 0.210 mol L<sup>-1</sup> hydrochloric a HCl, to 25.0 mL of 0.168 mol L<sup>-1</sup> methanamine,  $CH_3NH_2$ .

The equation for the reaction is:  $HCI + CH_3NH_2 \rightarrow CH_3NH_3^+ + CI^-$ 

 $pK_a(CH_3NH_3^+) = 10.6$   $K_a(CH_3NH_3^+) = 2.51 \times 10^{-11}$ 

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

Include an appropriate equation in your answer.

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

```
CH_3NH_2 + H_3O^+ \rightarrow CH_3NH_3^+ + H_2O
```

OR

```
CH_3NH_2 + HCI \rightarrow CH_3NH_3^+ + CI^-
```

Since the  $H_3O^+$  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 mol L<sup>-1</sup> methanoic acid, HCOOH, to make a buffer solution. Assume there is no change in the total volume.

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

(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.

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

The solution will function as a buffer over a pH range 2.74 - 4.74 (p $K_a + / - 1$ ).

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

 $[H_3O^+] = 3.18 \times 10^{-5} \text{ mol } \text{L}^{-1}$ 

 $pH = -log [H_3O^+] = 4.50$ 

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

Excellence

Question



Calculate the pH of this buffer solution.  $pK_a(CH_3COOH) = 4.76$ 

 $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ 

$$K_{a} = \frac{\left[CH_{3}COO^{-}\right]\left[H_{3}O^{+}\right]}{\left[CH_{3}COOH\right]}$$
$$10^{-4.76} = 2 \times \frac{\left[H_{3}O^{+}\right]}{5}$$
$$\left[H_{3}O^{+}\right] = 4.34 \times 10^{-5} \text{ mol } L^{-5}$$
$$pH = -\log 4.34 \times 10^{-5} = 4.36$$



#### NCEA 2019 Buffers

Excellence Question

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, CH<sub>3</sub>COONa

Your answer should include an equation to show how the buffer neutralises added strong base.

 $[CH_3COOH] > [CH_3COO^-] / pH < pK_a$ 

Therefore the buffer solution is more effective at neutralising strong base:

 $CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$ 

(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  $CH_3COOH$  to  $CH_3COO^-$  is unchanged, so the pH of the buffer solution is unaffected.

#### NCEA 2020 Buffers

Merit Question

Question: 1a An aqueous solution containing a mixture of ammonium chloride,  $NH_4CI$ , and ammonia,  $NH_3$ , can act as a buffer solution.

 $K_a(NH_4^+) = 5.75 \times 10^{-10}$   $pK_a(NH_4^+) = 9.24$ 

(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,  $HNO_3$ , to this buffer solution will not result in a significant change in pH.

Y our answer should include relevant equation(s).

The  $H_3O^+$  ions from the HNO<sub>3</sub> solution are neutralised /removed from the solution by the basic component of the buffer,  $NH_3$ , according to the equation below:

 $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$ 

 $(HNO_3 + NH_3 \rightarrow NH_4^+ + NO_3^-)$ 

The pH of the solution does not significantly change since the  $H_3O^+$  are removed from the solution /  $NH_4^+$  produced is a much weaker acid than  $HNO_3$ .

#### NCEA 2020 Buffers

**Question: 1b** (i) Calculate the mass of  $NH_4CI$  that must be added to 200 mL of 0.0500 mol L<sup>-1</sup>  $NH_3$  to give a buffer solution with a pH of 8.75.

Assume there is no change in volume when the solid is added.

 $M(NH_4CI) = 53.5 \text{ g mol}^{-1}$ 

$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$$

$$K_{a} = \frac{\left\lfloor \mathrm{NH}_{3} \right\rfloor \left\lfloor \mathrm{H}_{3}\mathrm{O}^{+} \right\rfloor}{\left[ \mathrm{NH}_{4}^{+} \right]}$$
  
5.75 × 10<sup>-10</sup> 0.0500 × 10<sup>-8</sup>



 $5.75 \times 10^{-10} = \frac{0.0500 \times 10^{-8.75}}{\left[ \text{NH}_4^+ \right]}$ 

 $[NH_4^+] = 0.155 \text{mol L}^{-1}$   $n(NH_4Cl) = cV = 0.155 \times 0.200 = 0.0309 \text{ mol}$  $m(NH_4Cl) = n \times M = 0.0309 \times 53.5 = 1.65 \text{ g}$  (ii) Explain whether the buffer in part (i) will be more effective at neutralising strong acid or strong base.

Merit Question

Excellence

Question

Since the pH of the buffer is less than the  $pK_a$  (8.75 < 9.24),  $[NH_4^+] > [NH_3]$ . 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

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

GZ Science Resources



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

 $HCOO^- + H_2O \iff HCOOH + OH^-$ 



Resources

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. acid of unknown



800

## Neutralisation of acids

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

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

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

- 1. Start pH of acid The initial pH of the solution is due to the starting acid or base in the flask. This is where your titration curve begins
- 2. Equivalence point This is the point when all of the weak acid has reacted with the base being added. This will be the most vertical point on the graph.
- 3. Mid-point This will be exactly half way in volume to the equivalence point. The pk<sub>a</sub> 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

64

63

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

63

Strong Base added to Weak Acid



## Characteristics

Start point above pH 3

500

Equivalence point above 7

End of titration above pH12

Unsymmetrical shape
# Acid – base titration curves

63



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**Characteristics** 

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

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

The pH before any base is added
 The volume of the base at equivalence point
 The volume of base when pH = pKa
 The pH at equivalence point
 The pH after all of the base 30mL has been added

stepstonion curve

















Now we have the key data points:

The pH before any Base added = 2.90
The volume of NaOH at equivalence point: 17.9 mL
The volume of NaOH when pH = pKa: 8.96 mL
The pH at equivalence point: 8.72
The pH after 30mL of NaOH is added: 12.4

provingcune

## Plot these points on a graph



http://www.iq.usp.br/gutz/Curtipot\_.html#Download



Drowing curve







- a) Calculate the number of moles of known acid or base (the substance where the concentration has been given)
- b) Multiply the number of moles by U/K

Example – if concentration given for NaOH and you are calculating the concentration for 
$$H_2SO_4$$
  
 $H_2SO_4$  +  $2NaOH \rightarrow Na_2SO_4$  +  $2H_2O$   
 $KNOWN$   
Moles Unknown = Moles known x U/K = Mole Known x 1/2

c) Rearrange equation to calculate volume  $v = volume (L) c = concentration (molL^{-1})$ 



n = c x v

# Drawing titration curves (additional notes)

Step Three: Calculate the midpoint Volume of the buffer zone

- a) Volume ( x axis) = equivalence point volume / 2
- b) pH (y axis) =  $pK_a$  of the Weak Acid (or conjugate acid of Weak base)

The buffer zone is 1 pH either side of the mid-point

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

At this point half of the weak acid has reacted with the base to form equal quantities of conjugate. Acid + water  $\Rightarrow$  conjugate base +  $H_3O^+$ 

So  $K_a =$ [conjugate base]-[H<sub>3</sub>O<sup>+</sup>]

24.25

[acid]

If they are equal concentration they are cancelled and  $K_a = [H_3O^+]$ Therefore  $pK_a = pH$  as  $pK_a = -\log K_a$  and  $pH = -\log [H_3O^+]$ 



# Drawing titration curves (additional notes)

Step Four: Calculate pH of the equivalence point (end point)

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a) Use the number of moles (n) of base (as calculated in step two) required to completely react with n of acid present to reach equivalence.

Each 1 mole of base required to react with acid produces 1 mole of conjugate base.

Example

 $HCOOH_{(aq)} + NaOH_{(aq)} \Leftrightarrow HCOONa_{(aq)} + H_2O_{(l)}$ 

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

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

c) Use pH equations

$$[H_3O^+] = \sqrt{\frac{k_a \times k_w}{c(conjugate base)}}$$



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.



	[CH <sub>3</sub> COOH]	[NaOH]	[CH <sub>3</sub> COO-]
n			
Initial	n= 0.1 x 0.02	n = 0.2 x0.015 = 0.003 mol	O =0 mol
	= 0.002 mol		
Change	- 0.002 mol	- 0.002 mol	+ 0.002 mol
Equilibrium	≈ 0	= 0.001 mol	0.002 mol

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

# Making use of K<sub>a</sub> expressions

The equilibrium expressions are generated from an **acid dissociation** reaction - remember that is a weak acid dissociating in water

 $HA + H_2O \leftrightarrows A^- + H_3O^+$ 

$$K_a = [A^-] [H_3O^+]$$
  
[HA]

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<sub>a</sub> in the question will indicate the acid used

i.e.

 $K_a(CH_3NH_3^+) = [CH_3NH_2][H_3O^+]$ [CH\_3NH\_3^+]

The acid is the denominator

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

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The relationship of  $[H_3O^+] = K_w/[OH_-]$ 

 $[A^{-}] = [H_3O^{+}]$ , [HA] = c(HA) in acid dissociation

or 
$$pK_a = -logK_a$$
 and  $pH = -log[H_3O^+]$ 

can also be substituted into the expression as a short cut.

so  $[H_{3}O^{+}] = \sqrt{K_{a}} \times c(HA) \text{ for pH of acid}$ or  $[H_{3}O^{+}] = \sqrt{K_{a}} \times K_{w} \div c(B) \text{ for pH of base}$ or pH = pK<sub>a</sub> + log [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  $pK_a / K_a$  and mole ratio of equations can help.

Take the reaction:  $CH_3NH_2 + HBr \rightarrow CH_3NH_3^+ + Br^- K_a(CH_3NH_3^+) = 2.29 \times 10^{-11}$ 

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  $CH_3NH_2$  in water:

 $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$ 

 $CH_3NH_2$  is the base, therefore  $CH_3NH_3^+$  is the conjugate acid.

Also note that the concentration of  $CH_3NH_3^+$  and  $OH^-$  will be the same.

The  $K_a$  indicates that  $CH_3NH_3^+$  is the acid used in the  $K_a$  expression, so

 $CH_3NH_3^+ + H_2O \leftrightarrows CH_3NH_2 + H_3O^+$ 

 $K_a(CH_3NH_3^+) = \underline{[CH_3NH_2][H_3O^+]}$ [CH\_3NH\_3^+] pH can be used to calculate  $H_3O^+$ 

As per the equation above, the concentration of  $CH_3NH_3^+ = OH^-$  and if you know  $H_3O^+$  then you also know  $OH^-$ 

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### Calculating the start concentration

GZ Scienc



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





### Equivalence point pH







(c(acid) x original v/total v)

If given v in the question (from graph)

# Summary of steps - Equivalence point pH – Q10 GZ Scienc Finish $pH = -log[H_3O^+]$ Need to find pH here $[H_3O^+] = \sqrt{K_a \times c(\text{conj acid})}$ Need to find H<sub>3</sub>O<sup>+</sup> You can work also backwards to find out what calculations you need to do c (conj acid)= n/total v n(base) = n(conj acid)Start v(base) + v(Acid) Need to find n(conj acid) Need to find v(conj acid) Start n(base) = c.v | n(base) = n(acid) |v(acid) = n/chere

Given conc of acid + base and volume start base

## NCEA 2013 Titrations- (PART ONE)



#### NCEA 2013 Titrations - (PART TWO)

Question: 3b: Halfway to the equivalence point of the titration, the pH = 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

[CH_3COOH] = [CH_3COO^-]

then K_a = [H_3O^+]

So pK_a = pH
```



500

Excellence

Question

### NCEA 2013 Titrations - (PART THREE)

Excellence Question

Question: 3c: (i) Discuss the <u>change in the concentration</u> 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.

 $NaOH(aq) + CH_3COOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$ 

- $\Box$  [CH<sub>3</sub>COO<sup>-</sup>] increases as it is formed in reaction
- □ [Na<sup>+</sup>] increases as NaOH is added
- □ [CH<sub>3</sub>COOH] decreases as it reacts with NaOH
- □  $[H_3O^+]$  decreases because  $[CH_3COO^-] / [CH_3COOH]$  increases and  $K_a$  is a constant.
- $\Box$  [OH<sup>-</sup>] increases because [H<sub>3</sub>O<sup>+</sup>] decreases and [H<sub>3</sub>O<sup>+</sup>] [OH<sup>-</sup>] is constant.

#### NCEA 2013 Titrations - (PART FOUR)

Excellence

Question

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

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

 $NaOH(aq) + CH_3COOH_{(aq)} \rightarrow NaCH_3COO_{(aq)} + H_2O_{(l)}$  $n(CH_3COOH \text{ at start}) = 0.0896 \times (20 \times 10^{-3}) = 1.79 \times 10^{-3} \text{ mol}$   $n = c \times v$  $n(\text{NaOH added}) = 0.1 \times (5 \times 10^{-3}) = 5 \times 10^{-4} \text{ mol}$ n = c x vAfter 5 mL NaOH added: (total 25mL) Step Four: Calculate pH of the equivalence point (end point)  $n(CH_3COOH) = 1.29 \times 10^{-3} \text{ mol}$ 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.  $(n(CH_3COOH - n(NaOH) after 5mL))$ Each 1 mole of base required to react with acid produces 1 mole of conjugate base.  $n(CH_{3}COO^{-}) = 5 \times 10^{-4} \text{ mol}$ Example  $HCOOH_{(aq)} + NaOH_{(aq)} \leftrightarrow HCOONa_{(aq)} + H_2O_{(l)}$  $[CH_3COOH] = 0.0516 \text{ mol } L^{-1}$  c = n / v b) Calculate c( conjugate base) using c = n/v $[CH_3COO^{-}] = 0.0200 \text{ mol } L^{-1}$  c = n / vV = initial volume in flask + volume added during titration to reach equivalence  $[H_3O^+] = 4.48 \times 10^{-5} \text{ mol } L^{-1}$ c) Use pH equations  $[H_3O^+] =$  $k_a \times k_w$ c(conjugate base) = 4.35 pН

#### NCEA 2014 Titrations - (PART ONE)

Question: 3a: A titration was carried out by adding hydrobromic acid, HBr, to 20.0 mL of aqueous methylamine,  $CH_3NH_2$ , solution.

The equation for the reaction is:

 $CH_3NH_2 + HBr \rightarrow CH_3NH_3 + + Br^-$ 

 $K_{\rm a}(\rm CH_3\rm NH_3^+) = 2.29 \times 10^{-11}$ 

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

At point A,  $[CH_3NH_2] \approx [CH_3NH_3^+]$ . So the solution has buffering properties in the proximity of point A. When HBr is added, the H<sub>3</sub>O<sup>+</sup> is consumed:

 $H_3O^+ + CH_3NH_2 \rightarrow CH_3NH_3^+ + H_2O$ 

Since the  $H_3O^+$  is removed from the solution (neutralised), the pH does not change significantly.



Excellence Question

#### NCEA 2014 Titrations - (PART TWO)

Question: 3b: A titration was carried out by adding hydrobromic acid, HBr, to 20.0 mL of aqueous methylamine,  $CH_3NH_2$ , solution.

The equation for the reaction is:  $CH_3NH_2 + HBr \rightarrow CH_3NH_3 + + Br^-$ 

 $K_{\rm a}(\rm CH_3\rm NH_3^+) = 2.29 \times 10^{-11}$ 

The aqueous methylamine,  $CH_3NH_2$ , 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  $L^{-1.}$ 

 $[H_{3}O^{+}] = 10^{-11.8} = 1.58 \times 10^{-12}$   $K_{8} = \frac{[CH_{3}NH_{2}][H_{3}O^{+}]}{[CH_{3}NH_{3}^{+}]}$   $= \frac{[CH_{3}NH_{2}][H_{3}O^{+}]}{[OH^{-}]}$   $2.29 \times 10^{-11} = \frac{[CH_{3}NH_{2}] \times (10^{-11.8})^{2}}{1 \times 10^{-14}}$   $[CH_{3}NH_{2}] = \frac{(2.29 \times 10^{-11}) \times (1 \times 10^{-14})}{(10^{-11.8})^{2}}$   $= 0.0912 \text{ mol } L^{-1}$ 



Excellence Question

### NCEA 2014 Titrations - (PART THREE)

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

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

In your answer you should include:

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





Excellence Question



At the start, before addition of HBr there is a solution of weak base ( $CH_3NH_2$ ) which only partially reacts with water to produce a relatively low concentration of ions.

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

 $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$ 

Therefore species present are  $CH_3NH_2 > OH^- \ge CH_3NH_3^+ > H_3O^+$ 

At point B, there is a solution of the salt  $CH_3NH_3Br$  present which is dissociated completely into ions. Therefore there is a relatively high concentration of ions ( $CH_3NH_3^+$  and  $Br^-$ ) present in the solution, so it will be a good electrical conductor / electrolyte.

 $CH_3NH_3Br \rightarrow CH_3NH_3^+ + Br^-$ 

 $CH_3NH_3^+$  reacts with water according to the equation

 $CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$ 

Species present are  $Br^- > CH_3NH_3^+ > H_3O^+ \ge CH_3NH_2 > (OH^-)$ 

### NCEA 2015 Titrations - (PART ONE)

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

The equation for the reaction is:

 $HF + NaOH \rightarrow NaF + H_2O$ 

pKa(HF) = 3.17

Achieved

Question

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






#### NCEA 2015 Titrations - (PART THREE)

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

 $HF + NaOH \rightarrow NaF + H_2O \qquad pKa(HF) = 3.17$ 

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

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

 $[H_3O^+] = 2 \times 10^{-3.17} = 1.35 \times 10^{-3} \text{ mol } \text{L}^{-1}$ pH = -log (1.35 x 10<sup>-3</sup>) = 2.87.  $pH = pK_a + \log [F^-] / [HF]$ = 3.17 + log 0.5 = 2.87

**Alternative** 

method

Sp

Achieved

Question

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

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

#### NCEA 2015 Titrations - (PART FOUR)

Excellence

Question

S

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

 $HF + NaOH \rightarrow NaF + H_2O$   $pK_a(HF) = 3.17$ 

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

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

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

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

$$\text{Total volume}$$

$$[\text{H}_{3}\text{O}^{+}] = \frac{K_{w}}{[\text{OH}^{-}]} = \frac{1 \stackrel{?}{\leftarrow} 10^{-14}}{0.0235} = 4.26 \stackrel{?}{\leftarrow} 10^{-13} \text{ mol } \text{L}^{-1}$$

$$p\text{H must be higher than equivalence point after base added}$$

Excellence

Question

**Question: 3b:** In a second titration, a 0.258 mol L<sup>-1</sup> ethanoic acid, CH<sub>3</sub>COOH, solution was titrated with the NaOH solution.

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

 $pK_a(CH_3COOH) = 4.76$   $pK_a(HF) = 3.17$  No calculations are necessary.

 $\rightarrow$  larger pK<sub>a</sub>  $\rightarrow$  less dissociation  $\rightarrow$  weaker acid

Since  $CH_3COOH$  has a higher  $pK_{a'}$ , it is a weaker acid than HF. Therefore its conjugate base,  $CH_3COO^-$ , will be a stronger base than F<sup>-</sup>.

This means  $[OH^-]$  will be higher at the equivalence point for the  $CH_3COOH$  vs NaOH titration, so the equivalence point pH will be higher.

## NCEA 2016 Titrations - (PART ONE)

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

The equation for this reaction is:

 $NH_3 + HCI \rightarrow NH_4^+ + CI^- \qquad pK_a(NH_4^+) = 9.24$ 

The curve for this titration is given below.

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



(Ammonium chloride) is acidic  $NH_4^+ + H_2O \iff H_3O^+ + NH_3$ 

8.10

Merit

Question

So therefore

 $[H_3O^+] > [OH^-]$ 

When considering pH think about which ion,  $H_3O^+$  or  $OH^-_{,}$  will be at the higher concentration

# NCEA 2016 Titrations - (PART TWO)

Excellence

Question

Question 3b: 20.00 mL of 0.320 mol L<sup>-1</sup> ammonia, NH<sub>3</sub>, is titrated with 0.640 mol L<sup>-1</sup> hydrochloric acid, HCl.  $pK_a(NH_4^+) = 9.24$ 

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,  $[NH_4 +] = [NH_3]$ . OR

 $pK_a = pH + log [acid] \div [c.base]$ so  $K_a = [H_3O^+]$ therefore  $pK_a = pH$ .

#### NCEA 2016 Titrations - (PART THREE)

Question 3c: 20.00 mL of 0.320 mol L<sup>-1</sup> ammonia, NH<sub>3</sub>, is titrated with 0.640 mol L<sup>-1</sup> hydrochloric acid, HCl.  $pK_a(NH_4^+) = 9.24$ 

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

As HCl is twice as concentrated as NH<sub>3</sub>, only need <sup>1</sup>/<sub>2</sub> volume – so 20mL +10mL = total volume. Each mol of NH3 produces a mol of conjugate at equivalence point. Then need to calculate concentration after dilution

pH  

$$A \rightarrow f$$
  
 $7 \rightarrow f$   
 $0$   
Volume of HCl added  
 $pH = 4$ .  
 $pH = 4$ .

 $[NH_{4}^{+}] = 0.320 \times 20 / 30 = 0.213 \text{ molL}^{-1}$ 

So

Excellence

Question

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

$$[H_3O^+] = \sqrt{(5.75 \times 10^{-10} \times 0.213)}$$
$$= 1.11 \times 10^{-5} \text{ molL}^{-1}$$

log[H₃O+]

.96

#### NCEA 2016 Titrations - (PART THREE)

Question 3c: 20.00 mL of 0.320 mol L<sup>-1</sup> ammonia, NH<sub>3</sub>, is titrated with 0.640 mol L<sup>-1</sup> hydrochloric acid, HCl.  $pK_a(NH_4^+) = 9.24$ 

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

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Volume of HCl added  
 $pH = 4$ .  
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 $[NH_{4}^{+}] = 0.320 \times 20 / 30 = 0.213 \text{ molL}^{-1}$ 

So

Excellence

Question

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

$$[H_3O^+] = \sqrt{(5.75 \times 10^{-10} \times 0.213)}$$
$$= 1.11 \times 10^{-5} \text{ molL}^{-1}$$

log[H₃O+]

.96





The solution at the equivalence point is  $NH_4CI$ .

 $NH_4^+$  solution is acidic since,  $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ 

## NCEA 2017 Titrations - (PART ONE)

Question 3a: A titration was carried out by adding 0.112 mol L<sup>-1</sup> sodium hydroxide solution, NaOH<sub>(aq)</sub>, to 20.0 mL of ethanoic acid solution,  $CH_3COOH_{(aq)}$ .

The equation for the reaction is:

 $CH_{3}COOH_{(aq)} + NaOH_{(aq)} \rightarrow CH_{3}COONa_{(aq)} + H_{2}O_{(l)} \qquad K_{a}(CH_{3}COOH) = 1.74 \times 10^{-5}$ 



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

Sp

Achieved

Question

Indicator	р <i>К</i> а	Tick ONE box below
Methyl yellow	3.1	
Bromocresol purple	6.3	
Phenolphthalein	9.6	

Merit

Question

Question 3b (i) : The ethanoic acid solution,  $CH_3COOH_{(aq)}$ , has a pH of 2.77 before any NaOH is added.

Show by calculation that the concentration of the  $CH_3COOH$  solution is 0.166 mol  $L^{-1}$ .

 $CH_{3}COOH_{(aq)} + NaOH_{(aq)} \Leftrightarrow CH_{3}COONa_{(aq)} + H_{2}O_{(l)} \qquad K_{a}(CH_{3}COOH) = 1.74 \times 10^{-5}$ 

 $CH_{3}COOH + H_{2}O \Leftrightarrow CH_{3}COO^{-} + H_{3}O^{+}$   $K_{a} = \underline{[CH_{3}COO^{-}][H_{3}O^{+}]}$   $[CH_{3}COOH]$  Use standard weak acid pH method and re-arrange to find [acid]  $1.74 \times 10^{-5} = (10^{-2.77})^{2}$   $[CH_{3}COOH]$ 

 $[CH_3COOH] = 0.166 \text{ mol } L^{-1}$ 

NCEA 2017 Titrations - (PART THREE) Excellence 80 Question Question 3b (ii) : Calculate the pH of the solution in the flask after 10.0 mL of 0.112 mol L<sup>-1</sup> NaOH has been added to 20.0 mL of ethanoic acid solution,  $CH_3COOH_{(aa)}$ .  $CH_3COOH_{(aq)} + NaOH_{(aq)} \rightarrow CH_3COONa_{(aq)} + H_2O_{(l)}$   $K_a(CH_3COOH) = 1.74 \times 10^{-5}$  $n(NaOH) added = 0.112 mol L^{-1} \times 0.01 L$ [CH<sub>3</sub>COO<sup>-</sup>][H<sub>3</sub>O<sup>+</sup>] [CH<sub>3</sub>COOH]  $K_a =$  $= 1.12 \times 10^{-3}$  mol  $n(CH_3COO^-)$  in 30 mL = 1.12 × 10<sup>-3</sup> mol  $1.12 \times 10^{-3}$ c=n/v $[H_3O^+]$ 0.03 As  $n(CH_3COO^-) = n(NaOH)$ 1.74×10<sup>-5</sup>  $2.2 \times 10^{-3}$ Initial  $n(CH_3COOH) = 0.166 \text{ mol } L^{-1} \times 0.02 \text{ L}$ c=n/v0.03  $= 3.32 \times 10^{-3}$  mol  $[H_3O^+] = 3.42 \times 10^{-5}$  $n(CH_3COOH)$  remaining in 30 mL  $pH = -\log 3.42 \times 10^{-5}$  $= 3.32 \times 10^{-3} \text{ mol} - 1.12 \times 10^{-3} \text{ mol}$ pH = 4.47

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

Achieved

Question

**Question 3c:** 

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

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

(ii) In a second titration, a 0.166 mol L<sup>-1</sup> methanoic acid solution, HCOOH<sub>(aq)</sub>, is titrated with the NaOH solution. The equivalence point pH for this titration is 8.28.

The equivalence point pH for the  $CH_3COOH$  titration is 8.79.

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

 $K_{a}(HCOOH) = 1.82 \times 10^{-4} K_{a}(CH_{3}COOH) = 1.74 \times 10^{-5}$ 

No calculations are necessary.

CH<sub>3</sub>COO<sup>-</sup>, Na<sup>+</sup>, CH<sub>3</sub>COOH, OH<sup>-</sup>, H<sub>3</sub>O<sup>+</sup>



Both titrations produce a basic salt at the equivalence point because [OH<sup>-</sup>] >  $[H_3O^+] / pH > 7 / equations$ .

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

The methanoic acid titration has a lower pH than the ethanoic acid titration at the equivalence point because: methanoate ions are a weaker base / produce fewer OH<sup>-</sup> ions than ethanoate ions

OR HCOOH has a larger  $K_a$  than CH<sub>3</sub>COOH, as it is a stronger acid. As a result, its conjugate base, HCOO<sup>-</sup>, is weaker than CH<sub>3</sub>COO<sup>-</sup>, 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 mol L<sup>-1</sup> hydrochloric a HCl, to 25.0 mL of 0.168 mol L<sup>-1</sup> methanamine,  $CH_3NH_2$ .

The equation for the reaction is:  $HCI + CH_3NH_2 \rightarrow CH_3NH_3^+ + CI^-$ 

 $p_{Ka}(CH_3NH_3^+) = 10.6$   $K_a(CH_3NH_3^+) = 2.51 \times 10^{-11}$ 

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

Do not include water.



 $CI^{-} > CH_{3}NH_{3}^{+} > CH_{3}NH_{2} = H_{3}O^{+} > OH^{-}$ 

Merit

## NCEA 2018 Titrations (Part TWO)



Excellence Question

Question: 2. A titration was carried out by adding 0.210 mol L<sup>-1</sup> hydrochloric acid, HCl, to 25.0 mL of 0.168 mol L<sup>-1</sup> methanamine,  $CH_3NH_2$ .

The equation for the reaction is:  $HCI + CH_3NH_2 \rightarrow CH_3NH_3^+ + CI^-$ 

 $pK_a(CH_3NH_3^+) = 10.6$   $K_a(CH_3NH_3^+) = 2.51 \times 10^{-11}$ 

(ii) Calculate the pH at the equivalence point.

Remember – at equivalence point the source of  $H_3O^+$  ions is the conjugate acid reacting with water



$$K_{\rm a} = 2.51 \times 10^{-11} = \frac{\left[{\rm H}_{3}{\rm O}^{+}\right]^{2}}{\left(0.168 \times \frac{25}{45}\right)}$$
  
Original conc of base with dilution factor

 $CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$ 

 $[H_3O^+] = 1.53 \times 10^{-6} \text{ mol } \text{L}^{-1}$ pH = -log 1.53 × 10<sup>-6</sup> = 5.82

Question: 2a A titration was carried out by adding 0.140 mol L<sup>-1</sup> sodium hydroxide, NaOH, to 20.0 mL of 0.175 mol L<sup>-1</sup> methanoic acid, HCOOH.

The equation for the reaction is:

 $HCOOH + NaOH \rightarrow HCOONa + H_2O$ 

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

(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 [HCOOH] = [HCOO<sup>-</sup>].
```

Therefore pH equals  $pK_{a}$ .



Merit Questior

Merit

Question

Question: 2b (i) A titration was carried out by adding 0.140 mol L<sup>-1</sup> sodium hydroxide, NaOH, to 20.0 mL of 0.175 mol L<sup>-1</sup> methanoic acid, HCOOH.

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

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	р <i>К</i> <sub>а</sub>	Tick ONE box below	
Thymol blue	1.70		ج <sup>8</sup>
Bromocresol green	4.70		4
Cresol red	8.30		
			Volume of NaOH added (mL)

Indicators change colour at a pH  $\pm 1$  of the pK<sub>a</sub> / near the pK<sub>a</sub>. 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: 2b A titration was carried out by adding 0.140 mol L<sup>-1</sup> sodium hydroxide, NaOH, to 20.0 mL of 0.175 mol L<sup>-1</sup> methanoic acid, HCOOH.  $pK_a$ (HCOOH) = 3.74  $K_a$ (HCOOH) = 1.82 × 10<sup>-4</sup> (ii) Calculate the pH at the equivalence point. V(NaOH) = 25mL from graph



0.0035 mol

0.0035 mol

Excellence

Question

Excellence Question

Question: 2c A titration was carried out by adding 0.140 mol L<sup>-1</sup> sodium hydroxide, NaOH, to 20.0 mL of 0.175 mol L<sup>-1</sup> methanoic acid, HCOOH.

63

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

Calculate the pH of the solution after 28.0 mL of 0.140 mol L<sup>-1</sup> NaOH has been added.



## NCEA 2020 Titrations - (PART ONE)

Question 3a: A titration was carried out by adding 0.280 mol L<sup>-1</sup> hydrochloric acid, HCl, to 25.0 mL of 0.224 mol L<sup>-1</sup> sodium ethanoate solution, CH<sub>3</sub>COONa.

The equation for the reaction is:

 $CH_3COONa + HCI \rightarrow CH_3COOH + NaCI$ 

 $K_a(CH_3COOH) = 1.74 \times 10^{-5}$ 

#### Titration curve for CH<sub>3</sub>COONa versus HCl



 $pK_{a}(CH_{3}COOH) = 4.76$ 

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

600

Achieved Question

Do not include water

#### NCEA 2020 Titrations - (PART TWO)

Merit

Question

600

Question 3a: A titration was carried out by adding 0.280 mol L<sup>-1</sup> hydrochloric acid, HCl, to 25.0 mL of 0.224 mol L<sup>-1</sup> sodium ethanoate solution, CH<sub>3</sub>COONa.

The equation for the reaction is:  $CH_3COONa + HCI \rightarrow CH_3COOH + NaCI$ 

 $pK_a (CH_3COOH) = 4.76 K_a (CH_3COOH) = 1.74 \times 10^{-5}$ 

(ii) Calculate the pH of the 0.224 mol L–1 sodium ethanoate solution before any hydrochloric acid is added.

For this solution:  $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ 

```
[CH_3COO^-] = 0.224 \text{ mol } L^{-1}
```

```
K_a = [H_3O^+] [CH_3COO^-]
```



 $[H_3O^+] = 8.81 \times 10^{-10} \text{ molL}^{-1}$ 

pH = 9.05

### NCEA 2020 Titrations - (PART THREE)

Question 3c: A titration was carried out by adding 0.280 mol L<sup>-1</sup> hydrochloric acid, HCl, to 25.0 mL of 0.224 mol L<sup>-1</sup> sodium ethanoate solution, CH<sub>3</sub>COONa.

The equation for the reaction is:  $CH_3COONa + HCI \rightarrow CH_3COOH + NaCI$ 

 $pK_a (CH_3COOH) = 4.76 K_a (CH_3COOH) = 1.74 \times 10^{-5}$ 

(i) Calculate the pH at the equivalence point.

For this solution:  $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ 



Titration curve for CH<sub>4</sub>COONa versus HCl

Sp

Excellence

Question

(i) And (ii)



## NCEA 2020 Titrations - (PART FOUR)

Excellence



At the equivalence point, the weak acid is present, i.e. either  $CH_3NH_3^+$  or  $CH_3COOH$ . Since  $CH_3NH_3^+$  has a smaller  $K_a$  (larger  $pK_a$ ), it is a weaker acid than  $CH_3COOH$  and will therefore dissociate to a lesser extent to produce a lower  $[H_3O^+]$ . As a result, the pH at the equivalence point will be higher for  $CH_3NH_3^+$ .