Anglo-Chinese Junior College
Department of Chemistry

Ionic Equilibrium I -
Theories of Acids & Bases
Acid-Base Equilibria

THE BEST IS YET TO BE

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Guiding Questions

- **Theories of Acids and Bases**

  What are acids and bases?

  What models can be used to classify substances as acids and bases?

- **Acid-base Equilibria**

  What is a strong or weak acid/base? How can the strength of acids and bases be represented and determined? What is the relationship between concentration of acid (base), pH (pOH) and strength of acid (base)?

  What are buffers? How do buffers work? How can the pH of buffers be determined?

  What are the changes in pH during acid-base titrations? How can these pH changes be explained?

1 Introduction

1.1 Types of equilibria

- Chemical equilibrium
- **Dissociation equilibrium** - the equilibrium between a dissolved undissociated molecule and its dissociated ions which mainly involve either acids or bases.
- **Solubility equilibrium** - the equilibrium between an undissolved solid and its dissolved species in solution.
- **Complex ion equilibrium**

1.2 Strength of electrolytes

Ionic equilibrium deals with electrolytes both weak and strong. Electrolytes are compounds which, when molten or in aqueous solution, will conduct an electric current and can be decomposed by it at the electrodes.

- **Strong electrolytes** are ionic compounds which dissociate *completely* into free ions in solution. Strong acids, e.g. HCl, HNO_3, strong bases, e.g., $NaOH$, and soluble salts, eg, $NaCl$, NH_4Cl, $CH_3COO^-Na^+$, can be classified as strong electrolytes.

$$NaCl\,(s) + aq \longrightarrow Na^+(aq) + Cl^-(aq)$$

- **Weak electrolytes** are compounds that dissociate *partially* when dissolved in water e.g. ethanoic acid, aqueous ammonia, organic acids and bases

$$CH_3COOH\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

2 Theories of Acids and Bases

2.1 History of the acid/base models

The acid-base concept has broadened over time as chemists seek to propose a more comprehensive model to classify, rationalise and predict acid-base chemistry. The current understanding of acids and bases is primarily based on the historical contributions of chemists such as Svante Arrhenius, Johannes Brønsted, Thomas Lowry, and Gilbert Newton Lewis.

Arrhenius theory was introduced in 1887 by the Swedish scientist Svante Arrhenius. The Arrhenius acid-base model studied at O-level can be used to classify and explain many substances as acids and bases, but this model has its limitations. One limitation is that this model cannot explain why certain compounds such as ammonia behave like bases even though they do not contain a hydroxide as part of their structure. This limitation could be addressed by the introduction of the Brønsted-Lowry acid-base model. Johannes Nicolaus Brønsted and Thomas Martin Lowry independently proposed the Brønsted–Lowry theory in 1923. The Brønsted-Lowry theory does not go against the Arrhenius theory in any way - it just adds to it. Through this process, you can understand how one theory has built on another to provide a more inclusive model of acids and bases. The Brønsted-Lowry acid-base model though more inclusive than the Arrhenius model, still could not explain why substances such as BF_3 or $AlCl_3$ that do not have any hydrogen atoms but are known to behave as acids. This called for an even more encompassing model of Lewis acid-base model which was proposed by G.N. Lewis from UC Berkeley in 1923. This theory extends well beyond the things one normally thinks of as acids and bases.

It is hence important to understand that science is an evidence-based, model-building enterprise about the natural world. Science knowledge is reliable and durable, yet it is subject to revision in the light of new evidence.

2.2 Definition of Acids and Bases

Learning Outcome:

(1) Show understanding of, and apply the Arrhenius theory of acids and bases

Recalling prior knowledge (Arrhenius Theory)

In the O-level syllabus, acids and bases were defined using the Arrhenius Theory.

Arrhenius Theory	
Acids	substances that give out protons (H^+) in water
Bases	substances that give out hydroxide (OH^-) in water

For example, $HCl\,(aq) \longrightarrow Cl^-\,(aq) + H^+\,(aq)$

More accurately, $HCl\,(aq) + H_2O\,(l) \longrightarrow Cl^-\,(aq) + H_3O^+\,(aq)$ because protons cannot exist independently in aqueous solution.

However, the Arrhenius Theory is limited in its use when acid-base reactions do not take place in aqueous solutions. Considering Arrhenius Theory, can the role of NH_3 and HNO_3 in equations 1 and 2 respectively be defined?

Equation 1: $HCl\,(g) + NH_3\,(g) \longrightarrow NH_4Cl\,(s)$

Equation 2: $HNO_3\,(l) + H_2SO_4\,(l) \longrightarrow H_2NO_3^+\,(l) + HSO_4^-\,(l)$

Learning Outcome:

(2) Show understanding of, and apply the Brønsted-Lowry theory of acids and bases, including the concept of conjugate acids and conjugate bases

Brønsted-Lowry Theory of Acids and Bases

Scientists Brønsted and Lowry proposed another definition of acids and bases that addresses the limitation of Arrhenius Theory.

Brønsted-Lowry Theory	
Acids	substances which will donate protons (H^+) to a base
Bases	substances that will accept protons (H^+) from an acid

Using the Brønsted-Lowry Theory, the roles of NH_3 in equation 1 and HNO_3 in equation 2 can now be defined. They are both acting as bases because they accept H^+ during the respective reactions.

Question: Using the Bronsted-Lowry Theory, explain the role of water in the following equations.

Equation 3: $HCl\,(aq) + H_2O\,(l) \longrightarrow Cl^-\,(aq) + H_3O^+\,(aq)$

Water is the base as it acts as a H^+ acceptor.

Equation 4: $NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$

Water is the acid as it acts as a H^+ donor.

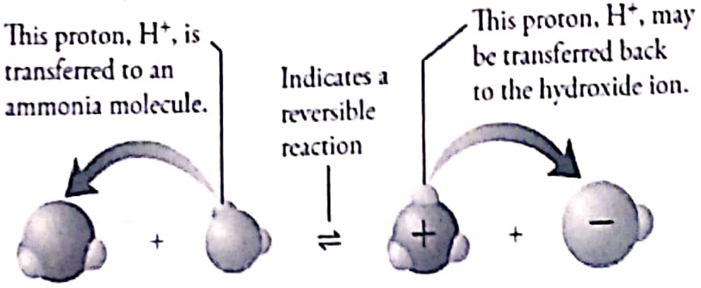
Conjugate acid-base pair

When using the Bronsted-Lowry Theory, the conjugate acid-base pair of each reaction can also be identified. The **conjugate acid-base pair** refers to *an acid and a base which have chemical formulae differing by the presence or absence of one proton.*

Using equation 3,

$$\underset{\textbf{acid}}{HCl\,(aq)} + H_2O\,(l) \longrightarrow \underset{\textbf{conjugate base}}{Cl^-\,(aq)} + H_3O^+\,(aq)$$

Illustrating equation 4 diagramatically,



$$\underset{\textbf{base}}{NH_3(aq)} + H_2O(l) \rightleftharpoons \underset{\textbf{conjugate acid}}{NH_4^+(aq)} + OH^-(aq)$$

Test Your Understanding!!

Identify the acid and the conjugate base in the pairs given below.

(a) HS^- and S^{2-} **(acid, conjugate base)**

(b) $CH_3CH_2O^-$ and CH_3CH_2OH **(conjugate base, acid)**

More examples for conjugate acid-base pairs (Do not memorise order of acid strength!)

		Acid		Conjugate base		
Acid strength increases	Strong acids	perchloric acid	$HClO_4$	ClO_4^-	perchlorate ion	Base strength increases
		hydrochloric acid	HCl	Cl^-	chloride ion	
		sulfuric acid	H_2SO_4	HSO_4^-	hydrogen sulfate ion	
		nitric acid	HNO_3	NO_3^-	nitrate ion	
		hydronium ion	H_3O^+	H_2O	water	
	Weak acids	hydrofluoric acid	HF	F^-	fluoride ion	
		nitrous acid	HNO_2	NO_2^-	nitrite ion	
		acetic acid	$HC_2H_3O_2$	$C_2H_3O_2^-$	acetate ion	
		ammonium ion	NH_4^+	NH_3	ammonia	
		hydrocyanic acid	HCN	CN^-	cyanide ion	
		carbonic acid	H_2CO_3	HCO_3^-	hydrogencarbonate ion	
		hydrosulfuric acid	H_2S	HS^-	hydrogensulfide ion	
		hydrogencarbonate ion	HCO_3^-	CO_3^{2-}	carbonate ion	
		water	H_2O	OH^-	hydroxide ion	
		ammonia	NH_3	NH_2^-	amide ion	
		hydroxide ion	OH^-	O^{2-}	oxide ion	

Table 1. A list of conjugate acid-base pairs that are ranked according to acid strength. Acids that are stronger than H_3O^+ will dissociate completely in water while acids that are weaker than H_3O^+ will only dissociate partially.

Learning Outcome:

(3) Show understanding of, and apply the Lewis theory of acids and bases (including non-aqueous system e.g. reaction between BF_3 and NH_3)

Lewis Theory of Acids and Bases

Lewis proposed a more generalised approach to classify acids and bases.

Lewis Theory	
Acids	substances that accept electron pair from a base
Bases	substances that donate electron pair to an acid

Let us revisit equation 4: $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
$NH_3(g)$ reacts with H^+ (from H_2O) by using its lone pair of electrons to form a co-ordinate bond with the empty 1s orbital on H^+. It has donated its electrons to H^+ and is considered the Lewis base.

In another reaction, $BF_3 + NH_3 \longrightarrow BF_3{\bullet}NH_3$
$NH_3(g)$ reacts with $BF_3(g)$ by using its lone pair of electrons to form a co-ordinate bond with the empty orbital on the boron. BF_3 is acting as the Lewis acid by accepting the nitrogen's lone pair of electrons.

Lewis acid-base theory is more general than Brønsted-Lowry Theory because a Lewis base can donate an electron pair to a Lewis acid which may not necessarily be H^+.

2.3 Basicity of Acids

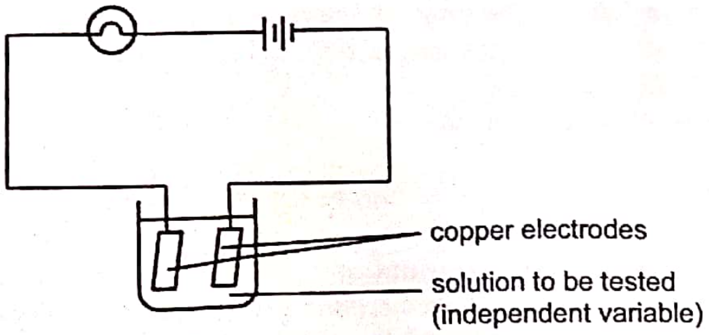
Basicity of an acid refers to the number of moles of ionisable H atoms per mole of the acid.

Basicity of acid	**No. of moles of ionisable H atoms per mole of acid**	**Examples**
Monobasic acids (monoprotic acids)	1	HC*l*, HNO_3, CH_3COOH
Dibasic acids (diprotic acids)	2	H_2SO_4, H_3PO_3 (Phosphorous acid)
Tribasic acids (triprotic acids)	3	H_3PO_4 (Phosphoric acid)

Bases which are soluble in water to form hydroxide ions (OH^-) are known as **alkalis**. Examples are NaOH, KOH and $Ba(OH)_2$. There are many insoluble bases which can react with acids in the solid state, such as CuO and $BaCO_3$.

Learning Outcome:
(4) Explain qualitatively the differences in behaviour between strong and weak acids and bases in terms of the extent of dissociation

2.4 Defining Strong and Weak Acids and Bases

Electrical conductivity of acid solutions	
Objective of experiment	To determine whether HC*l*(aq) and CH_3COOH(aq) with identical concentrations have identical electrical conductivity.
Experiment setup	
Solutions tested	1. Water (control) 2. 0.1 mol dm^{-3} CH_3COOH(aq) 3. 0.1 mol dm^{-3} HC*l*(aq)
Instructions	Immerse the copper electrodes into each of the solutions and observe how the brightness of the light bulb changes.
Observations	No light was seen from the light bulb when water was used. The light bulb is brighter when HC*l*(aq) is used and less bright when CH_3COOH(aq) is used.

Explanation	Both HC*l* and CH_3COOH molecules dissociate in water to form ions. The presence of mobile ions causes the solutions to show electrical conductivity. Although both solutions have the same concentration, HC*l* is a strong acid and dissociates fully while CH_3COOH is a weak acid which dissociates partially, giving rise to different concentration of ions. $HCl \longrightarrow H^+ + Cl^-$ $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Strong acids (e.g. HC*l*, HNO_3) *dissociate completely* in water to form ions.

Equation 5: $HCl\,(aq) \longrightarrow H^+\,(aq) + Cl^-\,(aq)$

Weak acids (e.g. CH_3COOH) *dissociate partially* in water to form a mixture of the acid molecules and ions. The undissociated acid molecules are present in a larger amount than the ions.

Equation 6: $CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + H^+\,(aq)$

The extent of dissociation indicates the strength of an acid. For weak acids, this strength is often described by a K_a value (see section 5).

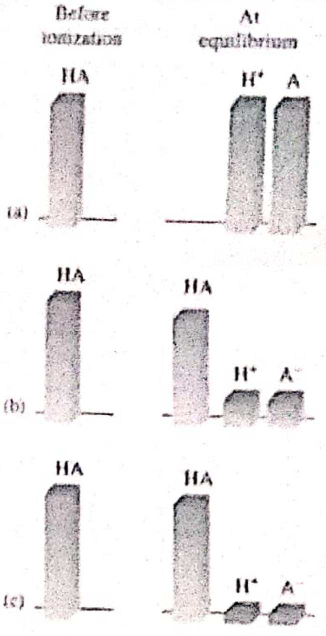


Figure 1. *(right)* The extent of ionisation of
(a) a strong acid that undergoes 100 percent ionisation,
(b) a weak acid, and
(c) a very weak acid

The above description can also be applied to bases.

Test Your Understanding!!

Write equations to show the dissociation (ionisation) of the following acids and bases in water, making sure to use the correct arrows to represent the strength of the acids and bases. Include state symbols in your answers. *(Hint - refer to Table 1)*

(a) H_2CO_3
$H_2CO_3\,(aq) + H_2O\,(l) \rightleftharpoons HCO_3^-\,(aq) + H_3O^+\,(aq)$

(b) HCO_3^- (behaving as an acid)
$HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons CO_3^{2-}\,(aq) + H_3O^+\,(aq)$

(c) HCO_3^- (behaving as a base)
$HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) + OH^-\,(aq)$

(d) CO_3^{2-}
$CO_3^{2-}\,(aq) + H_2O\,(l) \rightleftharpoons HCO_3^-\,(aq) + OH^-\,(aq)$

(e) $HClO_4$

$$HClO_4\,(aq) + H_2O\,(l) \longrightarrow ClO_4^-\,(aq) + H_3O^+\,(aq)$$

(f) HS^- (behaving as an acid)

$$HS^-\,(aq) + H_2O\,(l) \rightleftharpoons S^{2-}\,(aq) + H_3O^+\,(aq)$$

Learning Outcome:

(5) Explain the terms pH; K_a; pK_a; K_b; pK_b; K_w and apply them in calculations, including the relationship $K_w = K_aK_b$

3 The p-scale

Calculating pH from [H⁺]

In aqueous solutions, the concentration of H^+ takes on a large range from about 10 to 10^{-15} mol dm^{-3}. To handle the values with negative powers in a convenient manner, we convert them to positive numbers using a numerical system called the **p-scale**. This is a mathematical function.

Definition of pH	$pH = -\lg [H^+]$

Hence the concentration of H^+ can also be found from pH using **$[H^+] = 10^{-pH}$**

Other p-scales

A p-scale is used for other quantities too.

(a) Hydroxide ion concentration, $[OH^-]$

Definition of pOH	$pOH = -\lg [OH^-]$

(b) Equilibrium constants such as ionic product of water (K_w), acid dissociation constants (K_a) and base dissociation constants (K_b)

You will be learning about pK_w, pK_a and pK_b in sections 4 and 5.

Practice Questions:

1. Find the pH of solutions with the following $[H^+]$ in mol dm^{-3}.

(a) 1.33×10^{-12} **(11.9)**

(b) 5×10^{-3} **(2.30)**

2. Find the $[H^+]$ in mol dm^{-3} for solutions with the following pH.

(a) 7.6 **(2.51×10^{-8})**

(b) 4.42 **(3.80×10^{-5})**

4 Self-Ionisation of Water

When the pH of water changes with temperature, it shows that the concentration of H^+ is changing. This is because water dissociates very slightly into ions, which exist in equilibrium. This process is known as **self-ionisation or autoionisation.** The equilibrium is shown below.

Challenge yourself: Use Equation 7a below to explain why self-ionisation is known as a reaction whereby water undergoes an acid-base reaction with other water molecules.

Answer: Water behaves as an acid, giving out a proton to form OH^-. This proton is accepted by another water molecule which behaves as the base, forming H_3O^+.

Equation 7a $\quad H_2O\,(l) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$

A simplified version of equation 7a is

Equation 7b $\quad H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$

The equilibrium constant for this reaction is

$$K_c = \frac{[H^+][OH^-]}{[H_2O]}$$ where $[H_2O]$ is a large constant,

Multiplying $[H_2O]$ on both sides, $\quad K_c\,[H_2O] = [H^+][OH^-]$

$$K_w = [H^+][OH^-]$$

Taking log on both sides, $\quad \boxed{pK_w = pH + pOH}$

K_w, ionic product of water, is the equilibrium constant for the self-ionisation of water.

At 25 °C,

$$K_w = 1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$$

and consequently $\quad pK_w = 14.0$

Hence for pure water at 25 °C,

$$[H^+] = [OH^-]$$
$$[H^+] = [OH^-] = \sqrt{(1.00 \times 10^{-14})}$$
$$[H^+] = [OH^-] = 1.00 \times 10^{-7}\ \text{mol dm}^{-3}$$
$$pH = 7.00 \text{ and } pOH = 7.00$$

Consequences of the self-ionisation equilibrium of water

a) $[H^+]$ and $[OH^-]$ are present in all aqueous solutions

Both acidic and alkaline solutions contain both $[H^+]$ and $[OH^-]$. Hence the terms 'acidic solution' and 'alkaline solution' must be defined in the following way.

Defining acidic, neutral and alkaline solutions	
Acidic solution	$[H^+] > [OH^-]$
Neutral solution	$[H^+] = [OH^-]$
Alkaline solution	$[H^+] < [OH^-]$

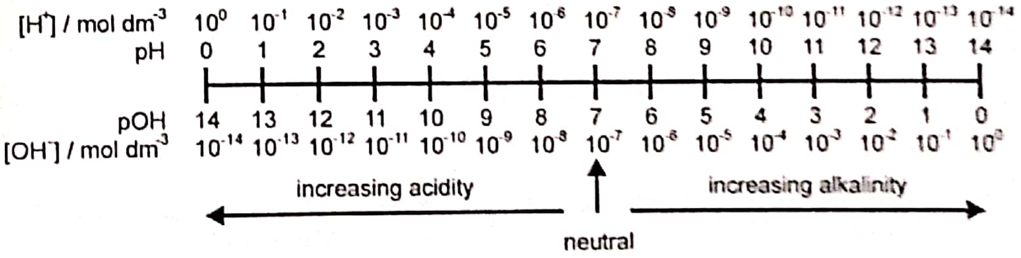
b) An inverse relationship exists between $[H^+]$ and $[OH^-]$

$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$ $\qquad$ $K_w = [H^+]\,[OH^-] = 1.0 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$ (at 25 °C)

At a constant temperature, the equilibrium for the self-ionisation of water shows an inverse relationship between $[H^+]$ and $[OH^-]$. This is because K_w is a constant when temperature is constant.

When an acid dissolves in water, $[H^+]$ increases and causes the above equilibrium to shift to the left. This results in decrease of $[OH^-]$. Similarly, when an alkali dissolves in water, $[OH^-]$ increases and the equilibrium shifts to the left. $[H^+]$ will decrease.

The figure below relates the pH scale to the hydrogen ion concentration and to the changing acidity and alkalinity at 25 °C.



c) Like all equilibrium constants, K_w is temperature dependent.

Equation 7b $H_2O\,(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ $\Delta H > 0$

Recalling Le Chatelier's Principle, it is expected that increasing the temperature of water favours the forward reaction to absorb excess heat. The position of equilibrium shifts to the right and more H^+ and OH^- ions are form. Hence pH and pOH both decrease and causes pK_w to decrease.

When temperature decreases, the backward reaction is favoured to give out heat. The position of equilibrium shifts to the left and less H^+ and OH^- ions are form. Hence pH and pOH both increase and causes pK_w to increase.

(Do not memorise this table)

Temperature / °C	K_w / mol² dm⁻⁶	$[H^+]$ for pure water	pH of pure water (where $pH = -\log[H^+]$)
10	0.29×10^{-14}	5.39×10^{-8}	7.27
20	0.68×10^{-14}	8.25×10^{-8}	7.08
25	$\mathbf{1.00 \times 10^{-14}}$	$\mathbf{1.00 \times 10^{-7}}$	**7.00**
30	1.47×10^{-14}	1.21×10^{-7}	6.92
40	2.92×10^{-14}	1.71×10^{-7}	6.77
50	5.48×10^{-14}	2.34×10^{-7}	6.63
100	51.3×10^{-14}	7.16×10^{-7}	6.15

Table 2. Variation of K_w, ionic product of water, with temperature. Note that pH of pure water (neutral) does not remain at 7 when temperature is higher or lower than 25 °C.

Practice Questions:

1. Calculate the value of pOH for solutions having these pH values. (assuming 25 °C)
   (a) 13.5 (**0.500**) **(b)** 4.6 (**9.40**)

2. Calculate the value of $[OH^-]$ for solutions having these pH values. (assuming 25 °C)
   (a) 1.8 (**6.31×10^{-13}**) **(b)** 7.6 (**3.98×10^{-7}**)

Learning Outcome:

(6) Calculate [$H^+(aq)$] and pH values for strong acids, weak monobasic (monoprotic) acids, strong bases, and weak monoacidic bases

5 Measuring Variation in Acid Strength and Base Strength

Although pH of solutions provides some measure of the strength of the acid or base solution, the use of pH is very limited since its value changes with concentration changes. This section will introduce acid dissociation constant (K_a) and base dissociation constant (K_b) which are more effective measures for the strength of Brønsted-Lowry acids and bases.

5.1 Acid dissociation constant (K_a) and the strength of acids

There are relatively few acids that are strong acids and a wide variety of acids are weak acids. When a weak acid (represented by HA) dissolves in water, an equilibrium is set up between undissociated HA molecules, and the ions H_3O^+ and A^-. This can be represented by this general equation:

Equation 8a $\quad$ $\mathbf{HA\,(aq) \rightleftharpoons H^+\,(aq) + A^-\,(aq)}$

Since the dissociation of HA occurs in water, the reactive H^+ ions associate with H_2O molecules to form **hydronium ions, H_3O^+**. This can be shown in the dissociation of HA by adding H_2O to both sides of **Equation 8a**, thus giving:

Equation 8b $\quad$ $\mathbf{HA\,(aq) + H_2O\,(\mathit{l}) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)}$

By writing the K_c expression for ***Equation 8b***,

$$K_c = \frac{[H_3O^+\,(aq)]\,[A^-(aq)]}{[HA\,(aq)]\,[H_2O\,(l)]}$$

$$K_c\,[H_2O] = \frac{[H_3O^+\,(aq)]\,[A^-(aq)]}{[HA\,(aq)]}$$

$$\boxed{K_a = \frac{[H_3O^+\,(aq)]\,[A^-(aq)]}{[HA\,(aq)]} \qquad \text{(units: mol dm}^{-3}\text{)}}$$

The expression on the right is a constant known as **acid dissociation constant, K_a**. The acid dissociation constant, K_a, is a measure of the strength of an acid.

- The stronger the acid, the greater will be the extent of dissociation, hence the larger the value of K_a.
- The weaker the acid, the lesser will be the extent of dissociation, hence the smaller the value of K_a.

Table 3: K_a values for selected acids (Do not memorise)

Acid	K_a / mol dm^{-3}	pK_a	
$HCl(aq)$	1×10^{7}	−7	acid strength decreases ↓
$HF(aq)$	5.6×10^{-4}	3.25	
$HNO_2(aq)$	4.5×10^{-4}	3.35	
$C_6H_5COOH(aq)$	6.3×10^{-5}	4.20	
$CH_3COOH(aq)$	1.8×10^{-5}	4.74	
$NH_4^+(aq)$	5.7×10^{-10}	9.24	
$HCN(aq)$	4.9×10^{-10}	9.31	

- The larger the K_a value, the stronger the acid
- The larger the pK_a value, the weaker the acid

Practice Questions:

1(a) A solution of benzoic acid, $C_6H_5COOH(aq)$, with the concentration of 0.35 mol dm^{-3} was found to be at pH 2.35 at 25 °C. Calculate the acid dissociation constant of $C_6H_5COOH(aq)$.

$[H_3O^+] = 10^{-2.35}$
$= 0.00447$ mol dm^{-3}

	$C_6H_5COOH(aq)$ +	$H_2O(l)$ ⇌	$H_3O^+(aq)$ +	$C_6H_5COO^-(aq)$
Initial conc / mol dm^{-3}	0.35		0	0
Change	−0.00447		+0.00447	+0.00447
Eqm conc / mol dm^{-3}	0.35−0.00447		0.00447	0.00447

Assumptions:

(i) $[H_3O^+(aq)] = [C_6H_5COO^-(aq)]$ Ignore self-ionisation of water

(ii) As the acid is a weak acid, the degree of dissociation is small. Therefore the equilibrium concentration of the acid is nearly equal to its initial concentration. i.e. $(0.35 - 0.00447) \approx 0.35$

$$K_a = \frac{[H_3O^+][C_6H_5COO^-]}{[C_6H_5COOH]}$$

$$= \frac{(0.00447)(0.00447)}{(0.35)}$$

$$= \underline{\mathbf{5.71 \times 10^{-5}\ mol\ dm^{-3}}}$$

(b) Using the value of acid dissociation constant calculated in **(a)**, find the pH of 0.50 mol dm^{-3} $C_6H_5COOH(aq)$ at 25 °C.

	$C_6H_5COOH(aq)$ +	$H_2O(l)$ $\rightleftharpoons$	$H_3O^+(aq)$ +	$C_6H_5COO^-(aq)$
Initial conc / mol dm^{-3}	0.50		0	0
Change	−x		+x	+x
Eqm conc / mol dm^{-3}	0.50−x		+x	+x

Assumptions:

(i) $[H_3O^+(aq)] = [C_6H_5COO^-(aq)]$ Ignore self-ionisation of water

(ii) As the acid is a weak acid, the degree of dissociation is small. Therefore the equilibrium concentration of the acid is nearly equal to its initial concentration. i.e. $(0.50 - x) \approx 0.50$

$$K_a = \frac{[H_3O^+][C_6H_5COO^-]}{[C_6H_5COOH]}$$

$$5.71 \times 10^{-5} = \frac{x^2}{(0.50)}$$

$$x = 5.34 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg(5.34 \times 10^{-3})$$
$$= \underline{2.27}$$

Challenge yourself: Why is it valid to assume that the weak acid dissociates to a negligible extent / the equilibrium concentration of the weak acid is the initial concentration?

5.2 Base dissociation constant (K_b) and the strength of bases

Similarly for a weak base, B, that is partially ionised in aqueous solution,

$$B\,(aq) \quad + \quad H_2O\,(l) \rightleftharpoons BH^+\,(aq) \quad + \quad OH^-\,(aq)$$

$$\boxed{K_b = \frac{[BH^+\,(aq)]\,[OH^-\,(aq)]}{[B\,(aq)]} \qquad \text{(units: mol dm}^{-3}\text{)}}$$

The base dissociation constant, K_b, is a measure of the strength of a base.

- The stronger the base, the greater the extent of dissociation of B to form BH^+, hence the larger the value of K_b.
- The weaker the base, the lesser will be the extent of dissociation, hence the smaller the value of K_b.

Table 4: K_b values for selected bases (Do not memorise)

Base	K_b / mol dm^{-3}	pK_b	
$CH_3CH_2NH_2(aq)$	5.1×10^{-4}	3.29	base strength decreases
$CO_3^{2-}(aq)$	2.1×10^{-4}	3.68	
$NH_3(aq)$	1.8×10^{-5}	4.74	
$HS^-(aq)$	1.8×10^{-7}	6.74	
$CH_3COO^-(aq)$	5.7×10^{-10}	9.24	
 NH_2 (aq)	4.2×10^{-10}	9.38	

- The larger the K_b value, the stronger the base
- The larger the pK_b value, the weaker the base

The dissociation constants, K_a and K_b, are equilibrium constants. **They are unaffected by concentration changes but are influenced by temperature changes.**

Question:

1(a) Determine K_b of $NH_3(aq)$ given that a 0.80 mol dm^{-3} solution has pH of 11.6 at 25 °C.

pOH = 14 – 11.6 = 2.4

$[OH^-] = 10^{-2.4}$

= 0.00398 mol dm^{-3}

	NH_3 (aq) +	H_2O (*l*) $\rightleftharpoons$	NH_4^+ (aq) +	OH^- (aq)
Initial conc / mol dm^{-3}	0.80		0	0
Change	–0.00398		+0.00398	+0.00398
Eqm conc / mol dm^{-3}	0.80 – 0.00398		0.00398	0.00398

Assumptions:

(i) $[NH_4^+(aq)] = [OH^-(aq)]$ Ignore self-ionisation of water

(ii) As the NH_3 is a weak base, the degree of dissociation is small. Therefore the equilibrium concentration of the base is nearly equal to its initial concentration. i.e. (0.80 – 0.00398) ≈ 0.80

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$= \frac{(0.00398)(0.00398)}{(0.80)}$$

$$= \underline{\mathbf{1.98 \times 10^{-5}\ mol\ dm^{-3}}}$$

(b) Using your answer from **(a)**, calculate the pH of 0.40 mol dm^{-3} NH_3 (aq) at the same temperature.

	NH_3 (aq) +	H_2O (*l*) $\rightleftharpoons$	NH_4^+ (aq) +	OH^- (aq)
Initial conc / mol dm^{-3}	0.40		0	0
Change	–x		+x	+x
Eqm conc / mol dm^{-3}	0.40 – x		x	x

Assumptions:

(i) $[NH_4^+(aq)] = [OH^-(aq)]$ Ignore self-ionisation of water

(ii) As the NH_3 is a weak base, the degree of dissociation is small. Therefore the equilibrium concentration of the base is nearly equal to its initial concentration. i.e. (0.40 – x) ≈ 0.40

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$1.98 \times 10^{-5} = \frac{x^2}{(0.40)}$$

$$x = 0.00282\ \text{mol dm}^{-3}$$

pOH = – lg 0.00282 = 2.55

pH = 14 – 2.55 = **<u>11.5</u>**

5.3 The relationship between K_a of acids and K_b of their conjugate base

Consider the dissociation of the conjugate acid-base pair (NH_3 and NH_4^+) in water.

e.g **Equation 9a** $NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$

$$K_b = \frac{[NH_4^+\,(aq)]\,[OH^-\,(aq)]}{[NH_3\,(aq)]}$$

Equation 9b $NH_4^+\,(aq) + H_2O\,(l) \rightleftharpoons NH_3\,(aq) + H_3O^+\,(aq)$

$$K_a = \frac{[NH_3\,(aq)]\,[H_3O^+\,(aq)]}{[NH_4^+(aq)]}$$

Taking the product of K_a and K_b,

$$K_a \times K_b = \frac{[NH_3\,(aq)]\,[H_3O^+\,(aq)]}{[NH_4^+(aq)]} \times \frac{[NH_4^+\,(aq)]\,[OH^-\,(aq)]}{[NH_3\,(aq)]}$$

$$= [H_3O^+\,(aq)]\,[OH^-\,(aq)] = K_w$$

Hence **for a conjugate acid-base pair,** $\boxed{K_w = K_a \times K_b}$

The relationship of $K_w = K_a \times K_b$ for a conjugate acid-base pair shows that:

- The stronger an acid (the larger the K_a), the weaker its conjugate base (the smaller the K_b), and vice versa. (Refer to Section 2.2 under conjugate acid-base pair)

6 Degree of dissociation, α

Consider the following reaction where α **is the degree of ionisation of a weak electrolyte.**

	$HA(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$A^-(aq)$
Initial conc	c		0		0
Change	$-c\alpha$		$+c\alpha$		$+c\alpha$
Eqm conc	$c(1-\alpha)$		$c\alpha$		$c\alpha$

According to the equilibrium law, $K_a = \dfrac{[H^+(aq)][A^-(aq)]}{[HA(aq)]}$

$$= \frac{(c\alpha)(c\alpha)}{c(1-\alpha)}$$

$$= \frac{c\alpha^2}{1-\alpha}$$

For a weak electrolyte at low concentrations, α is very small. i.e. $(1-\alpha) \sim 1$.

Hence, $K = c\alpha^2$ or $\alpha = \sqrt{(K/c)}$

For a weak acid, $K_a = c\alpha^2$ or $\alpha = \sqrt{(K_a/c)}$

For a weak base, $K_b = c\alpha^2$ or $\alpha = \sqrt{(K_b/c)}$

Note that the degree of dissociation increases as the concentration decreases with dilution.

7 Salt Hydrolysis

7.1 Definition of a salt

A salt may be defined as a compound formed by the reaction of an acid and a base. It contains a cation which originates from the base and an anion which originates from the acid.

Many salts dissolve in water to give neutral solutions. However, some salts react with water to form acidic or alkaline solutions due to **salt hydrolysis**. This is a reversible reaction between salt ions and water.

7.2 Neutral salts

Neutral salts (eg. $NaCl(aq)$) are formed from the reaction between a strong acid and strong, base.

Neutral salts (eg. $NaCl(s)$) dissolve in water to form neutral solutions. When added to water, the salt fully dissociates and the concentration of Na^+ ions equals the concentration of Cl^- ions.

$$NaCl(s) + aq \longrightarrow Na^+(aq) + Cl^-(aq)$$

Neither ion undergoes hydrolysis and therefore the solution is neutral. Na^+ does not undergo hydrolysis due to its relatively low charge density. Cl^- is a weak conjugate base of HCl and does not undergo hydrolysis.

7.3 Acidic salts

Acidic salts (eg. $NH_4Cl(aq)$) are formed from the reaction between a strong acid and weak base. Acidic salts (eg. $NH_4Cl(s)$) dissolve in water and the cations undergoes hydrolysis to form acidic solutions.

E.g. NH_4Cl

Hydration: $NH_4Cl\,(s) + aq \longrightarrow NH_4^+(aq) + Cl^-(aq)$

Hydrolysis: $NH_4^+(aq) + H_2O\,(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

This phenomenon is known as ***cation hydrolysis***. The pH of the solution is **lower than pH 7.**

Do you know?

A salt (e.g. $FeCl_3(aq)$, $AlCl_3(aq)$, $CrCl_3(aq)$) that contains a metallic cation of **high charge density** (small size and high charge) can undergo hydrolysis in aqueous solution and give an acidic solution.

In aqueous solution, the Al^{3+} ion exists as an aqua complex ion, $[Al(H_2O)_6]^{3+}$. The Al^{3+} ion has a **high charge density** and is hence **strongly polarising**. It is able to distort the electron cloud of the H_2O molecules bonded to it, weakening the O–H bonds and enabling these H_2O molecules bonded to it to become proton donors. The free water molecules in the solution act as bases and the following equilibrium is established:

$$[Al(H_2O)_6]^{3+}(aq) + H_2O\,(l) \rightleftharpoons [Al(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq).$$

The Al^{3+} ion is said to undergo **appreciable hydrolysis** in aqueous solution. The production of H_3O^+ ions in the solution causes the solution to be **acidic**. *(This will be covered in more detail in J2 topics Chemical Periodicity & Transition metals)*

7.4 Basic salts

Basic salts (eg. $CH_3COO^-Na^+(aq)$) are formed from the reaction between a strong base and a weak acid. Basic salts (eg. $CH_3COO^-Na^+(s)$) dissolve in water and the anions undergoes hydrolsis to form alkaline solutions.

E.g. $CH_3COO^-Na^+$

Hydration: $CH_3COO^-Na^+\,(s) + aq \longrightarrow CH_3COO^-(aq) + Na^+(aq)$

Hydrolysis: $CH_3COO^-(aq) + H_2O\,(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

E.g. Na_2CO_3

Hydration: $Na_2CO_3\,(s) + aq \longrightarrow 2\,Na^+(aq) + CO_3^{2-}(aq)$

Hydrolysis: $CO_3^{2-}(aq) + H_2O\,(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$

This phenomenon is known as ***anion hydrolysis***. The pH of these solutions are **higher than pH 7.**

7.5 Salts formed from neutralisation of weak acid and weak base

Ammonium ethanoate is an example of this type of salt. When dissolved in water, solid ammonium ethanoate undergoes complete dissociation.

$$CH_3COO^-NH_4^+\,(s) + aq \longrightarrow CH_3COO^-\,(aq) + NH_4^+\,(aq)$$

The NH_4^+ ion undergoes hydrolysis to generate H_3O^+ ions:

$$NH_4^+\,(aq) + H_2O\,(l) \rightleftharpoons NH_3\,(aq) + H_3O^+\,(aq) \qquad K_a$$

The CH_3COO^- ion undergoes hydrolysis to generate OH^- ions:

$$CH_3COO^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3COOH\,(aq) + OH^-\,(aq) \qquad K_b$$

Whether the solution is acidic or alkaline depends on the relative values of the dissociation constants of NH_4^+ and CH_3COO^-.
If $K_a > K_b$, then the salt is acidic.
If $K_b > K_a$, then the salt is basic.

For ammonium ethanoate, since $K_a \approx K_b$, $[H_3O^+(aq)] \approx [OH^-(aq)]$. Hence, ammonium ethanoate solution is approximately neutral.

Summary table of different types of salts		
Reaction of acid and base	**Salt formed**	**Nature and pH of solution (25 °C)**
strong acid + strong base $HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)$	$NaCl\,(aq)$	**Neutral** pH = 7
strong acid + weak base $HCl\,(aq) + NH_3\,(aq) \longrightarrow NH_4Cl\,(aq)$	$NH_4Cl\,(aq)$	**Acidic** pH < 7
weak acid + strong base $CH_3COOH\,(aq) + NaOH\,(aq) \longrightarrow CH_3COO^-Na^+\,(aq) + H_2O\,(l)$	$CH_3COO^-Na^+\,(aq)$	**Alkaline** pH > 7
weak acid + weak base $CH_3COOH\,(aq) + NH_3\,(aq) \longrightarrow CH_3COO^-NH_4^+\,(aq) + H_2O\,(l)$	$CH_3COO^-NH_4^+\,(aq)$	very slightly acidic Note: Acidic if K_a of cation > K_b of anion Neutral if K_a of cation = K_b of anion Alkaline if K_a of cation < K_b of anion

Practice Questions:

1. Calculate the pH of 0.30 mol dm^{-3} NH_4Cl(aq), given that the K_b of NH_3(aq) is 1.67 x 10^{-5} mol dm^{-3}.

	$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$			
Initial conc / mol dm^{-3}	0.30		0	0
Change	−x		+x	+x
Eqm conc / mol dm^{-3}	0.30 − x		x	x

Assumptions:

(i) $[NH_3(aq)] = [H_3O^+(aq)]$ Ignore self-ionisation of water

(ii) As NH_4^+ is a weak acid, the degree of disssociation is small.

$\therefore [NH_4^+(aq)]_{int} = [NH_4^+(aq)]_{eqm}$

$K_a = 1 \times 10^{-14} \div 1.67 \times 10^{-5}$

$= 5.988 \times 10^{-10}$ mol dm^{-3}

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$$5.988 \times 10^{-10} = \frac{x^2}{0.30}$$

$[H_3O^+] = 1.34 \times 10^{-5}$ mol dm^{-3}

pH = $-\lg(1.34 \times 10^{-5})$ = **<u>4.87</u>**

2. Calculate the pH of 0.60 mol dm^{-3} $CH_3COO^-Na^+$(aq), given that the K_a of CH_3COOH(aq) is 1.75 x 10^{-5} mol dm^{-3}.

	$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$			
Initial conc / mol dm^{-3}	0.60		0	0
Change	−x		+x	+x
Eqm conc / mol dm^{-3}	0.60 − x		x	x

Assumptions:

(i) $[CH_3COOH(aq)] = [OH^-(aq)]$ Ignore self-ionisation of water

(ii) As CH_3COO^- is a weak base, the degree of disssociation is small.

$\therefore [CH_3COO^-(aq)]_{int} = [CH_3COO^-(aq)]_{eqm}$

$K_b = 1 \times 10^{-14} \div 1.75 \times 10^{-5}$

$= 5.71 \times 10^{-10}$ mol dm^{-3}

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$5.71 \times 10^{-10} = \frac{x^2}{0.60}$$

$[OH^-] = 1.851 \times 10^{-5}$ mol dm^{-3}

pOH = $-\lg(1.851 \times 10^{-5}) = 4.73$

pH = 14 − 4.73 = **<u>9.27</u>**

8 Buffer solutions

- A buffer solution is a solution containing a weak acid and its conjugate base or a weak base and its conjugate acid which resists and does not show significant changes in pH when **small amounts of strong acid or strong alkali are added to it.**

- An **acidic buffer** solution consists:
  (i) a weak acid
  (ii) the salt of the same weak acid (conjugate base)
- An **alkaline buffer** solution consists:
  (i) a weak base
  (ii) the salt of the same weak base (conjugate acid)

Learning Outcome:
(9) Explain how buffer solutions control pH

8.1 Acidic buffer: CH_3COOH and $CH_3COO^-Na^+$

In an aqueous solution of CH_3COOH (weak acid) and $CH_3COO^-Na^+$ (conjugate base of CH_3COOH), $CH_3COO^-Na^+$ exists as the separate ions, CH_3COO^- and Na^+. We can represent the equation when $CH_3COO^-Na^+$ dissolves in water:

$$CH_3COO^-Na^+ (s) + aq \longrightarrow CH_3COO^- (aq) + Na^+ (aq) \text{ ---- } (1)$$

CH_3COOH, being a weak acid, exists in equilibrium with its ions according to the equation:

$$CH_3COOH (aq) \rightleftharpoons H^+ (aq) + CH_3COO^- (aq) \text{ ---- } (2)$$

Notice that in both equations, CH_3COO^- is formed. The contribution of CH_3COO^- by (1) is far greater than (2). This suppresses the dissociation of CH_3COOH and therefore the position of equilibrium of (2) lies far to the left. Hence, the mixture contains **a high concentration of both undissociated ethanoic acid molecules and ethanoate ions.**

Let us examine how the conjugate acid – base pair is responsible for the ability of buffer to minimise pH changes when small amounts of strong acid or alkali are added.
On addition of a little acid to the buffer,

$$CH_3COO^- (aq) + H^+ (aq) \longrightarrow CH_3COOH (aq)$$

the hydrogen ions from the acid react with the ethanoate ions to form ethanoic acid molecules. Thus the increase in the hydrogen ion concentration is not as great and pH does not significantly change.

On the addition of a little alkali to the buffer,

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

the added hydroxide ions react with the ethanoic acid molecules. The decrease in hydrogen ion concentration is not as great and the pH does not significantly change.

There are minimal changes to the relative concentrations of both the weak acid and its conjugate base in both cases.

Thus the stable pH of an acidic buffer is maintained effectively due to:

(i) a **high concentration of A^-** which traps any added $H^+(aq)$

(ii) a **high concentration of HA** which supplies $H^+(aq)$ to remove any added $OH^-(aq)$

8.2 Alkaline buffer: NH_3 and NH_4Cl

An alkaline buffer containing NH_3 (weak base) and NH_4Cl (conjugate acid of NH_3) works in a similar way as an acidic buffer. In an aqueous mixture of $NH_3(aq)$ and $NH_4Cl(aq)$, each compound behaves according to the equations below:

$$NH_4Cl\ (aq) \longrightarrow NH_4^+\ (aq) + Cl^-\ (aq) \text{ ---- } (3)$$

$$NH_3\ (aq) + H_2O\ (l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq) \text{ ---- } (4)$$

The NH_4^+ ion from the fully ionised ammonium chloride of (3) suppresses the ionisation of the ammonia solution of (4) so that the mixture contains a **high concentration of both ammonia molecules and ammonium ions.**

On addition of a little acid to the buffer,

$$NH_3\ (aq) + H^+\ (aq) \longrightarrow NH_4^+\ (aq)$$

the hydrogen ions from the acid react with ammonia to form ammonium ion. Thus the increase in the hydrogen ion concentration is not as great as when the acid is added to pure water alone and pH does not significantly change.

On the addition of a little alkali to the buffer,

$$NH_4^+\ (aq) + OH^-\ (aq) \longrightarrow NH_3\ (aq) + H_2O\ (l)$$

the added hydroxide ions react with the ammonium ions. The decrease in hydrogen ion concentration is not as great when the alkali is added to pure water alone and the pH does not significantly change.

There are minimal changes to the relative concentrations of both the weak base and its conjugate acid in both cases.

Thus the stable pH of an alkaline buffer is due to:

(i) a **high concentration of $NH_3(aq)$** which traps added $H^+(aq)$

(ii) a **high concentration of $NH_4^+(aq)$** which supplies $H^+(aq)$ to remove added $OH^-(aq)$

Learning Outcome:

(11) Calculate the pH of buffer solutions, given appropriate data

8.3 Calculating pH of a buffer

In buffer composed of a weak acid (HA) and its salt (MA),

$$HA\ (aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

$$MA\ (s) + aq \longrightarrow M^+\ (aq) + A^-\ (aq)$$

We can construct the K_a expression as follows:

$$K_a = \frac{[H^+\ (aq)]\ [A^-(aq)]}{[HA\ (aq)]}$$

The value of **[HA] is taken as the initial concentration of the acid** since the acid is only slightly dissociated in the presence of its salt. The value of **$[A^-]$ is effectively the concentration of the salt taken** since the salt is fully dissociated into ions. Thus for a buffer,

$$[H^+(aq)] = \frac{K_a \times [HA(aq)]}{[A^-(aq)]}$$

$$[H^+(aq)] = \frac{K_a \times [acid]}{[salt]}$$

By taking log on both sides,

pH of acidic buffers is $$\boxed{\mathbf{pH = pK_a + \log \frac{[salt]}{[acid]}}}$$

The following equation can be deduced for pOH of alkaline buffers

$$\boxed{\mathbf{pOH = pK_b + \log \frac{[salt]}{[base]}}}$$

The pH of a buffer is **slightly affected by dilution** since the ratio $\frac{[salt]}{[acid]}$ (or [base]) will remain constant on dilution. Hence buffers work best when there is a high concentration of both species.

8.4 Maximum buffering capacity

A buffer solution at maximum buffering capacity shows the smallest change in pH when a small amount of strong acid or strong base is added to it.

The maximum buffering capacity of each solution occurs when the concentration of the acid is the same as the concentration of its conjugate base. i.e. [salt] = [acid] or [salt] = [base]

For an acidic buffer at maximum buffering capacity, since [salt] = [acid]

$$\mathbf{pH = pK_a}$$

For an alkaline buffer at maximum buffering capacity, since [salt] = [base]

$$\mathbf{pOH = pK_b}$$

Practice Questions:

1(a) Calculate the pH of a solution containing 0.10 mol dm^{-3} of propanoic acid and 0.20 mol dm^{-3} of sodium propanoate. K_a for propanoic acid is 1.34 x 10^{-5} mol dm^{-3}.

	$CH_3CH_2COOH(aq)$ + $H_2O(l)$ ⇌		$CH_3CH_2COO^-(aq)$ +	$H_3O^+(aq)$
Initial conc / mol dm^{-3}	0.10		0.20	0
Change	−x		+x	+x
Eqm conc / mol dm^{-3}	0.10 − x		0.20 + x	x

Assumptions:

(i) $[CH_3CH_2COO^-(aq)]$ = $[CH_3CH_2COO^-Na^+(aq)]$ since dissociation of CH_3CH_2COOH is very small.

(ii) As the CH_3CH_2COOH is a weak acid, the degree of dissociation is small. Therefore the equilibrium concentration of the acid is nearly equal to its initial concentration. i.e. $(0.10 - x) \approx 0.10$

$$K_a = \frac{[H_3O^+(aq)]\,[CH_3CH_2COO^-(aq)]}{[CH_3CH_2COOH(aq)]} = \frac{[H_3O^+(aq)]\,[\text{sodium propanoate}]}{[\text{propanoic acid}]}$$

$$1.34 \times 10^{-5} = \frac{[H_3O^+(aq)]\,(0.2)}{(0.1)}$$

$[H_3O^+] = 6.70 \times 10^{-6}$ mol dm^{-3}

pH = $-\lg(6.70 \times 10^{-6})$ = **5.17**

Or

$$pH = pK_a + \lg\frac{[\text{sodium propanoate}]}{[\text{propanoic acid}]}$$

$= -\lg(1.34 \times 10^{-5}) + \lg\left(\frac{0.2}{0.1}\right)$
$= \underline{5.17}$

(b) Calculate the change in the pH when 1 cm^3 of 1.0 mol dm^{-3} NaOH is added to 1 dm^3 of the buffer in **(a)** above.

Total volume = 1.001 dm^3 ≈ 1.000 dm^3
Amt of NaOH added = 0.001 mol

$$NaOH + CH_3CH_2COOH \longrightarrow CH_3CH_2COO^-Na^+ + H_2O$$

Amount of salt formed = 0.001 mol

$$CH_3CH_2COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CH_2COO^-(aq)$$

	$CH_3CH_2COOH(aq)$	$CH_3CH_2COO^-(aq)$
Initial conc / mol dm^{-3}	0.100	0.200
Change	−0.001	+0.001
Equilibrium / mol dm^{-3}	0.099	0.201

$$K_a = \frac{[H_3O^+(aq)]\,[CH_3CH_2COO^-(aq)]}{[CH_3CH_2COOH(aq)]} = \frac{[H_3O^+(aq)]\,[\text{sodium propanoate}]}{[\text{propanoic acid}]}$$

$$1.34 \times 10^{-5} = \frac{[H_3O^+](0.201)}{(0.099)}$$

$[H_3O^+] = 6.60 \times 10^{-6}$ mol dm^{-3}

pH = $-\lg(6.60 \times 10^{-6})$ = **5.18**

Change in pH = 5.18 – 5.17
= **0.0100**

Or

$$pH = pK_a + \lg \frac{[\text{sodium propanoate}]}{[\text{propanoic acid}]}$$

$$= -\lg (1.34 \times 10^{-5}) + \lg \left(\frac{0.201}{0.099}\right)$$

$$= \underline{5.18}$$

Change in pH = 5.18 – 5.17
= **0.0100**

2 Calculate the pH of a buffer solution made by mixing 750 cm^3 of a 0.20 mol dm^{-3} of NH_4Cl and 750 cm^3 of 0.10 mol dm^{-3} of ammonia solution. Assume that K_b for the NH_3 is 1.67×10^{-5} mol dm^{-3}.

Total volume = 750 + 750 = 1500 cm^3
Conc of NH_4^+ = (0.20 x 0.75)/1.5 = 0.10 mol dm^{-3}
Conc of NH_3 = (0.10 x 0.75)/1.5 = 0.05 mol dm^{-3}

	NH_3 (aq) + H_2O (*l*)	⇌	NH_4^+ (aq)	+ OH^- (aq)
Initial conc / mol dm^{-3}	0.05		0.10	0
Change	−x		+x	+x
Eqm conc / mol dm^{-3}	0.05 − x		0.10 + x	x

Assumptions:

(i) $[NH_4^+ (aq)] = [NH_4Cl (aq)]$ since dissociation of NH_3 is very small.

(ii) As the NH_3 is a weak base, the degree of dissociation is small. Therefore the equilibrium concentration of the base is nearly equal to its initial concentration. i.e. $(0.05 - x) \approx 0.05$

$$K_b = \frac{[NH_4^+(aq)]\,[OH^-(aq)]}{[NH_3\,(aq)]}$$

$$1.67 \times 10^{-5} = \frac{(0.10)\,[OH^-]}{0.05}$$

$[OH^-] = 8.35 \times 10^{-6}$ mol dm^{-3}

$pOH = -\lg (8.35 \times 10^{-6}) = 5.08$
pH = 14 – 5.08
= **8.92**

Or

$$pOH = pK_b + \lg \frac{[\text{ammonium chloride}]}{[\text{ammonia}]}$$

$$= -\lg (1.67 \times 10^{-5}) + \lg \left(\frac{0.10}{0.05}\right)$$

$$= 5.08$$

pH = 14 – 5.08
= **8.92**

8.5 Importance of buffers

Learning Outcome:

(10) Describe and explain the uses of buffers, including the role of H_2CO_3/HCO_3^- in controlling pH in blood

- **Control of pH in blood by H_2CO_3/HCO_3^- buffer**
  Blood is buffered at a pH of 7.4 by a number of mechanisms. The most important buffer system is the **carbonic acid-bicarbonate buffer** system:
  $H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$ (or $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$)

When $[H^+]$ increases *(from lactic acid produced during vigorous exercise)*, the HCO_3^- present removes the additional H^+ to form H_2CO_3 and the pH remains almost constant.

$$H^+(aq) + HCO_3^-(aq) \longrightarrow H_2CO_3(aq)$$

When $[OH^-]$ increases, the H_2CO_3 present removes the additional OH^- to form HCO_3^- and the pH remains almost constant.

$$OH^-(aq) + H_2CO_3(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$$

- **Buffers are important in many industrial processes** where the pH must not deviate very much from the optimum value. Several synthetic and processed foods must be prepared in a buffered form so that they may be eaten and digested in our bodies without undue changes in pH.

- **Control of the pH of a solution is also important in medicine and agriculture.** This is because many metabolic processes have to occur at strictly controlled pH. Intravenous injections must be buffered so as to maintain the pH of blood in the range of 7.0 – 7.9.

- The fermentation processes are also buffered as relatively small changes in pH may destroy the fermenting organisms. **Enzymes (biological proteins) function due to their structures which depend on pH.** Abrupt pH changes can rupture cells and denature enzymes. Buffering action is provided by the following systems:

  (i) H_2CO_3/HCO_3^- buffer (i.e. $H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$)
  (ii) $H_2PO_4^-/HPO_4^{2-}$ buffer (i.e. $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$)
  (iii) Proteins

- **Buffers play an important role in personal care products such as cosmetics.** Alpha hydroxy acids (AHAs) are found in many skin care products. They are used in anti-aging creams where the pH is below 5.5. AHAs function as pH adjusters, they are added to make sure skin-care products are not too acidic or basic and are therefore mild and non-irritating. AHAs are used to exfoliate and cleanse the skin, help reduce the appearance of skin wrinkling, even skin tones and soften the skin. They act on the surface of the skin by removing dead surface cells, thereby improving the appearance of the skin.

Learning Outcome:

(8) Explain the choice of suitable indicators for acid-base titrations, given appropriate data.

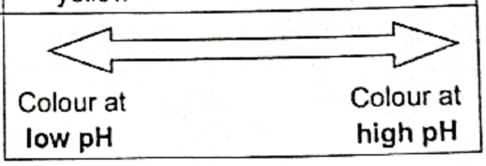
9 Acid-Base Indicators

Acid-base indicators are substances which change colour according to the hydrogen ion concentration of the solution in which they are placed.

- They are usually either weak bases or weak acids that have distinctly different colours in their dissociated and undissociated forms.
- The undissociated molecule is one colour and the anion (or cation) is a different colour.

E.g. An indicator, represented as HIn, dissociates according to the following equation:

Indicator (HIn)	$HIn (aq) \rightleftharpoons H^+(aq)$	$+ In^-(aq)$
Phenolphthalein	colourless	pink
Methyl orange	red	yellow
Bromothymol blue	yellow	blue



Consider **methyl orange** being used in an acid-base titration,

- Addition of acid (i.e. $H^+(aq)$) shifts the position of equilibrium to the *left*. $[HIn (aq)] > [In^-(aq)]$ the solution becomes *red*.
- Addition of alkali (i.e. $OH^-(aq)$) shifts the position of equilibrium to the *right*. $[HIn (aq)] < [In^-(aq)]$ and the solution becomes *yellow*.

Choosing an indicator for a titration

- The *equivalence point* is the point at which an acid is completely reacted with or been neutralised by the base. The indicator's role in a titration is to signal the equivalence point through a sharp change in colour, brought about by the sharp change in pH.

- The *end point* of a titration occurs when the indicator changes colour. A suitable indicator should have an end point that is close to the equivalence point of the titration.

- Consider the equilibrium for dissociation of HIn and its equilibrium constant, K_{Ind}:

$$HIn (aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

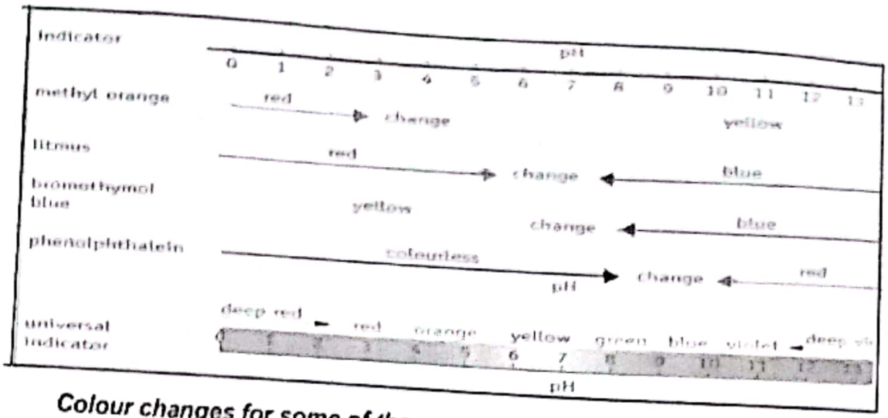
Since $$K_{Ind} = \frac{[H^+(aq)][In^-(aq)]}{[HIn(aq)]}$$ where K_{Ind} is the K_a of HIn

Under high $[H^+(aq)]$, $[HIn(aq)]$ is high. As base is added, $[H^+(aq)]$ decreases and position of equilibrium shifts right, increasing $[In^-(aq)]$. At a certain pH, the concentration of the dissociated and undissociated forms are nearly similar. At this point the colour of the indicator will be midway between the acid colour for HIn and the alkaline colour for In^-.

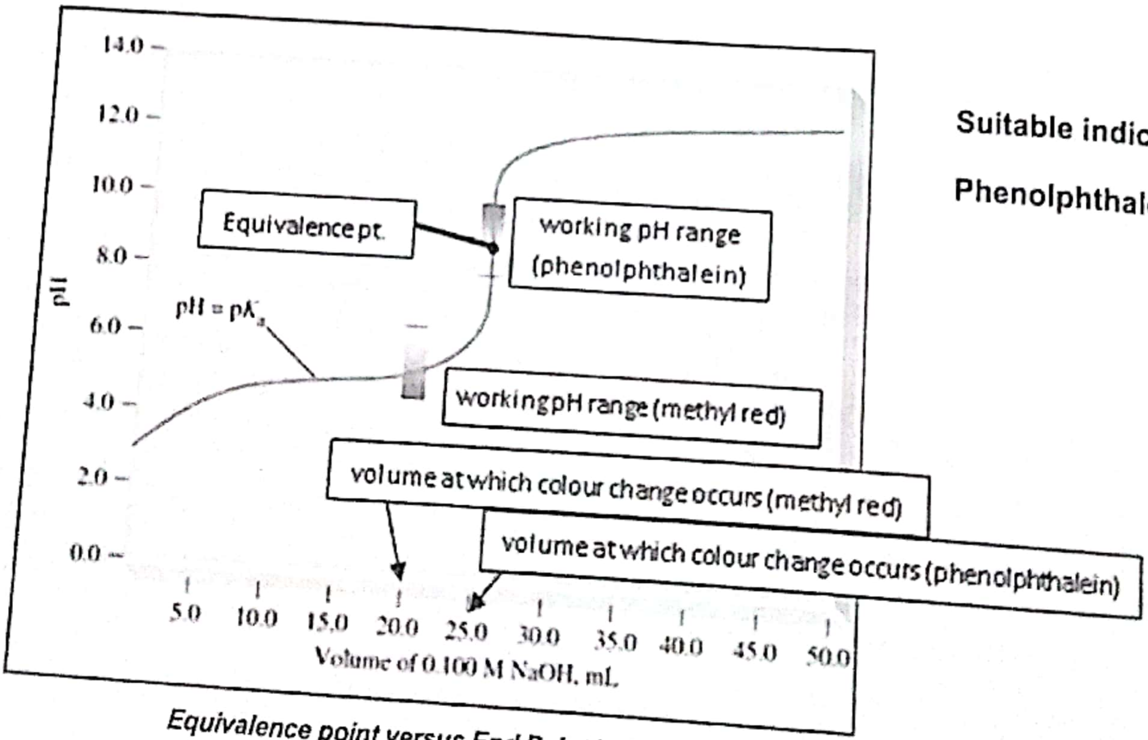
$$\text{i.e. } [HIn (aq)] = [In^-(aq)]$$
$$pH = pK_{Ind}$$

- Hence pK_{Ind} gives a good indication of the pH range where the indicator can be used to detect the equivalence point in a titration. In other words, **an indicator is chosen when its working pH range coincides with the equivalence point of a titration.** (See table below)

Indicator	pK_{Ind}	Working pH range of colour change*	Colour change		
			Colour in acid	Colour around pK_{Ind}	Colour in alkali
Methyl orange	3.7	**3.2 – 4.2**	Red	Orange	Yellow
Methyl red	5.1	**4.2 – 6.3**	Red	Orange	Yellow
Bromothymol blue	7.0	**6.0 – 7.6**	Yellow	Green	Blue
Phenol red	7.9	**6.8 – 8.4**	Yellow	Orange	Red
Phenolphthalein	9.3	**8.2 – 10.0**	Colourless	Pale pink	Red



Colour changes for some of the common indicators used for titrations



Suitable indicator:

Phenolphthalein

Equivalence point versus End Point in an acid-base titration

Learning Outcome:

(7) Describe the changes in pH during acid-base titrations and explain these changes in terms of the strengths of the acids and bases

10 Titration Curves

A titration curve is a plot of pH versus the volume of titrant added in a titration. It indicates graphically the changes in pH as acid or base is added to a solution.

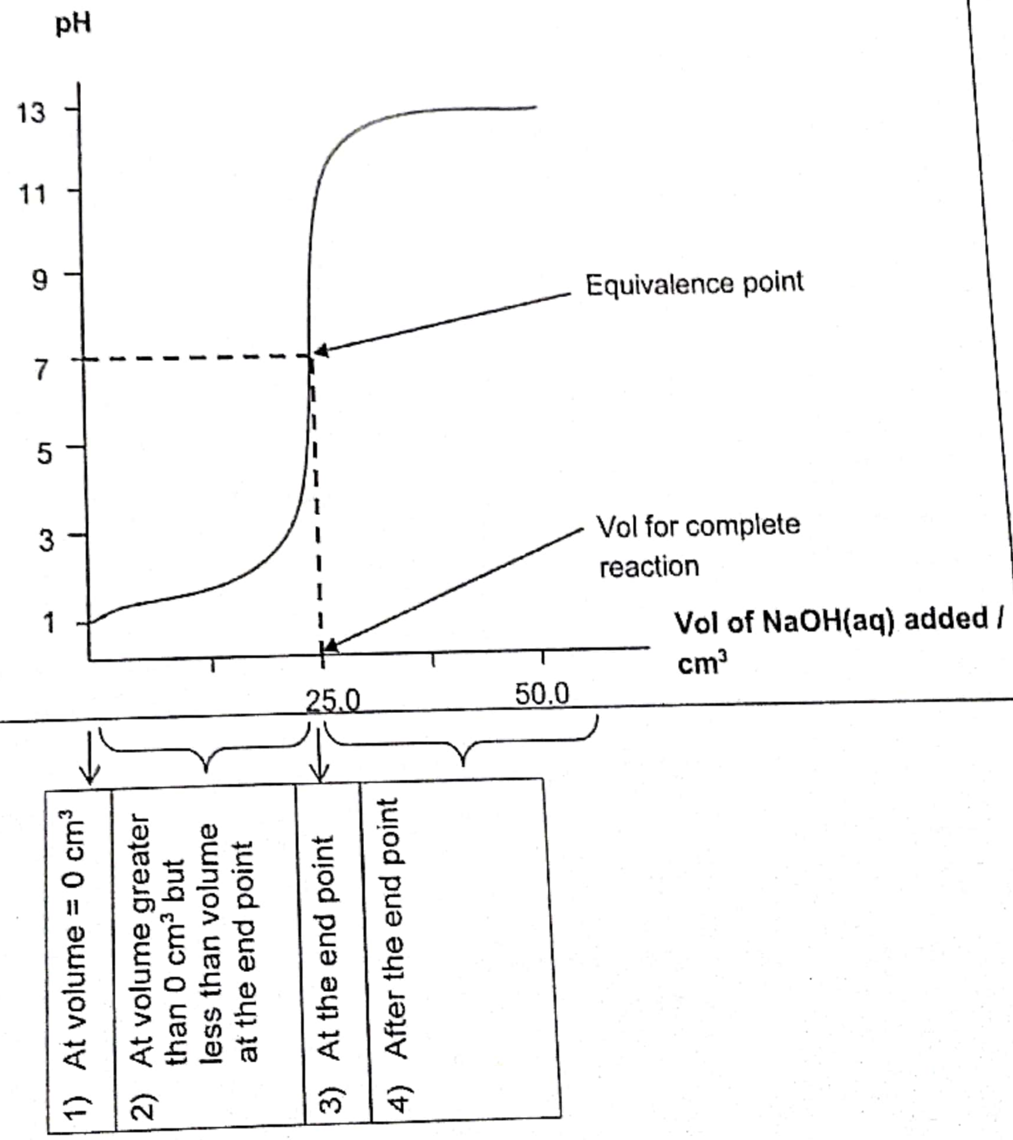
A titration curve consists of information on the volume of titrant added and corresponding pH at

- Maximum buffering capacity
- Equivalence point

10.1 Titration of strong acid with strong base

Solution 25.0 cm^3 of 0.100 mol dm^{-3} HC*l*(aq)	**Titrant** 0.100 mol dm^{-3} NaOH(aq)

Titration Curve



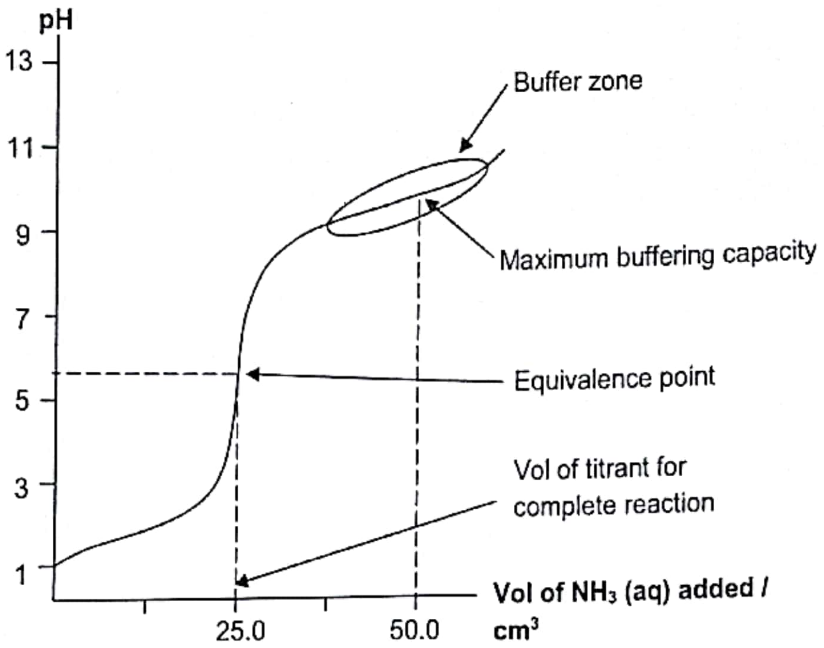
Important: To calculate the pH of the mixture during titration, we will start by considering the titration curve in 4 parts as shown above.

Section of the titration curve	Type of solution present	pH changes during titration
1) At volume of titrant = 0 cm^3	HCl(aq) (A solution of strong acid is present.)	**Initial pH** pH = $-\lg[H^+] = -\lg(0.100) = \mathbf{1.00}$
2) At volume greater than 0 cm^3 but less than 25 cm^3	NaCl(aq) and HCl(aq) (A solution of strong acid is present.)	**pH when a small amount of NaOH is added** When 5.00 cm^3 of NaOH has been added to the acid, the total volume of the mixture is 30.00 cm^3 Since $NaOH + HCl \longrightarrow NaCl + H_2O$ 1 mol NaOH ≡ 1 mol HCl No. of moles of unreacted acid $= \frac{25-5}{1000} \times 0.1 = 0.002$ mol $[H^+(aq)] = 0.002 \div 30/1000 = 0.0667$ mol dm^{-3} **pH = 1.18**
(same as above)	(same as above)	**pH just before the end point** When 24.90 cm^3 of NaOH has been added, the total volume of the mixture is 49.90 cm^3. No. of moles of unreacted acid = $0.10 \times 0.1 / 1000$ $= 1.00 \times 10^{-5}$ mol $[H^+(aq)] = 1.00 \times 10^{-5} \div 49.90/1000$ $= 2.00 \times 10^{-4}$ mol **pH = 3.70**
3) At the end point, when volume of titrant = 25 cm^3	NaCl(aq) (A solution of a neutral salt is present.)	**pH at equivalence point** When 25.00 cm^3 of NaOH has been added, the acid is exactly neutralised. The salt formed, NaCl, does not undergo salt hydrolysis. pH now depends on the self-ionisation of water, $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ **pH = 7.00**
4) After the end point, when volume of titrant is more than 25 cm^3	NaCl(aq) and NaOH(aq) (A solution of strong base is present.)	**pH after the end point** When 25.10 cm^3 of NaOH has been added, the total volume of mixture is 50.10 cm^3. The number of moles of unreacted alkali $= 0.10 \times 0.1 / 1000 = 1.00 \times 10^{-5}$ mol $[OH^-] = 1.00 \times 10^{-5} \div 50.10/1000$ $= 2.00 \times 10^{-4}$ mol pOH = 3.70 **pH = pK_w - pOH = 14 – 3.70 = 10.3**

10.2 Titration of strong acid with weak base

Solution 25.0 cm^3 of 0.100 mol dm^{-3} $HCl(aq)$ | **Titrant** 0.100 mol dm^{-3} $NH_3(aq)$

Titration Curve



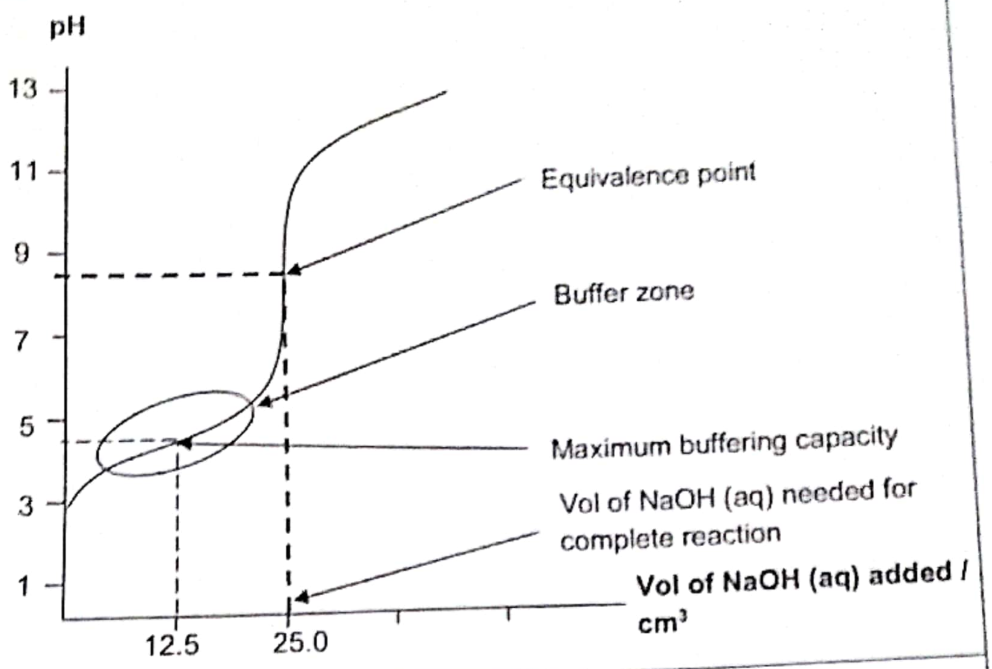
Section of the titration curve	Type of solution present	pH changes during titration
1) At volume of titrant = 0 cm^3	$HCl(aq)$ (A solution of strong acid is present.)	**Initial pH** **pH** = $-\lg [H^+(aq)] = -\lg (0.1) =$ **1.00**
2) At volume greater than 0 cm^3 but less than 25 cm^3	$HCl(aq)$ and $NH_4Cl(aq)$ (A solution of strong acid is present.)	**pH when a small amount of $NH_3(aq)$ is added** When 5.00 cm^3 of $NH_3(aq)$ has been added to the acid, the total volume of the mixture is 30.00 cm^3. Since $NH_3 + HCl \longrightarrow NH_4Cl + H_2O$ 1 mol NH_3 ≡ 1 mol HCl No. of moles of unreacted acid $= (\frac{25}{1000} \times 0.1) - (\frac{5}{1000} \times 0.1) = 0.002$ mol $[H^+(aq)] = 0.002 \div 30/1000 = 0.0667$ mol dm^{-3} **pH = 1.18**
(Same as above)	(Same as above)	**pH just before end point** When 24.90 cm^3 of $NH_3(aq)$ has been added, the total volume of the mixture is 49.90 cm^3. No. of moles of unreacted acid $= (\frac{25}{1000} \times 0.1) - (\frac{24.90}{1000} \times 0.1)$ $= 1.00 \times 10^{-5}$ mol $[H^+(aq)]$ $= 1.00 \times 10^{-5} \div (\frac{49.90}{1000})$

		$= 2.00 \times 10^{-4}$ mol dm^{-3} **pH** $= -\lg (2.00 \times 10^{-4})$ **= 3.70**
3) At the end point, when volume of titrant is 25 cm^3	$NH_4Cl(aq)$ (A solution of an acidic salt is present.)	**pH at equivalence point** When 25.00 cm^3 of $NH_3(aq)$ has been added, the acid is exactly neutralised. Total volume of solution is 50.00 cm^3. pH now depends on the **hydrolysis of the NH_4Cl,** $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$ $n(NH_4^+) = 25/1000 \times 0.1 = 0.0025$ mol $[NH_4^+] = 0.0025 / 50.00 \times 1000 = 0.05$ mol dm^{-3} Given that K_a of $NH_4^+ = 5.7 \times 10^{-10}$ mol dm^{-3} Let $x = [H_3O^+(aq)]$ $K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]}$ (assuming $x << 0.05$) $5.7 \times 10^{-10} = x^2 / 0.05$ $x = 5.34 \times 10^{-5}$ mol dm^{-3} **pH = 5.27 (i.e. equivalence point pH < 7 ; salt formed is acidic)**
4) After the end point, when volume of titrant is more than 25 cm^3	$NH_4Cl(aq)$ and $NH_3(aq)$ (A solution of an alkaline buffer is present.) At vol = 50 cm^3, the solution achieves maximum buffering capacity (MBC).	**pH at maximum buffering capacity** When 50.00 cm^3 of $NH_3(aq)$ has been added, the total volume of mixture is 75.00 cm^3. For a buffer at maximum buffer capacity, since $[NH_4^+] = [NH_3]$ $pH = pK_a$ **pH** $= -\lg (5.7 \times 10^{-10})$ **= 9.24**

10.3 Titration of weak acid with strong base

Solution 25.0 cm^3 of 0.100 mol dm^{-3} $CH_3COOH(aq)$	**Titrant** 0.100 mol dm^{-3} $NaOH(aq)$

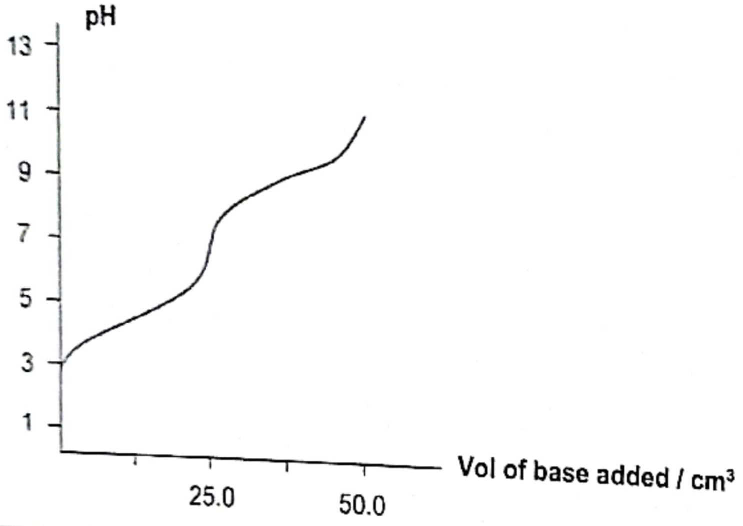
Titration Curve



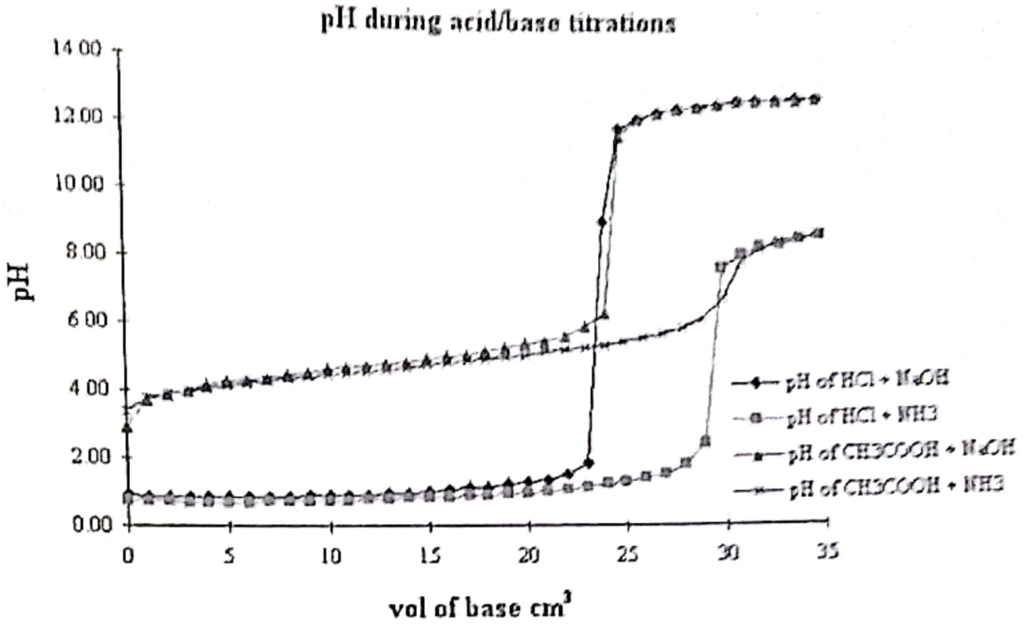
Section of the titration curve	**Type of solution present**	**pH changes during titration**
1) At volume of titrant = 0 cm^3	$CH_3COOH(aq)$ (A solution of a weak acid is present.)	**Initial pH** Given $K_a = 1.8 \times 10^{-5}$ mol dm^{-3}, let $[H^+]$ be x mol dm^{-3}. $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ $1.8 \times 10^{-5} = \frac{x^2}{0.1 - x} \approx \frac{x^2}{0.1}$ (assuming x <<0.1) $x = [H^+] = 1.342 \times 10^{-3}$ mol dm^{-3} **pH** = −lg (1.342×10^{-3}) = **2.87**
2) At volume greater than 0 cm^3 but less than 25 cm^3	$CH_3COOH(aq)$ and $CH_3COO^-Na^+(aq)$ (A solution of an acidic buffer is present.) At vol = 12.5 cm^3, the solution achieves MBC.	**pH at maximum buffering capacity** Maximum buffer capacity is reached, the total volume of the mixture is 37.50 cm^3. For a buffer at maximum buffer capacity, since $[CH_3COOH] = [CH_3COO^-]$ $pH = pK_a$ **pH** = − lg (1.8×10^{-5}) = **4.74**

3) At the end point, when volume of titrant = 25 cm^3	$CH_3COO^-Na^+(aq)$ (A solution of a basic salt is present.)	**pH at equivalence point** When 25.00 cm^3 of NaOH has been added, the acid is exactly neutralised. pH now depends on the **hydrolysis of the salt**, $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$ $[CH_3COO^-] = \frac{25}{1000} \times 0.1 \div \frac{50}{1000} = 0.05 \text{ mol dm}^{-3}$ $K_b = 5.56 \times 10^{-10} \text{ mol dm}^{-3} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$ $5.56 \times 10^{-10} \times 0.05 = x^2$ $x = [OH^-] = 5.27 \times 10^{-6} \text{ mol dm}^{-3}$ $pOH = -\lg(5.27 \times 10^{-6}) = 5.28$ pH = 14 – 5.28 = **8.72**

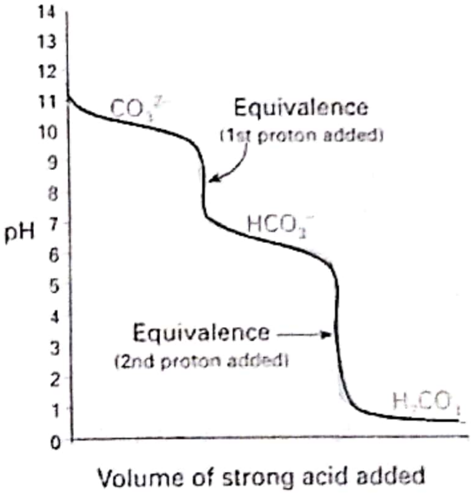
10.4 Titration of weak acid with weak base

Solution 25.0 cm^3 of 0.100 mol dm^{-3} $CH_3COOH(aq)$	**Titrant** 0.100 mol dm^{-3} $NH_3(aq)$
Titration Curve 	

Comparison of 4 titration curves on the same set of axes



10.5 pH curves of diacidic bases and polyprotic acids (self – reading)



The titration curve for the weak base, Na_2CO_3 and the strong acid HC*l* shows two separate equivalence points.

The first equivalence point corresponds to

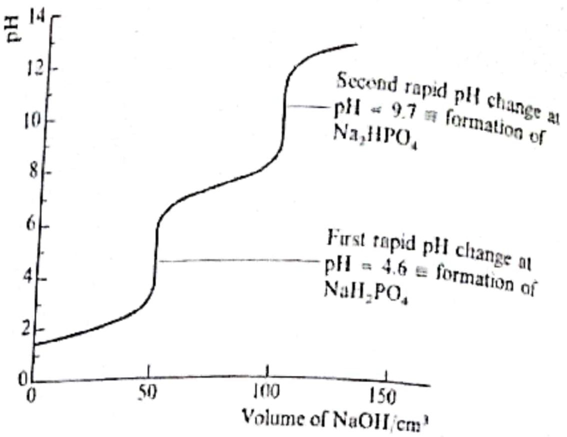
$$CO_3^{2-}(aq) \quad + \quad H_3O^+(aq) \longrightarrow HCO_3^-(aq) \quad + \quad H_2O\,(l)$$

The second equivalence point corresponds to

$$HCO_3^-(aq) \quad + \quad H_3O^+(aq) \longrightarrow H_2CO_3(aq) \quad + \quad H_2O\,(l)$$

Titration of a polyprotic acid

FIGURE 12.10 Changes in pH during Titration (of 50.0 cm³ of Phosphoric(V) acid (0.100 mol dm⁻³) with sodium hydroxide (0.100 mol dm⁻³)



Second rapid pH change at pH ≈ 9.7 ≡ formation of Na_2HPO_4

First rapid pH change at pH ≈ 4.6 ≡ formation of NaH_2PO_4

The titration curve for H_3PO_4 and NaOH shows two obvious equivalence points.

The **first equivalence point** corresponds to

$$NaOH(aq) + H_3PO_4(aq) \longrightarrow NaH_2PO_4(aq) + H_2O(l)$$

The **second equivalence point** corresponds to

$$NaOH(aq) + NaH_2PO_4(aq) \longrightarrow Na_2HPO_4(aq) + H_2O(l)$$

However, for the **third stage** of titration of titration

$$NaOH(aq) + Na_2HPO_4(aq) \longrightarrow Na_3PO_4(aq) + H_2O(l)$$

the curve is very flat and **no suitable indicator** will detect an end-point.

pH calculations of carbonic acid

The concentration of a solution of carbonic acid (a diprotic acid) is 0.00370 mol dm^{-3}. Given that

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_{a1} = 4.3 \times 10^{-7}$$
$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \qquad K_{a2} = 5.6 \times 10^{-11}$$

Calculate

(i) the pH of the carbonic acid solution and

(ii) the carbonate ion concentration.

(i) Since $K_{a1} >> K_{a2}$, K_{a1} is used for the calculation.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_{a1} = 4.3 \times 10^{-7}$$

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

Let $[H^+] = x$ mol dm^{-3}

$$= \frac{x^2}{(0.00370 - x)}$$

$$\approx x^2 / 0.00370$$

$x = 3.989 \times 10^{-5}$

pH = 4.40

(ii) K_{a2} now needs to be used. $K_{a2} = \dfrac{[\cancel{H^+(aq)}]\,[CO_3^{2-}]}{[\cancel{HCO_3^-}\,(aq)]}$ Assume: $[H^+] \approx [HCO_3^-]$

$$5.60 \times 10^{-11}\ \text{mol dm}^{-3} = [CO_3^{2-}]$$