

Pioneer Junior College
Higher 2 Chemistry (9647)
Ionic Equilibria I: Acid – Base Equilibria

References

1. Chemistry The Molecular Nature of Matter and Change by M S Silberberg
2. Chemistry Principles and Applications by Atkins, Clugston, Frazer, Jones

Assessment Objectives

Candidates should be able to:

- (a) show understanding of, and apply the Bronsted-Lowry theory of acids and bases, including the concept of conjugate acids and conjugate bases
- (b) explain qualitatively the differences in behaviour between strong and weak acids and bases in terms of the extent of dissociation
- (c) explain the terms pH; K_a ; pK_a ; K_b ; pK_b ; K_w and apply them in calculations, including the relationship $K_w = K_a \times K_b$
- (d) calculate $[H^+(aq)]$ and pH values for strong acids, weak monobasic (monoprotic) acids, strong bases, and weak monoacidic bases
- (e) explain the choice of suitable indicators for acid-base titrations, given appropriate data
- (f) describe the changes in pH during acid-base titrations and explain these changes in terms of the strengths of the acids and bases
- (g) (i) explain how buffer solutions control pH
(ii) describe and explain their uses, including the role of H_2CO_3/HCO_3^- in controlling pH in blood
- (h) calculate the pH of buffer solutions, given appropriate data

Lecture Outline

1. Theories about Acids and Bases
2. The pH Scale and the ionic product of water, K_w
3. Acids in water
 - (i) Strong vs. Weak Acids
 - (ii) Acid dissociation constant, K_a and pK_a
 - (iii) Calculating pH of weak acid solutions
4. Bases in water
 - (i) Strong vs. Weak Bases
 - (ii) Base dissociation constant, K_b and pK_b
 - (iii) Calculating the pH of weak basic solutions
5. Strength of Acids and Bases
6. Conjugate Acid – Base Pairs
7. Salt Solutions
 - (i) Relationship between K_a , K_b and K_w (also between pK_a , pK_b and pK_w)
 - (ii) Calculating pH of salt solutions
8. Buffer Systems
 - (i) Action of buffers
 - (ii) Calculating pH of buffer solutions
 - (iii) Buffering capacity and effective buffer range
9. Acid-Base Titration Curves
 - (i) Titration curves
 - (ii) Indicators

1. Theories about Acids and Bases

Definition	Remarks/ Limitations
1. The Arrhenius Theory of Acids and Bases	
<p>An <u>acid</u> is a substance that ionises in water to give $H^+(aq)$. $HCl(g) + aq \rightarrow H^+(aq) + Cl^-(aq)$</p> <p>A <u>base</u> is a substance that ionises in water to give $OH^-(aq)$. $NaOH(s) + aq \rightarrow Na^+(aq) + OH^-(aq)$</p>	<p>The acid definition limits acids to those of formula H_nX and bases to those of $M(OH)_n$.</p> <p>Common bases such as NH_3 and Na_2CO_3 are excluded. It is also restricted to aqueous solutions only.</p>
2. The Brønsted-Lowry Theory of Acids and Bases	
<p>An acid is a proton (H^+) <u>donor</u>.</p> <p>A base is a proton (H^+) <u>acceptor</u>.</p> <p>Acid Base</p> $HCl + H_2O \rightarrow H_3O^+ + Cl^-$ $H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$ $HCl + NH_3 \rightarrow NH_4Cl$ <div style="border: 1px dashed black; padding: 10px; margin-top: 10px;"> <p>We are primarily concerned with aqueous solutions, in which acid-base phenomena involve proton transfer and so the Brønsted-Lowry Theory in which acids and bases are defined as proton donors and acceptors is of most use to us.</p> </div>	<p>For this definition, the acid - base property is shown only when an acid is present together with a base.</p> <p><u>Advantages:</u> A broader definition which includes bases without $-OH$ group. It is not limited to acids and bases in aqueous solutions only.</p> <p><u>Disadvantages:</u> It is restricted to substances containing protons (H^+).</p>
3. Lewis acids and bases	
<p>An acid is an electron-pair <u>acceptor</u>.</p> <p>A base is an electron-pair <u>donor</u>.</p> $\underset{\text{Lewis acid}}{BF_3} + \underset{\text{Lewis base}}{:NH_3} \longrightarrow H_3N: \rightarrow BF_3$ $\underset{\text{Lewis acid}}{H^+} + \underset{\text{Lewis base}}{H_2O:} \longrightarrow H_3O^+$ $\underset{\text{Lewis acid}}{AlCl_3} + \underset{\text{Lewis base}}{:Cl^-} \longrightarrow AlCl_4^-$	<p>The Lewis theory is much broader than the Arrhenius and the Brønsted - Lowry definitions. It extends the range of acid-base reactions to include those who do not include protons.</p> <p><i>*Note:</i> All Brønsted-Lowry acids are Lewis acids, but not all Lewis acids are Brønsted-Lowry acids. The same can be said of the bases.</p>

2. The pH Scale and the Ionic Product of Water

The pH Scale

The concentration of hydrogen ions in a solution is a measure of acidity or alkalinity of the solution. Most H^+ concentrations fall between the values of 10^0 mol dm^{-3} (i.e. pH 0) and $10^{-14} \text{ mol dm}^{-3}$ (i.e. pH 14). This wide range of hydrogen ion concentrations could conveniently be expressed by the numbers 0 to 14 using the **pH scale**.

Definition of pH

The pH of a solution is a measure of the acidity or alkalinity of the solution. It is the negative logarithm to base 10 of the hydrogen ion concentration in mol dm^{-3} of the solution, i.e.

$$\text{pH} = -\lg[H^+(\text{aq})] = -\lg[H_3O^+(\text{aq})]$$

$$[H^+(\text{aq})] = 10^{-\text{pH}}$$

- A solution that has a lower pH has a **higher** concentration of hydrogen ions than a solution with a higher pH.
- A solution with a lower pH is **more acidic** than a solution with a higher pH.
- An aqueous solution with pH = 7 at 298 K is considered to be neutral.

Definition of pOH

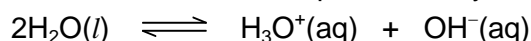
Similarly, the concentration of hydroxide ions (in mol dm^{-3}) in aqueous solution can be expressed in terms of pOH.

$$\text{pOH} = -\lg[OH^-(\text{aq})]$$

$$[OH^-(\text{aq})] = 10^{-\text{pOH}}$$

Ionic Product of water, K_w

- The electrical conductivity of even the purest water never falls to exactly zero. This is due to the self-ionisation of water. This can be represented by:



- At equilibrium, $K_c = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]}$
- Since water is a weak electrolyte, the amount of water ionised is very small, such that $[H_2O]$ remains virtually constant.
 $\Rightarrow K_c \cdot [H_2O]^2 = [H_3O^+][OH^-] = \text{another constant, } K_w$
- The **ionic product of water**, K_w is the product of the concentrations of H_3O^+ and OH^- ions.

Hence,

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

$$\text{At 298 K, } K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

- K_w has units of $\text{mol}^2 \text{ dm}^{-6}$.

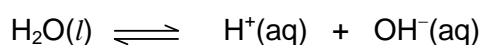
- Since $K_w \ll 1$, equilibrium position lies to the left. Hence, we can deduce that H_2O is a weaker base than OH^- , and H_2O is a weaker acid than H^+ .
- The exact value of K_w depends on temperature.

****Recall: Values of K_c and K_p are only affected by T . Same for K_w .**
- At a given temperature, $[H_3O^+][OH^-] = K_w$ at all times. Thus, when $[H_3O^+]$ becomes larger, $[OH^-]$ becomes smaller and vice versa.

Lecture E.g. 1:

Temp / °C	18	25	40	75
$K_w / \text{mol}^2 \text{dm}^{-6}$	0.61×10^{-14}	1.00×10^{-14}	2.92×10^{-14}	16.9×10^{-14}

Is the self-ionisation of water exothermic or endothermic? Explain.



- As temperature is increased, K_w **increases**.
i.e. more water molecules dissociate, giving rise to higher concentrations of H^+ and OH^- ions.
- The equilibrium position shifts to the **right** to absorb the heat energy supplied. (*in accordance to LCP*)

⇒ Hence the forward reaction is **endothermic** ($\Delta H > 0$).

Relationship between pK_w , pH and pOH at 298 K

- Since $K_w = [H_3O^+][OH^-]$,
Taking $-\lg$ on both sides, $-\lg K_w = (-\lg [H_3O^+]) + (-\lg [OH^-])$
Therefore, **$pK_w = pH + pOH$**

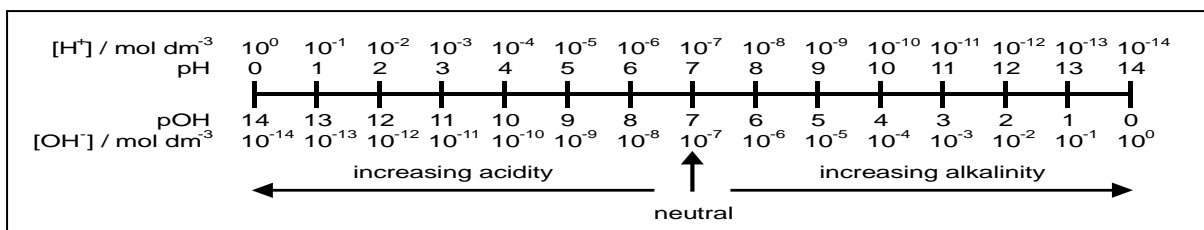
At 298 K, $pK_w = -\lg K_w = -\lg (1.0 \times 10^{-14}) = 14$

At 298 K, **$pH + pOH = 14$**

pH of neutral solution at 298 K = 7

- For a neutral solution, $[H_3O^+] = [OH^-]$
- Since $K_w = [H_3O^+][OH^-]$,
 $[H_3O^+]^2 = 1.0 \times 10^{-14} \text{ mol}^2 \text{dm}^{-6}$ (at 298 K)
 $[H_3O^+] = \sqrt{(1.0 \times 10^{-14})}$
 $= 1.0 \times 10^{-7} \text{ mol dm}^{-3}$
 Therefore, **$pH = -\lg [H_3O^+] = -\lg (1.0 \times 10^{-7}) = 7$**
- Since $[OH^-] = [H_3O^+] = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$,
 $pOH = -\lg [OH^-] = -\lg (1.0 \times 10^{-7}) = 7$

At 298 K, **pH of a neutral solution = 7**



In summary:

Neutral solution	$[H^+] = [OH^-]$	pH = 7 at 298 K
Acidic solution	$[H^+] > [OH^-]$	pH < 7 at 298 K
Basic solution	$[H^+] < [OH^-]$	pH > 7 at 298 K

Measurement of pH of a solution

- For an approximate value, use universal indicator paper or solution.
- For an accurate determination, use a pH meter.

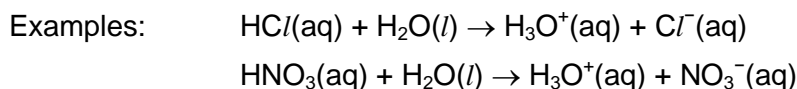
3. Acids in water

Acids typically have the following properties:

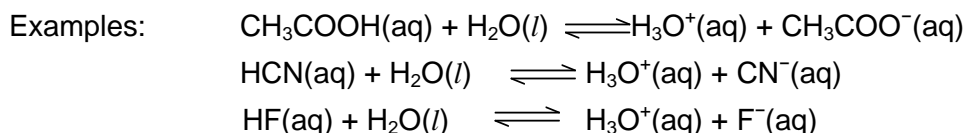
- They have a strong sharp, sour taste.
- They do not conduct electricity when pure but becomes an electrical conductor when in aqueous solutions.
- Aqueous solutions of acids change the colour of indicators.
- Aqueous solutions of acids undergo the following reactions:
 - they react with metal oxides to produce salts and water,
 - they react with more reactive metals to produce salts and hydrogen, and
 - they react with carbonates to produce salts, carbon dioxide and water.

Strong and Weak Acids

- A strong acid is one that undergoes **complete** dissociation in aqueous solution.



- A weak acid is one that undergoes **partial** dissociation in aqueous solution.



Due to incomplete dissociation, the undissociated species of the weak acids still exist in relatively large amounts in the dilute solutions.

Dissociation of strong acid
E.g. HCl (aq)

Before Dissociation

No. of moles

HCl

After Dissociation

No. of moles

H^+ Cl^-

Consider a $0.100 \text{ mol dm}^{-3}$ HCl (aq),
 $\text{HCl}(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

Initial amt/ mol	0.100	0	0
Final amt/ mol	0	0.100	0.100

In this solution,
 $[\text{H}^+] = [\text{Cl}^-] = 0.100 \text{ mol dm}^{-3}$

Note:
 There are no more H-Cl molecules present in solution!

Dissociation of weak acid
E.g. HF (aq)

Before Dissociation

No. of moles

HF

After Dissociation

No. of moles

HF H^+ F^-

Consider a $0.100 \text{ mol dm}^{-3}$ HF (aq),
 $\text{HF}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{F}^-(\text{aq})$

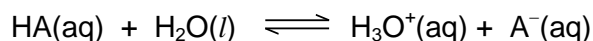
Initial amt/ mol	0.100	0	0
Final amt/ mol	$0.100 - a$	a	a

In this solution, $[\text{H}^+] = [\text{F}^-]$
 And $[\text{HF}] \gg [\text{H}^+] = [\text{F}^-]$

Note:
 Equilibrium constant, $K_a \ll 1$
 (equilibrium position lies to the left)

Acid dissociation constant, K_a

- Consider the dissociation of a weak monobasic acid HA (e.g. CH_3COOH) in aqueous solution:



- At equilibrium, $K_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$
 - In aqueous solution, water is present in such large excess, that its concentration stays essentially constant.
 - Rearranging the above expression, we get:

$$K_c \cdot [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \text{constant} = K_a$$

$$\text{Acid dissociation constant, } K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]}$$

- K_a is called the **acid dissociation constant**.
 - It is a measure of the **STRENGTH** of the acid HA as it provides a quantitative indication of the extent of dissociation of the acid.
 - It has units of mol dm^{-3} .
 - Its value is constant at a constant temperature and changes only with temperature.
- The K_a values of different acids can be used to compare the strength of the acids. However, it is sometimes more convenient to compare the strength of acids using $\text{p}K_a$ values:

$$\text{p}K_a = -\lg K_a$$

- The K_a and pK_a of some acids (at 298 K) are shown below.

Acid	$K_a / \text{mol dm}^{-3}$	pK_a
HCl	1×10^7	-7
HF	5.6×10^{-4}	3.25
HNO ₂	4.5×10^{-4}	3.35
C ₆ H ₅ COOH	6.3×10^{-5}	4.20
CH ₃ COOH	1.8×10^{-5}	4.74
NH ₄ ⁺	5.7×10^{-10}	9.24
HCN	4.9×10^{-10}	9.31
H ₂ O	1.8×10^{-16}	15.7

Acid strength decreases.

The stronger the acid, the **larger** the K_a value, the **smaller** the pK_a value.

Acid dissociation constants of a weak polyprotic acid

- An acid that donates 1 proton is called a monobasic acid. E.g. HCl, HNO₃, CH₃COOH.
- An acid that donates 2 protons is called a dibasic acid. E.g. H₂SO₄, H₂CO₃
- An acid that donates 3 protons is called a tribasic acid. E.g. H₃PO₄, H₃BO₃
- In general, acids that donate more than 1 proton are called **polyprotic acids**.
 - For example, phosphoric(V) acid, a tribasic acid, has three acids dissociation constants. These are called first (K_{a1}), second (K_{a2}) and third (K_{a3}) dissociation constants respectively.

Dissociation	Equilibrium in aqueous solution	$K_a / \text{mol dm}^{-3}$	pK_a
First	$\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$	7.5×10^{-3}	2.1
Second	$\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HPO}_4^{2-}$	6.2×10^{-8}	7.2
Third	$\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{PO}_4^{3-}$	4.5×10^{-13}	12.3

where $K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$ $K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$ $K_{a3} = \frac{[\text{H}_3\text{O}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$

- Note: $K_{a1} > K_{a2} > K_{a3}$
 - Its value is temperature dependent (i.e. K_a remains constant at a constant temperature).
 - First proton, H⁺, is lost from a **neutral** molecule.
 - Subsequent dissociations involve the removal of H⁺ (a **positive ion**) from anions with increasing **negative charge**.
 ⇒ Hence, increasing energy is needed for successive dissociations, causing extent of dissociation (as seen from K_a values) to decrease.

Acid	Dissociation	K_a	pK_a
Sulfuric(VI) acid, H ₂ SO ₄ (aq)	First	Large	-
	Second	1.2×10^{-2}	1.92
Phosphoric(V) acid, H ₃ PO ₄ (aq)	First	7.5×10^{-3}	2.14
	Second	6.2×10^{-8}	7.21
	Third	4.5×10^{-13}	12.35
Carbonic acid, H ₂ CO ₃ (aq)	First	4.2×10^{-7}	6.38
	Second	4.8×10^{-11}	10.32

Calculations involving pH and K_a values

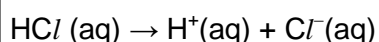
pH of Strong acid solutions

- Strong acids ionise completely in water.
- For a strong acid H_nA with basicity n , $[H^+(aq)] = n \times [H_nA(aq)]$

Note:

- No matter how dilute an acidic solution is, its pH (at 25 °C) is always less than 7.
- Self-ionisation of water is ignored for concentrated strong acid.

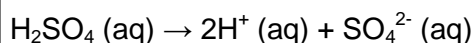
Lecture E.g. 2: Calculate the pH of 0.100 mol dm⁻³ hydrochloric acid solution.



$$[H^+] = [HCl]_{\text{initial}} = 0.100 \text{ mol dm}^{-3}$$

$$pH = -\lg(0.100) = \underline{\underline{1.00}}$$

Lecture E.g. 3: Calculate the pH of 4.20 x 10⁻³ mol dm⁻³ sulfuric acid solution.



$$[H^+] = 2 \times [H_2SO_4]_{\text{initial}} = 8.40 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pH = -\lg(8.40 \times 10^{-3}) = \underline{\underline{2.08}}$$

pH of Weak acid solutions

- Weak acids ionise only partially in water.
- For a solution containing a weak acid, $[H_3O^+(aq)] \ll [\text{acid}]$.
- In order to simplify the calculation, we make an assumption:
 $[H_3O^+] = [HA]_{\text{dissociated}} \ll [HA]_{\text{initial}}$, such that $[HA]_{\text{eqm}} \approx [HA]_{\text{initial}}$.
 This approximation is valid and approximation can be used only if:

$$\frac{[H^+]}{[HA]_{\text{initial}}} \times 100\% \leq 5\%$$

Lecture E.g. 4: Calculate the pH of 0.100 mol dm⁻³ ethanoic acid solution. ($K_a = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$)

Let $[H^+] = [CH_3COO^-] = x \text{ mol dm}^{-3}$ at equilibrium

	$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$		
Initial concentration / mol dm ⁻³	0.100	0	0
Concentration at eqm / mol dm ⁻³	$0.100 - x$	x	x

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{x^2}{0.100 - x}$$

Since ethanoic acid is a weak acid, the extent of dissociation is very small.

⇒ Hence x is negligible compared to 0.100 mol dm⁻³. Therefore, $(0.100 - x) \approx 0.100$

$$K_a = \frac{x^2}{0.100} = 1.8 \times 10^{-5}$$

Solving, $x = 1.34 \times 10^{-3} \text{ mol dm}^{-3}$
Hence, $\text{pH} = -\lg [\text{H}^+ (\text{aq})] = \underline{\underline{2.87}}$

**Note: $[\text{CH}_3\text{COOH}]$ at equilibrium (i.e. those remaining undissociated)
 $= 0.100 - 1.34 \times 10^{-3}$
 $= 0.0987 \text{ mol dm}^{-3} \approx 0.100 \text{ mol dm}^{-3}$
The assumption stated earlier is, hence, valid.*

Compare the above with the previous exercise with $0.100 \text{ mol dm}^{-3}$ hydrochloric acid.

- Note:** The pH of a weak acid is higher than that of a strong acid of the same concentration.

Lecture E.g. 5: The pH of an acid solution containing $0.350 \text{ mol dm}^{-3}$ of HF is 1.82.

Calculate the K_a of HF(aq).

$\text{pH} = 1.82$

$\Rightarrow [\text{H}_3\text{O}^+] = 10^{-1.82} = 0.0151 \text{ mol dm}^{-3}$

At equilibrium, $[\text{H}_3\text{O}^+] = [\text{F}^-]$

	$\text{HF(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{F}^-(\text{aq})$		
Initial concentration / mol dm^{-3}	0.35	0	0
Concentration at eqm / mol dm^{-3}	$0.35 - 0.0151$	0.0151	0.0151

$$K_a = \frac{[\text{F}^-][\text{H}_3\text{O}^+]}{[\text{HF}]} \quad K_a = \frac{(0.0151)(0.0151)}{(0.35 - 0.0151)} = \underline{\underline{6.84 \times 10^{-4} \text{ mol dm}^{-3}}}$$

4. Bases in water

Bases typically have the following properties:

- They have a characteristic bitter taste and slippery to the touch.
- Not all bases are soluble in water. Bases which are soluble in water are called alkali.
- Aqueous solutions of alkalis are electrical conductors.
- Aqueous solutions of bases change the colour of indicators.

Strong and Weak Bases

- A strong base is one that undergoes **complete** ionisation in aqueous solution.

Example: $\text{NaOH(s)} + \text{aq} \rightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq}); [\text{OH}^-] = [\text{Na}^+] = \text{initial } [\text{NaOH}]$

- A weak base is one that undergoes slight or **partial** ionisation in aqueous solution.

Examples: $\text{NH}_3(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
 $\text{CH}_3\text{CH}_2\text{NH}_2(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{CH}_3\text{CH}_2\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$

Base dissociation constant, K_b

- Consider the ionisation of a weak monoacidic base B (e.g. NH_3) in aqueous solution:

$$\text{B(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{BH}^+\text{(aq)} + \text{OH}^-\text{(aq)}$$

- At equilibrium, $K_c = \frac{[\text{OH}^-][\text{BH}^+]}{[\text{H}_2\text{O}][\text{B}]}$
 - Note: In aqueous solution, water is present in such large excess, that its concentration stays essentially constant.
 - Rearranging the above expression, we get:

$$K_c \cdot [\text{H}_2\text{O}] = \frac{[\text{OH}^-][\text{BH}^+]}{[\text{B}]} = \text{another constant} = K_b$$

$$\text{Base dissociation constant, } K_b = \frac{[\text{OH}^-(\text{aq})][\text{BH}^+(\text{aq})]}{[\text{B(aq)}]}$$

- K_b is called the **base dissociation constant**.
 - It is a measure of the **STRENGTH** of the weak base B.
 - It has units of mol dm^{-3} .
 - Its value is constant at a constant temperature and changes only with temperature.
- Just as K_a and $\text{p}K_a$ values of different acids can be used to compare the strength of the weak acids, we can also use K_b and $\text{p}K_b$ values of different bases to compare the strength of weak bases.

$$\text{p}K_b = -\lg K_b$$

- The K_b and $\text{p}K_b$ of some bases (at 298 K) are shown below.

Base	$K_b / \text{mol dm}^{-3}$	$\text{p}K_b$	<div style="border: 1px solid black; padding: 10px; text-align: center;"> Base strength decreases </div>
$(\text{CH}_3)_2\text{NH}$	5.9×10^{-4}	3.23	
CH_3NH_2	4.8×10^{-4}	3.32	
$(\text{CH}_3)_3\text{N}$	6.3×10^{-5}	4.20	
NH_3	1.8×10^{-5}	4.74	
N_2H_4	9.8×10^{-7}	6.01	
HONH_2	1.1×10^{-8}	7.96	
$\text{C}_6\text{H}_5\text{NH}_2$	4.2×10^{-10}	9.38	

The stronger the base, the **larger** the K_b value, the **smaller** the $\text{p}K_b$ value.

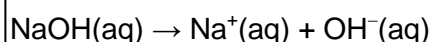
Calculations involving pOH and K_b values

pH of Strong base solutions

- Strong bases ionise completely in water.
- Metal hydroxides such as NaOH, KOH, Ca(OH)_2 and Ba(OH)_2 are examples of strong bases.

$$\text{NaOH(s)} + \text{aq} \rightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$$
- Metal oxides such as Na_2O which react with water to form hydroxides are also considered strong bases. Such oxides include: Na_2O , K_2O and BaO .

Lecture E.g. 6: Calculate the pH of 0.100 mol dm⁻³ sodium hydroxide solution.



$$[\text{OH}^-] = [\text{NaOH}]_{\text{initial}} = 0.100 \text{ mol dm}^{-3}$$

$$\text{pOH} = -\lg(0.100) = 1.00$$

$$\text{At 298K, pH} = 14 - \text{pOH} = \underline{\underline{13.0}}$$

pH of Weak base solutions

- Weak bases ionise only partially in water.
- For a solution containing a weak base, $[\text{OH}^-(\text{aq})] \ll [\text{base}]$.
- In order to simplify the calculation, we make an assumption:
 $[\text{OH}^-] = [\text{B}]_{\text{ionised}} \ll [\text{B}]_{\text{initial}}$, such that $[\text{B}]_{\text{eqm}} \approx [\text{B}]_{\text{initial}}$.

Lecture E.g. 7: Calculate the pH of 0.100 mol dm⁻³ aqueous NH_3 at 298 K. ($K_b = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$)

Let $[\text{OH}^-] = [\text{NH}_4^+] = y \text{ mol dm}^{-3}$ at equilibrium

	$\text{NH}_3(\text{aq})$	$+$	$\text{H}_2\text{O(l)}$	\rightleftharpoons	$\text{NH}_4^+(\text{aq})$	$+$	$\text{OH}^-(\text{aq})$
Initial concentration / mol dm ⁻³	0.100	-			0		0
Concentration at eqm / mol dm ⁻³	$0.100 - y$	-			y		y

$$K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]} = \frac{(y)(y)}{(0.100 - y)}$$

Since ammonia is a weak base, the extent of dissociation is very small. Hence y is negligible compared to $0.100 \text{ mol dm}^{-3}$. Therefore, $(0.100 - y) \approx 0.100$

$$K_b = \frac{(y)(y)}{(0.100)} = 1.8 \times 10^{-5}$$

Solving, $y = 1.34 \times 10^{-3} \text{ mol dm}^{-3} = [\text{OH}^-]$

$$\text{pOH} = -\lg [\text{OH}^-(\text{aq})] = 2.87$$

$$\text{Hence pH} = 14 - \text{pOH} = 11.12 \approx \underline{\underline{11.1}}$$

Compare the above with the previous exercise with $0.100 \text{ mol dm}^{-3}$ sodium hydroxide.

Note: The pH of a weak base is lower than that of a strong base of the same concentration.

5. Strength of Acids and Bases

Degree of dissociation, α

- The degree of dissociation (or degree of ionisation), α , is the fraction of the original undissociated molecules that have dissociated (or ionised) at equilibrium.

$$\alpha = \frac{\text{no. of moles of molecules which are dissociated (or ionised) at equilibrium}}{\text{initial no. of moles of molecules}}$$

- The degree of dissociation may also be expressed in percentage.
- For strong acids/ bases which dissociate completely, $\alpha = 1$ (or 100%).
- For weak acids/ bases which dissociate partially, $0 < \alpha < 1$ (or $< 100\%$).
- Note:** α is temperature and concentration dependent.

Lecture E.g. 8: Calculate the degree of dissociation, α of a $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ benzoic acid solution at 298 K. (K_a of benzoic acid = $6.16 \times 10^{-5} \text{ mol dm}^{-3}$)

At equilibrium, let $[\text{H}_3\text{O}^+(\text{aq})] = [\text{C}_6\text{H}_5\text{COO}^-(\text{aq})] = x$

	$\text{C}_6\text{H}_5\text{COOH}(\text{aq})$	$+$	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{C}_6\text{H}_5\text{COO}^-(\text{aq})$	$+$	$\text{H}_3\text{O}^+(\text{aq})$
Initial concentration / mol dm^{-3}	5.0×10^{-3}		-		0		0
Concentration at eqm / mol dm^{-3}	$5.0 \times 10^{-3} - x$		-		x		x

$$K_a = \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{(x)^2}{(5.0 \times 10^{-3} - x)} = 6.16 \times 10^{-5}$$

Since benzoic acid is a weak acid, the extent of dissociation is very small.

\Rightarrow Hence x is negligible compared to $5.0 \times 10^{-3} \text{ mol dm}^{-3}$.

Therefore, $(5.0 \times 10^{-3} - x) \approx 5.0 \times 10^{-3}$

Solving, $x = 5.55 \times 10^{-4} \text{ mol dm}^{-3} = [\text{H}_3\text{O}^+]$

In 1 dm^3 of solution,

Initial amount of $\text{C}_6\text{H}_5\text{COOH} = 5.0 \times 10^{-3} \text{ mol}$

Amount of $\text{C}_6\text{H}_5\text{COOH}$ dissociated = amount of H_3O^+ formed = $5.55 \times 10^{-4} \text{ mol}$

Hence $\alpha = 5.55 \times 10^{-4} / 5.0 \times 10^{-3} = \mathbf{0.111 \text{ (3sf)}}$

Measure of acid/ base strength

Which is a better indicator of the strength of an acid: pH, α or K_a ? Why?

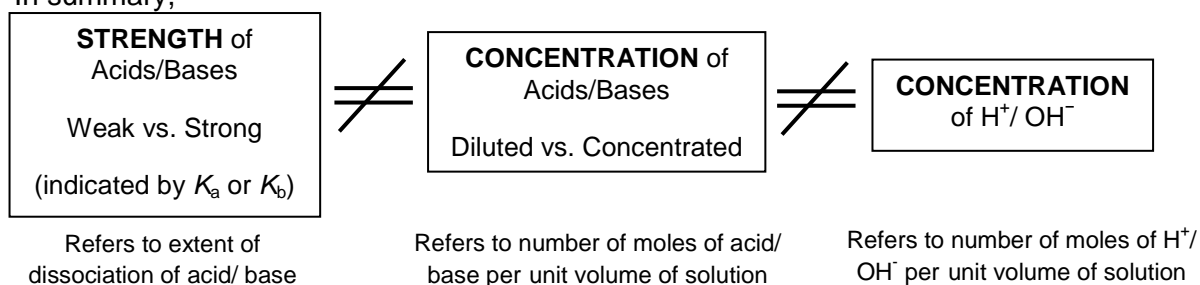
The following table shows how the respective pH and degree of dissociation changes with concentration:

$[\text{CH}_3\text{COOH}] / \text{mol dm}^{-3}$	0.200	0.010	2.0×10^{-4}
pH	2.72	3.39	4.29
Degree of dissociation, α	9.75×10^{-4}	0.041	0.259
$K_a / \text{mol dm}^{-3}$	1.8×10^{-5}	1.8×10^{-5}	1.8×10^{-5}

Conclusion:

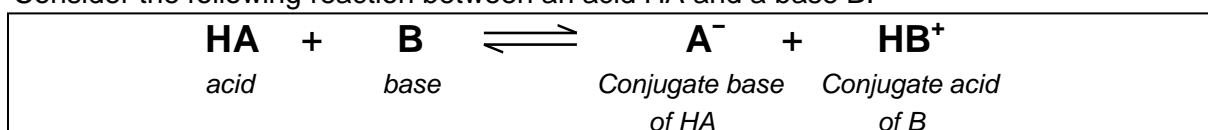
- ① The acid dissociation constant, K_a , is the best indicator of the acid strength as it is a constant at constant temperature, and does NOT vary with concentration.
 \Rightarrow Hence, at the same temperature, K_a of a stronger acid is **HIGHER** than the K_a of a weak acid, regardless of their concentrations.
- ② However, pH of an acid varies with the concentration of the acid.
 i.e. pH of a stronger acid need not be lower than pH of a weaker acid if their concentrations are different.
E.g. pH of $0.200 \text{ mol dm}^{-3} \text{CH}_3\text{COOH}$ ($= 2.72$) $<$ pH of $1.00 \times 10^{-5} \text{ mol dm}^{-3} \text{HCl}$ ($= 5$), even though HCl is the stronger acid.
- ③ For pH to be a good indicator of acid strength between two acids, the two acids to be compared must be of the same concentration, then the pH of the stronger acid is always lower than that of the weaker acid.
- ④ Similarly, the degree of dissociation, α increases with decreasing concentrations of acids.

In summary,



6. Conjugate acid – base pairs

Consider the following reaction between an acid HA and a base B.



Considering the forward reaction,	Considering the backward reaction,
HA donates a proton to B . \Rightarrow HA is an acid. B accepts a proton from HA . \Rightarrow B is a base.	HB⁺ is an acid since it donates a proton to A⁻ . \Rightarrow HB⁺ is the conjugate acid of the base B . A⁻ is a base since it accepts a proton from HB⁺ . \Rightarrow A⁻ is the conjugate base of the acid HA .

- There are two conjugate acid-base pairs in the above reaction:
 - **HA** and **A⁻** constitute a conjugate acid-base pair.
 - **HB⁺** and **B** constitute another conjugate acid-base pair.
- Notice that in each conjugate pair, the acid and base differ from one another by a proton.
 - *Example 1:*

$$\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$

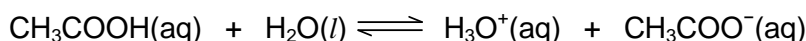
Acid 1
Base 2
Conjugate base 1
Conjugate acid 2

- *Example 2:* $\text{NH}_3(\text{aq}) + \text{HCl}(\text{l}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$

Base 1
Acid 2
Conjugate acid 1
Conjugate base 2
- In general, every acid has a conjugate base and every base has a conjugate acid.
 - A **strong acid** has a **weak conjugate base** (and vice versa).
 - A **strong base** has a **weak conjugate acid** (and vice versa).

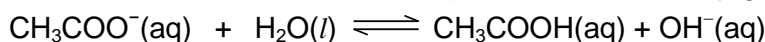
Relationship between K_a , K_b and K_w

- ① In a solution of ethanoic acid:



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} \quad \text{————— ①}$$

- ② In a solution of sodium ethanoate (CH_3COO^- is the conjugate base of ethanoic acid):



$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \quad \text{————— ②}$$

- ③ Multiply ① by ②:

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

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

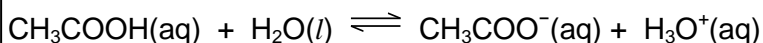
- Hence, the K_b of the conjugate base of an acid (A^-) is related to the K_a of the acid (HA) by the relationship:

$$K_w = K_a (\text{of HA}) \times K_b (\text{of conjugate base } \text{A}^-)$$

A similar relationship exists between a base and its conjugate acid.

$$K_b (\text{of base B}) \times K_a (\text{of conjugate acid of } \text{BH}^+) = K_w$$

Lecture E.g. 9: Calculate $K_b(\text{CH}_3\text{COO}^-)$ at 298 K. ($K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$ at 298 K)



CH_3COO^- is the conjugate base of CH_3COOH

Since $K_w = K_a \times K_b = 1.0 \times 10^{-14}$ (at 298 K)

$$\text{Hence, } K_b(\text{CH}_3\text{COO}^-) = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = \underline{\underline{5.6 \times 10^{-10} \text{ mol dm}^{-3}}}$$

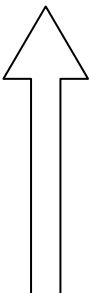
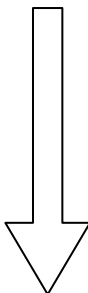
Relative strengths of conjugate acid-base pairs

- At 25 °C, $K_a \times K_b = K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$
 $\text{p}K_a + \text{p}K_b = \text{p}K_w = 14$
 - The larger the K_a of an acid, the smaller is the K_b of its conjugate base.
 \Rightarrow the stronger is the acid, the **weaker** is the conjugate base.
 E.g. HCl is a strong acid. Cl^- is a weak conjugate base.

⇒ the weaker is the acid, the **stronger** is its conjugate base.

E.g. CH_3COOH is a weak acid. CH_3COO^- is a strong conjugate base.

- Conversely, the larger the K_b of a base, the smaller is the K_a of its conjugate acid.

Strength of Acid	Acid	Conjugate Base	Strength of Base
Strong acids 	HClO_4 HCl H_3O^+ H_3PO_4 CH_3COOH H_2CO_3 NH_4^+ HCN HCO_3^- H_2O NH_3	ClO_4^- Cl^- H_2O H_2PO_4^- CH_3COO^- HCO_3^- NH_3 CN^- CO_3^{2-} OH^- NH_2^-	Weak bases 
Weak acids			Strong bases

7. Salt hydrolysis

- Salts are produced when acids react with bases. A salt is made up of a cation (which comes from the base), and an anion (which comes from the acid).
- When salts dissolve to form solutions, the resultant cations/ anions become hydrated (i.e. form ion-dipole interactions with the surrounding water molecules).
- These cations/ anions may react with the water molecules present to form acidic or alkaline solutions.
 - This phenomenon is known as **salt hydrolysis**.
- Whether the salt dissolves to form a neutral, acidic or alkaline solution depends on the acid and the base which react to give the salt.

Nature of Salt	Example	Aqueous solution
① Salt of Strong Acid & Strong Base	Na^+Cl^-	Neutral
② Salt of Strong Acid & Weak Base	NH_4^+Cl^-	Acidic
③ Salt of Weak Acid & Strong Base	$\text{CH}_3\text{COO}^-\text{Na}^+$	Alkaline
④ Salt of Weak Acid & Weak Base	$\text{CH}_3\text{COO}^-\text{NH}_4^+$	** (depends on K_a & K_b) Acidic if K_a (cation) > K_b (anion) Neutral if K_a (cation) = K_b (anion) Alkaline if K_a (cation) < K_b (anion)

** (Use $K_a \times K_b = K_w$ to calculate the acid or base dissociation constant of the conjugate acid or base).

Predicting the nature of aqueous solutions of salts: 4 cases

Case ①: Salt of a strong base and strong acid (e.g. sodium chloride, Na^+Cl^-)

- This type of salt dissolves in water to form a **neutral** solution.
When added to water, the salt, being a strong electrolyte, is fully dissociated.
 $\text{NaCl(s)} + \text{aq} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- Both Na^+ and Cl^- ions get hydrated, but neither undergoes hydrolysis.
 - Na^+ has low charge density (q/r) \Rightarrow does not hydrolyse in water.
 - Cl^- is a weak conjugate base of a strong acid, $\text{HCl} \Rightarrow$ does not hydrolyse in water.
- Hence, resulting salt solution remains neutral.

Case ②: Salt of a strong base and weak acid (e.g. sodium ethanoate, $\text{CH}_3\text{COO}^-\text{Na}^+$)

- This type of salt dissolves in water to form an **alkaline** solution.
When added to water, complete dissociation of $\text{CH}_3\text{COO}^-\text{Na}^+$ occurs:
 $\text{CH}_3\text{COO}^-\text{Na}^+(\text{s}) + \text{aq} \rightarrow \text{Na}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$
- Both Na^+ and CH_3COO^- ions get hydrated.
 - Na^+ has low charge density (q/r) \Rightarrow does not hydrolyse in water.
 - CH_3COO^- is a strong conjugate base of a weak acid, $\text{CH}_3\text{COOH} \Rightarrow$ hydrolyses to give OH^- :
 $\text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{CH}_3\text{COOH(aq)} + \text{OH}^-(\text{aq})$
- Hence, OH^- generated by **anion hydrolysis** causes solution to be alkaline.

Case ③: Salt of a strong acid and weak base (e.g. ammonium chloride, NH_4^+Cl^-)

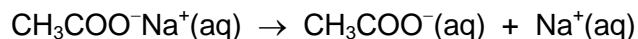
- This type of salt dissolves in water to form an **acidic** solution.
When added to water, complete dissociation of NH_4^+Cl^- occurs:
 $\text{NH}_4\text{Cl(s)} + \text{aq} \rightarrow \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- Both NH_4^+ and Cl^- ions get hydrated.
 - NH_4^+ is a strong conjugate acid of a weak base, $\text{NH}_3 \Rightarrow$ hydrolyses to give H_3O^+ :
 $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
 - Cl^- is a weak conjugate base of a strong acid, $\text{HCl} \Rightarrow$ does not hydrolyse in water.
- Hence, H_3O^+ generated by **cation hydrolysis** causes solution to be acidic.

Case ④: Salt of a weak acid and weak base (e.g. ammonium ethanoate, $\text{CH}_3\text{COO}^-\text{NH}_4^+$)

- This type of salt dissolves in water to form a slightly acidic solution.
When added to water, complete dissociation of $\text{CH}_3\text{COO}^-\text{NH}_4^+$ occurs:
 $\text{CH}_3\text{COONH}_4(\text{s}) + \text{aq} \rightarrow \text{NH}_4^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$
- Both NH_4^+ and CH_3COO^- ions get hydrated, and both undergo cation and anion hydrolysis in water respectively.
 - NH_4^+ is a strong conjugate acid of a weak base, $\text{NH}_3 \Rightarrow$ hydrolyses in water to give H_3O^+ :
 $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
 - CH_3COO^- is a strong conjugate base of a weak acid, $\text{CH}_3\text{COOH} \Rightarrow$ hydrolyses in water to give OH^- :
 $\text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{CH}_3\text{COOH(aq)} + \text{OH}^-(\text{aq})$
- Since $K_a(\text{NH}_4^+) > K_b(\text{CH}_3\text{COO}^-)$, $[\text{H}_3\text{O}^+] > [\text{OH}^-]$, solution is slightly acidic.

Calculating pH of salt solutions

Lecture E.g. 10: Calculate the pH of 0.50 mol dm⁻³ sodium ethanoate solution at 298 K.
(K_a of ethanoic acid = 1.8 x 10⁻⁵ mol dm⁻³ at 298 K)



Let [OH⁻] = x mol dm⁻³ at equilibrium.

	$\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$		
Initial concentration / mol dm ⁻³	0.500	0	0
Concentration at eqm / mol dm ⁻³	0.500 - x	x	x

$$K_b \text{ of } \text{CH}_3\text{COO}^- = \frac{K_w}{K_a(\text{CH}_3\text{COOH})} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} \text{ mol dm}^{-3}$$

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

$$5.56 \times 10^{-10} = \frac{x^2}{0.500 - x}$$

Since ethanoic acid is a weak acid, the extent of dissociation is very small.

⇒ Hence x is negligible compared to 0.500 mol dm⁻³. Therefore, (0.500 - x) ≈ 0.500

Solving, $x = 1.67 \times 10^{-5} \text{ mol dm}^{-3} = [\text{OH}^-]$

$$\text{pOH} = -\lg(1.67 \times 10^{-5}) = 4.78$$

$$\text{pH} = 14 - \text{pOH} = \underline{\underline{9.22}} \text{ (3sf)}$$

8. Buffer Solutions

- A buffer solution is one which is able to **resist** a change in pH (i.e. maintain an almost constant pH) upon the addition of a **small** amount of acid or alkali, or on dilution.
- A buffer solution contains large amounts of both an acidic species and a basic species (in large amounts) to react with any alkali or acid added respectively.
- Two types of buffer solutions exist:
 - Acidic** buffer solution: made up of a weak acid, and the salt of its conjugate base (e.g. CH_3COOH and $\text{CH}_3\text{COO}^-\text{Na}^+$)
 - Alkaline** buffer solution: made up of a weak base, and the salt of its conjugate acid (e.g. NH_3 and NH_4Cl)

Acidic buffer

An acidic buffer solution consists of a mixture of a weak acid, and the salt of its conjugate base.

- Consider a buffer solution made up of a mixture of CH_3COOH and $\text{CH}_3\text{COO}^-\text{Na}^+$.
Ethanoic acid, being a weak acid, is only partially dissociated:
Eqn ①: $\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$
- Sodium ethanoate, being a strong electrolyte, is fully ionised:
Eqn ②: $\text{CH}_3\text{COO}^-\text{Na}^+(\text{aq}) \rightarrow \text{Na}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$
- By Le Chatelier's Principle, the large quantity of the CH_3COO^- (formed from complete ionisation of sodium ethanoate) further suppresses the dissociation of CH_3COOH .
 \Rightarrow Equilibrium position for *Eqn ①* lies very much to the left.
- Hence, the buffer solution contains a large reservoir (high concentration) of the undissociated CH_3COOH molecules (i.e. weak acid) and the dissociated conjugate base, CH_3COO^- (i.e. salt of conjugate base).
- Relatively high concentrations of both the weak acid and the salt of its conjugate base enable the solution to function as a buffer.
- Action of acidic buffer**
 - Addition of acid (i.e. H^+ ions) to solution:
 - When a small amount of H^+ ions is added, neutralisation reaction occurs:
 $\text{CH}_3\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{CH}_3\text{COOH}(\text{aq})$
 - Presence of $\text{CH}_3\text{COO}^-\text{Na}^+$ in solution ensures a large reservoir of CH_3COO^- ions are present to cope with addition of H^+ ions.
 - Nearly all added H^+ ions are removed $\Rightarrow [\text{H}^+]$ does not increase significantly
 \Rightarrow pH is kept approximately constant.
 - Addition of alkali (i.e. OH^- ions) to solution:
 - When a small amount of OH^- ions is added, the following reaction occurs:
 $\text{CH}_3\text{COOH}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 - Presence of CH_3COOH in solution ensures a large reservoir of undissociated CH_3COOH molecules are present to cope with addition of OH^- ions.
 - Nearly all added OH^- ions are removed. $\Rightarrow [\text{OH}^-]$ does not increase significantly
 \Rightarrow pOH (and hence, pH) is kept approximately constant.

Alkaline buffer

An alkaline buffer solution consists of a mixture of a weak base, and the salt of its conjugate acid.

- Consider a buffer solution made up of a mixture of NH_3 and NH_4^+Cl^- .
Aqueous ammonia, being a weak base, undergoes only slight ionisation:
Eqn ①: $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
Ammonium chloride, being a strong electrolyte, is completely ionised:
Eqn ②: $\text{NH}_4^+\text{Cl}^-(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$
 - By Le Chatelier's Principle, the large quantity of the NH_4^+ (formed from complete ionisation of ammonium chloride) further suppresses the ionisation of NH_3 .
 \Rightarrow Equilibrium position for *Eqn ①* lies very much to the left.
 - Hence, the buffer solution contains a large reservoir (high concentration) of the NH_3 molecules (i.e. weak base) and NH_4^+ (i.e. salt of conjugate acid).
 - Relatively high concentrations of both the weak base and the salt of its conjugate acid enable the solution to function as a buffer.
- **Action of alkaline buffer**
 1. Addition of acid (i.e. H^+ ions) to solution:
 - When a small amount of H^+ ions is added, the following reaction occurs:
 $\text{NH}_3(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq})$
 - Presence of NH_3 in solution ensures a large reservoir of NH_3 molecules are present to cope with addition of H^+ ions.
 - Nearly all added H^+ ions are removed $\Rightarrow [\text{H}^+]$ does not increase significantly
 \Rightarrow pH is kept approximately constant.
 2. Addition of alkali (i.e. OH^- ions) to solution:
 - When a small amount of OH^- ions is added, the following reaction occurs:
 $\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 - Presence of NH_4^+ in solution ensures a large reservoir of NH_4^+ ions are present to cope with addition of OH^- ions.
 - Nearly all added OH^- ions are removed. $\Rightarrow [\text{OH}^-]$ does not increase significantly
 \Rightarrow pOH (and hence, pH) is kept approximately constant.

Lecture E.g. 11(a): State what is meant by a *buffer solution*. [J98/II/1, N2002/III/3 or]

A buffer solution is one which is able to **resist** a change in pH (i.e. maintain an almost constant pH) upon the addition of a **small** amount of **acid** or **alkali**, or on **dilution**.

Lecture E.g. 11(b): Explain, using equations, why an aqueous mixture of ethanoic acid (represented by HA) and sodium ethanoate (Na^+A^-) can act as a buffer solution

(i) on the addition of acid,

(ii) on the addition of alkali.

b i) When a small amount of H^+ ions is added: $\text{A}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{HA}(\text{aq})$

- Presence of **Na^+A^-** in solution ensures a large reservoir of **A^-** ions are present to cope with addition of H^+ ions.
- Nearly all added H^+ ions are removed $\Rightarrow [\text{H}^+]$ does not increase significantly
 \Rightarrow pH is kept approximately **constant**.

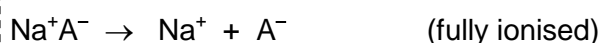
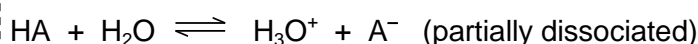
- b ii)** When a small amount of OH^- ions is added: $\text{HA(aq)} + \text{OH}^-(\text{aq}) \rightarrow \text{A}^-(\text{aq}) + \text{H}_2\text{O(l)}$
- Presence of **HA** in solution ensures a large reservoir of undissociated **HA** molecules are present to cope with addition of OH^- ions.
 - Nearly all added OH^- ions are removed. $\Rightarrow [\text{OH}^-]$ does not increase significantly \Rightarrow pOH (and hence, pH) is kept approximately **constant**.

Calculations involving buffer solutions

Relationship between pH, pK_a and composition of an acidic buffer

**Derivation below is not tested in the exams (for self-read).

Consider an acidic buffer solution containing a weak acid, HA, and a salt of the acid, Na^+A^- .



$$\begin{aligned} K_a &= \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \Rightarrow [\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]} \\ &\Rightarrow -\lg[\text{H}_3\text{O}^+] = -\lg K_a + \lg \frac{[\text{A}^-]}{[\text{HA}]} \\ &\Rightarrow \text{pH} = \text{pK}_a + \lg \frac{[\text{A}^-]}{[\text{HA}]} \end{aligned}$$

HA is a weak acid. In the presence of high $[\text{A}^-]$ from Na^+A^- , the dissociation of HA is suppressed (i.e. $[\text{A}^-]_{\text{acid}}$ and $[\text{HA}]_{\text{dissociated}}$ are very low).

Hence, we can assume $[\text{A}^-] \approx [\text{A}^-]_{\text{salt}}$ and $[\text{HA}] \approx [\text{HA}]_{\text{initial}}$

Therefore,
$$\text{pH} = \text{pK}_a + \lg \frac{[\text{salt}]}{[\text{acid}]}$$

- The Henderson – Hasselbach equation for an acidic buffer solution is hence obtained:

$$\text{pH} = \text{pK}_a + \lg \frac{[\text{salt}]}{[\text{acid}]}$$

- It can be used to calculate the following:
 - pH of a buffer solution,
 - how much acid or salt is needed to make a buffer solution of the required pH,
 - the effect on the pH of a buffer solution when a small amount of acid/ base is added.

Note:

- ① For a buffer made up of a weak acid (HA) and its salt (Na^+A^-), $[\text{H}_3\text{O}^+(\text{aq})] \neq [\text{A}^-(\text{aq})]$
Compare with solution of weak acid, where $[\text{H}_3\text{O}^+(\text{aq})] = [\text{A}^-(\text{aq})]$.
- ② When two different solutions containing substances **Y** and **Z** are mixed, their initial concentrations upon mixing would be **different** from their original concentrations of C_Y and C_Z respectively.

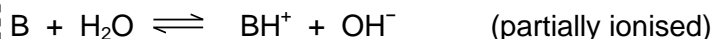
$$\text{The new initial concentration of Y} = \frac{V_Y}{V_Y + V_Z} \times C_Y$$

$$\text{The new initial concentration of Z} = \frac{V_Z}{V_Y + V_Z} \times C_Z$$

where V_Y and V_Z are volumes of **Y** and **Z** respectively.

Relationship between pOH, pK_b and composition of an alkaline buffer

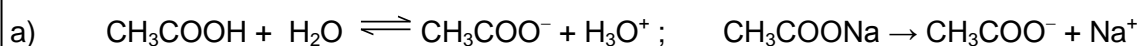
Consider a basic buffer solution containing a weak base, B, and a salt of the acid, BH⁺Cl⁻.



- In a similar manner, the Henderson – Hasselbach equation for alkaline buffer solution can be obtained:

$$pOH = pK_b + \lg \frac{[salt]}{[base]}$$

Lecture E.g. 12(a): Calculate the pH of a buffer solution containing 0.200 mol dm⁻³ CH₃COOH and 0.300 mol dm⁻³ CH₃COO⁻Na⁺ at 25°C. (K_a of ethanoic acid at 25°C = 1.80 × 10⁻⁵ mol dm⁻³)



Assuming negligible dissociation of the acid CH₃COOH, [CH₃COOH] = 0.200 mol dm⁻³

Assuming contribution of CH₃COO⁻ comes solely from CH₃COO⁻Na⁺, [CH₃COO⁻] = 0.300 mol dm⁻³

$$pH = pK_a + \lg \frac{[salt]}{[acid]}$$

$$pH = -\lg(1.80 \times 10^{-5}) + \lg \frac{0.300}{0.200}$$

$$pH = 4.921 \approx \underline{\underline{4.92}} \text{ (3sf)}$$

Lecture E.g. 12(b): Calculate the new pH if 1.00 × 10⁻³ mol of the following is added to 1 dm³ of the solution in the above exercise: (i) H⁺, (ii) OH⁻

b i) When H⁺ is added, CH₃COO⁻ + H⁺ → CH₃COOH

$$\text{new } [CH_3COO^-] = (0.300 - 1.00 \times 10^{-3}) / 1 = 0.299 \text{ mol dm}^{-3}$$

$$\text{new } [CH_3COOH] = (0.200 + 1.00 \times 10^{-3}) / 1 = 0.201 \text{ mol dm}^{-3}$$

$$pH = -\lg(1.80 \times 10^{-5}) + \lg \frac{0.299}{0.201} = 4.917 \approx \underline{\underline{4.92}} \text{ (3sf)}$$

b ii) When OH⁻ is added, CH₃COOH + OH⁻ → CH₃COO⁻ + H₂O

$$\text{new } [CH_3COOH] = (0.200 - 1.00 \times 10^{-3}) / 1 = 0.199 \text{ mol dm}^{-3}$$

$$\text{new } [CH_3COO^-] = (0.300 + 1.00 \times 10^{-3}) / 1 = 0.301 \text{ mol dm}^{-3}$$

$$pH = -\lg(1.80 \times 10^{-5}) + \lg \frac{0.301}{0.199} = 4.924 \approx \underline{\underline{4.92}} \text{ (3sf)}$$

****Note: the change in pH of the buffer solution is resisted.**

Lecture E.g. 13: What mass of sodium ethanoate must be added to 1 dm³ of 1.0 mol dm⁻³ ethanoic acid to produce a buffer of pH 4.5? (pK_a of ethanoic acid = 4.8)

For the required acidic buffer,

$$pH = pK_a + \lg \left(\frac{[CH_3COO^-]}{[CH_3COOH]} \right)$$

$$4.5 = 4.8 + \lg \frac{[CH_3COO^-]}{1.0}$$

$$[CH_3COO^-] = 0.501 \text{ mol dm}^{-3}$$

$$\begin{aligned} \text{Amount of } CH_3COO^-Na^+ \text{ needed} &= \text{amount of } CH_3COO^- \\ &= 1 \text{ dm}^3 \times 0.501 \text{ mol dm}^{-3} = 0.501 \text{ mol} \end{aligned}$$

$$\text{Hence mass of } CH_3COO^-Na^+ = 0.501 \text{ mol} \times 82.0 \text{ g/mol} = \underline{\underline{41.1 \text{ g (3sf)}}}$$

Buffering capacity and effective buffer range

(a) Buffering capacity

- Buffering capacity refers to the amount of acid or alkali that may be added to a buffer solution before its pH changes appreciably. It represents the ability of a buffer to resist changes in pH.
- A buffer solution is equally effective in resisting changes in pH when:
 - ① The number of moles of both the weak acid (or alkali) and its salt are **large**, relative to that of the acid/ alkali to be added to the buffer solution.
 - ② The weak acid (or base) to salt concentration is close to **1:1**.
- Hence, the **maximum buffering capacity** occurs when:

Acidic buffer	Alkaline buffer
$\frac{[A^-]}{[HA]} \approx 1 \quad \text{and} \quad pH = pK_a + \lg \frac{[A^-]}{[HA]} \approx pK_a$	$\frac{[BH^+]}{[B]} \approx 1 \quad \text{and} \quad pOH = pK_b + \lg \frac{[BH^+]}{[B]} \approx pK_b$

(b) Effective buffer range

- For a buffer to be effective, $0.1 \leq \frac{[salt]}{[acid]} \leq 10$

$$\begin{array}{ccc} pK_a + \lg 0.1 & \text{to} & pK_a + \lg 10 \\ \text{i.e.} & & \\ pK_a - 1 & \text{to} & pK_a + 1 \end{array}$$
- Hence, the effective buffer range of an acidic buffer is given by: $pH = pK_a \pm 1$
- Similarly, the effective buffer range of an alkaline buffer is given by: $pOH = pK_b \pm 1$

[RJC Prelim 2008/ P3]

Lecture E.g. 14: An aqueous mixture of sodium hydrogen carbonate and sodium carbonate can act as a buffer solution.

(i) Calculate the pH range in which the buffer is most effective. Take the K_a for HCO₃⁻ to be 5.61 x 10⁻¹¹ moldm⁻³ at 25°C.



For maximum buffering capacity, $\frac{[salt]}{[acid]} \approx 1$

$$pH = pK_a + \lg \frac{[salt]}{[acid]}$$

$$pH = -\lg(5.61 \times 10^{-11}) + 0$$

$$pH = 10.3 \text{ (3sf)}$$

$$pH \text{ range : } \underline{\mathbf{9.3 \text{ to } 11.3}}$$

(ii) Calculate the change in pH of the solution if the ratio of $\frac{[CO_3^{2-}]}{[HCO_3^-]}$ was increased from 0.30 to 0.96.

$$\text{Substitute } \frac{[salt]}{[acid]} = 0.30,$$

$$pH = pK_a + \lg \frac{[salt]}{[acid]}$$

$$pH = -\lg(5.61 \times 10^{-11}) + \lg(0.30)$$

$$pH = 9.73 \text{ (3sf)}$$

$$\text{Substitute } \frac{[salt]}{[acid]} = 0.96,$$

$$pH = pK_a + \lg \frac{[salt]}{[acid]}$$

$$pH = -\lg(5.61 \times 10^{-11}) + \lg(0.96)$$

$$pH = 10.2 \text{ (3sf)}$$

$$\Delta \text{ in pH} = pH_{\text{final}} - pH_{\text{initial}} = 10.2 - 9.73$$

$$\Delta \text{ in pH} = \underline{\mathbf{0.503}} \text{ (3sf)}$$

Uses of buffer solutions

Buffers have widespread applications. Some examples are:

- *Analysis* - Chemists use buffers for example, in the calibration of pH meters
- *Agriculture* – maintaining the pH of the soil for the proper growth of crops/plants.
- *Medicine* – Medication drugs are buffered to ensure their stability; Intravenous injections need to be buffered so as not to change the pH of blood from its normal value of 7.4
- *Food processing* – The pH of some processed food may need to be buffered so that they can be eaten and digested in the body without causing undue changes in pH.
- *Fermentation* – Fermenting organisms are sensitive to pH of the environment. Small changes in pH can kill the organisms and end the fermentation process prematurely, hence the need for buffer solution.

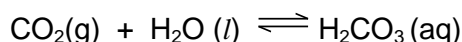
Buffers are also important in living systems:

- The pH of human blood is maintained between 7.35 and 7.45.
- The pH of tears is also maintained at 7.4 by use of buffers consisting of proteins.

Blood as a biological buffer

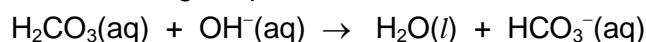
The pH of blood is kept constant at 7.4 so that the enzymes in the blood can function. Enzymes only work over a narrow pH range. This is achieved by a natural buffer system in blood. Death may result if the pH falls below 6.8 or rises above 7.8.

- The most important buffer in blood that regulates blood pH is the $\text{HCO}_3^-/\text{H}_2\text{CO}_3$ buffer system: $\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq})$
- Cell respiration produces CO_2 , which dissolves in water (body fluids) to form carbonic acid H_2CO_3 (a weak acid).



- If $[\text{H}^+]$ ions in the blood increases (e.g. from lactic acid produced from exercise), the HCO_3^- present reacts with the addition H^+ ions and thus resist change in pH:

$$\text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{CO}_3(\text{aq})$$
- If $[\text{OH}^-]$ ions in the blood increases, H_2CO_3 present reacts with the addition OH^- ions and thus resist change in pH:



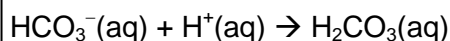
[HCI Prelim 2008/ P2]

Lecture E.g. 15: Many chemical reactions that occur in living systems are extremely sensitive to pH. As a result, the human body maintains a remarkably intricate system of buffers, both within tissue cells, and in the fluids that transport blood cells. Blood is one of the most prominent examples of a buffer in the human body. The major buffer system that is used to control the pH of blood is the carbonic acid – hydrogen carbonate buffer system.

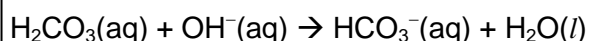


(a) Explain, with the aid of equations, how the buffer system in blood helps to control pH.

If concentration of H^+ ions in the blood increases (e.g. from lactic acid produced due to vigorous exercise), the HCO_3^- ions present react with the additional H^+ ions, and hence the pH remains virtually unchanged.



If concentration of OH^- ions in the blood increases, H_2CO_3 present reacts with the additional OH^- ions (neutralization) and hence, a constant pH is maintained.



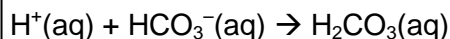
(b) The pH of human plasma is usually maintained at about 7.4. Calculate the ratio of concentrations of hydrogen carbonate ion and carbonic acid in plasma, given the $\text{p}K_a$ of carbonic acid is 6.10.

$$\text{pH} = \text{p}K_a + \lg \frac{[\text{salt}]}{[\text{acid}]}$$

$$7.4 = 6.10 + \lg \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 10^{7.4 - 6.1} = \underline{\underline{20.0}} \text{ (3sf)}$$

(c) Using your answer in (b), calculate the new pH of a 2.0 dm³ of the human plasma, which is 0.05 mol dm⁻³ with respect to carbonic acid, when 0.03 moles of H⁺ is added.



$$n(\text{H}^+) \text{ added} = 0.03 \text{ mol}$$

$$\text{new } n(\text{HCO}_3^-) = [(0.05 \times 20) \times 2] - 0.03 = 1.97 \text{ mol}$$

$$\text{new } [\text{HCO}_3^-] = 1.97 / 2 = 0.985 \text{ mol dm}^{-3}$$

$$\text{new } n(\text{H}_2\text{CO}_3) = (0.05 \times 2) + 0.03 = 0.13 \text{ mol}$$

$$\text{new } [\text{H}_2\text{CO}_3] = 0.13 / 2 = 0.065 \text{ mol dm}^{-3}$$

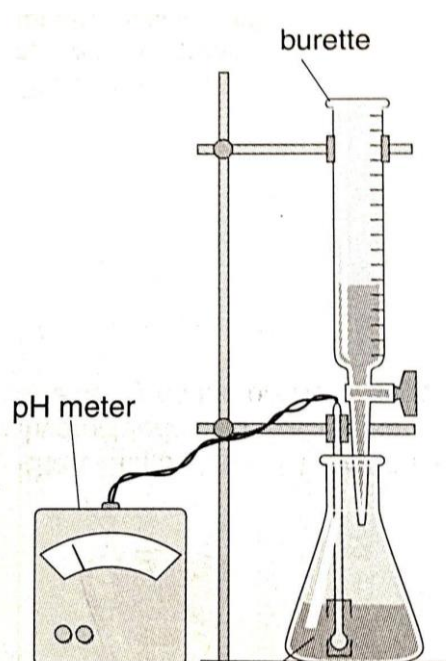
$$\text{pH} = \text{p}K_a + \lg \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{pH} = 6.10 + \lg \frac{0.985}{0.065} = \underline{\underline{7.28}} \text{ (3sf)}$$

9. Acid – Base Titrations

Equivalence point and End-point in a titration

- The aim of a titration is to determine the volumes of two solutions which just react with each other.
 - **Equivalence point** – the exact point during titration when the reaction between acid and base is just complete \Rightarrow can be calculated using stoichiometric ratios.
 - **End-point** – the point during titration when a distinct colour change is observed, brought about by use of a suitable indicator.
 - Use of an appropriate indicator allows end-point to coincide with equivalence point.



Types of Titration Curves

- A titration curve is a graphical plot of pH against volume of acid or base added. It shows how pH changes as the base is added to the acid (or vice versa).
 - Change in pH during the course of titration depends largely on the strength of acid and base used.
 - In summary, four types of titration curves can be obtained:

Types of titrations	Acid	Base	Region of distinct pH change	Suitable indicator
① Strong Acid – Strong Base SA – SB	HCl	NaOH	4.0 – 10.0	phenolphthalein (8.3 – 10.0) methyl orange (3.1 – 4.4) screened methyl orange methyl red
② Weak Base – Strong Acid WB – SA	HCl	NH ₃	3.5 – 6.5	methyl orange (3.1 – 4.4) screened methyl orange methyl red
③ Weak Acid – Strong Base WA – SB	CH ₃ COOH	NaOH	7.5 – 10.5	phenolphthalein (8.3 – 10.0)
④ Weak Base – Weak Acid WB – WA	CH ₃ COOH	NH ₃	no marked change	no suitable indicator

Half – Equivalence point

- A point on the WA–SB titration curve where half of the acid present in the reaction mixture is neutralised. i.e. $[HA]_{\text{reacted}} = \frac{1}{2}[HA]_{\text{initial}}$
- Vol at half-equivalence point = $\frac{1}{2}$ x Vol at equivalence point

- Given $HA(aq) + NaOH(aq) \rightarrow NaA(aq) + H_2O(l)$,

$$[A^-]_{\text{present}} = [HA]_{\text{reacted}} = \frac{1}{2}[HA]_{\text{initial}}$$

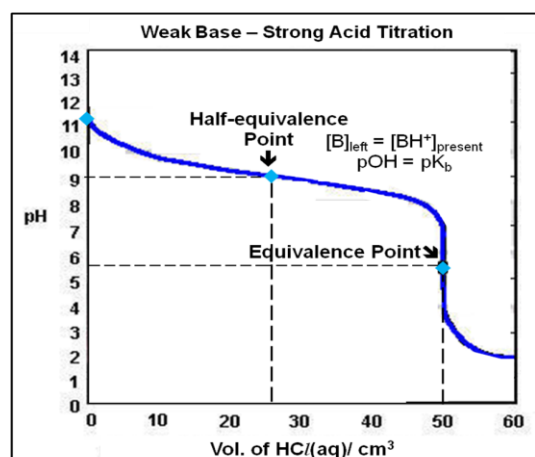
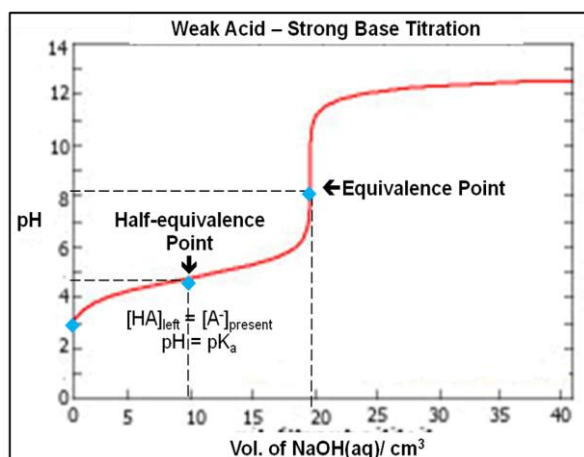
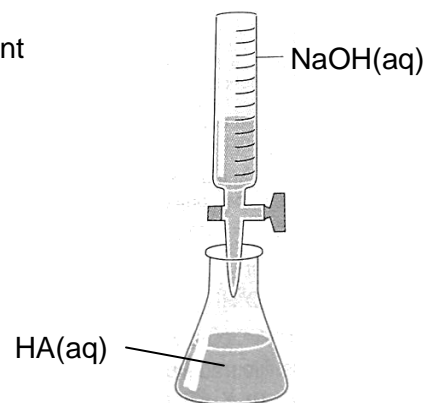
$$\Rightarrow [A^-]_{\text{present}} = [HA]_{\text{left}}$$

- Since $pH = pK_a + \lg \frac{[A^-]}{[HA]}$

At half-equivalence point, substitute $[A^-]/[HA] = 1$,

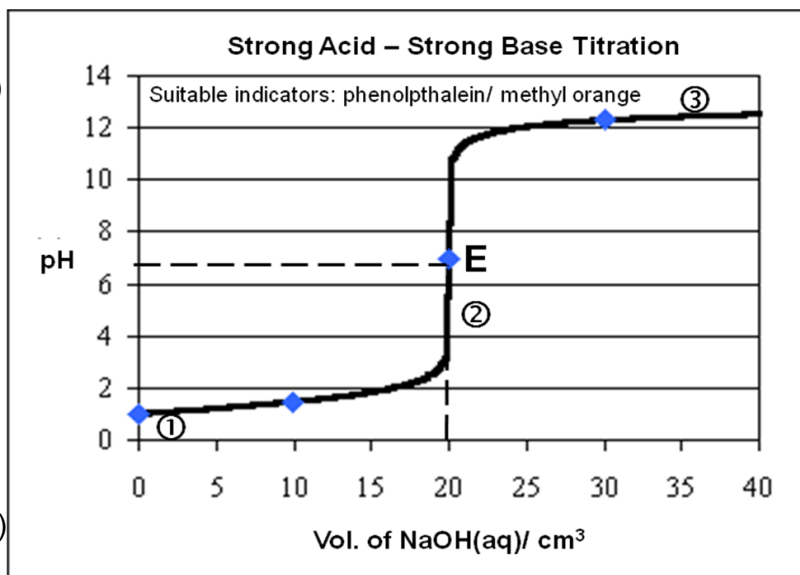
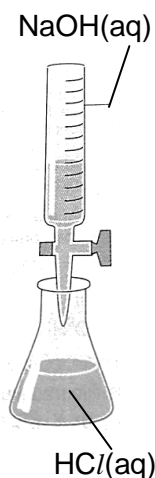
$$pH = pK_a \text{ (for WA–SB titration curve)}$$

- For a weak base–strong acid (WB–SA) titration curve, $pOH = pK_b$.



Type 1: Titration curve of a Strong Acid–Strong Base titration (SA – SB)

- E.g. 20.0 cm^3 of $0.100 \text{ mol dm}^{-3} \text{ HCl(aq)}$ titrated against $0.100 \text{ mol dm}^{-3} \text{ NaOH(aq)}$



③ After **E**, excess NaOH is added.

- The titration curve plateaus off at a high pH \Rightarrow strong base $[\text{NaOH}] = 0.100 \text{ mol dm}^{-3}$.

② This is the region of rapid pH change.

- There is a sudden increase in pH over the equivalence point (pH 4 to 10) when 1 or 2 drops of base are added from burette.
- At the **equivalence point (E)**, the pH of the resultant NaCl solution is 7.

① The **initial** pH is low (pH 1) \Rightarrow strong acid $[\text{HCl}] = 0.100 \text{ mol dm}^{-3}$.

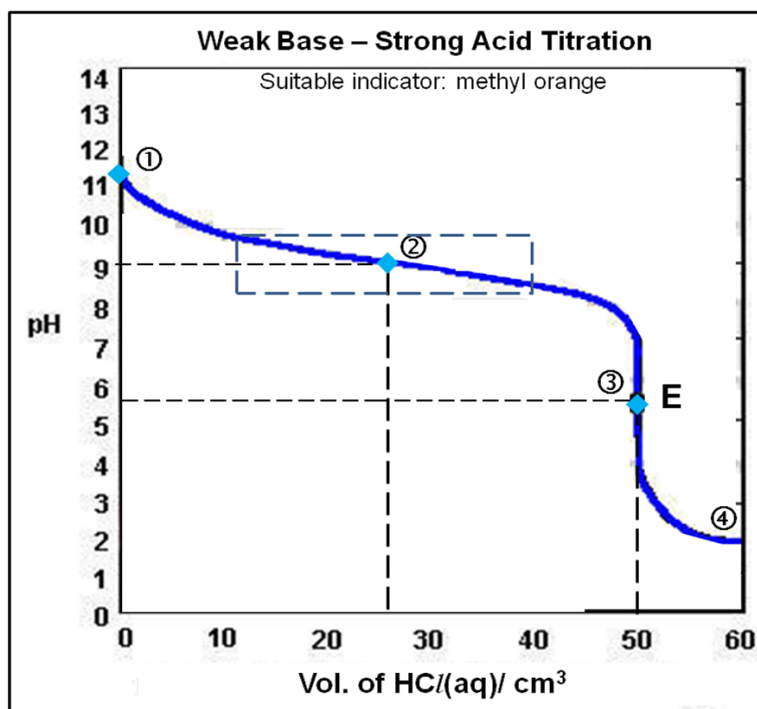
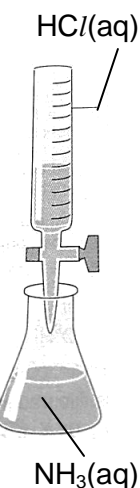
- As NaOH is added, the pH increases as some of the acid is neutralised: $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$
- The remaining acid is diluted by the increased volume of the solution, causing $[\text{H}^+]$ to decrease and pH to increase.

Note:

The equivalence point is found by extrapolating the linear portions of the titration curve (①, ② & ③) and taking the midpoint between the 2 intersections.

Type 2: Titration curve of a Weak Base – Strong Acid titration (WB – SA) Pg 30

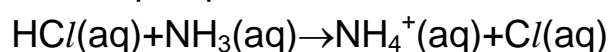
- E.g. 50.0 cm^3 of $0.100 \text{ mol dm}^{-3} \text{ NH}_3(\text{aq})$ titrated against $0.100 \text{ mol dm}^{-3} \text{ HCl}(\text{aq})$



① The **initial pH** is not high (pH 11)
 \Rightarrow weak base is used (compare with pH 13 for $0.1 \text{ mol dm}^{-3} \text{ NaOH}$).

② Alkaline buffer (buffering region)

- As $\text{HCl}(\text{aq})$ is added, some of the base gets neutralised, leading to a drop in pH:



- Change in pH is fairly constant due to the formation of an effective buffer when large amounts of the weak base and its salt are present.

- At **half-equivalence point**,

$$[\text{B}]_{\text{remaining}} = [\text{BH}^+]_{\text{formed}}$$

$\Rightarrow \text{pOH} = \text{pK}_b$ (maximum buffering capacity).

③ The region of rapid pH change

- Is shorter than that of a SA-SB titration.
- Occurs at lower pH range than that of a SA-SB titration.

At the **equivalence point (E)**, the pH of resultant solution is < 7 .

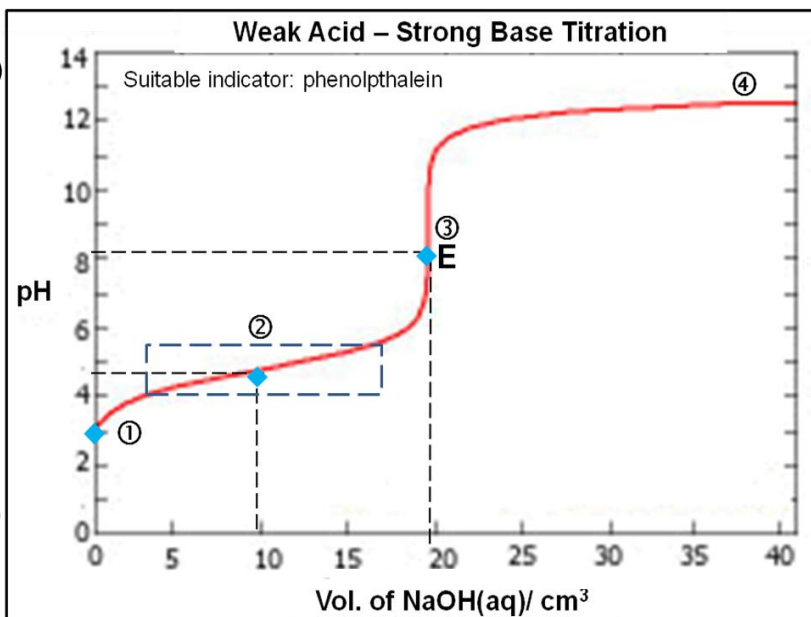
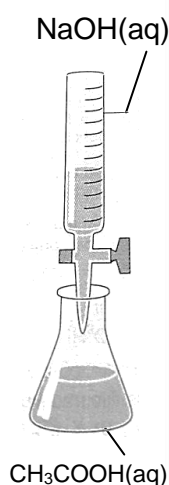
$\Rightarrow \text{NH}_4^+$ undergoes **salt (cation) hydrolysis**:
 $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

④ After E, excess HCl is added.

- The titration curve plateaus off at a low pH (pH 1.5)
 \Rightarrow strong acid of HCl used.

Type 3: Titration curve of a Weak Acid – Strong Base titration (WA – SB)

- E.g. 20.0 cm³ of 0.100 mol dm⁻³ CH₃COOH(aq) titrated against 0.100 mol dm⁻³ NaOH(aq)



④ After **E**, excess NaOH is added.

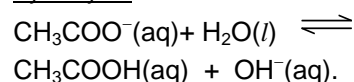
- The titration curve plateaus off at a high pH \Rightarrow strong base [NaOH] = 0.100 mol dm⁻³.

③ The region of rapid pH change

- Is shorter than that of a SA-SB titration.
- Occurs at higher pH range than that of a SA-SB titration.

At the **equivalence point (E)**, the pH of the resultant solution is > 7 .

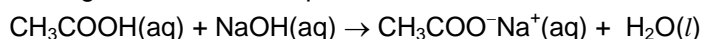
\Rightarrow CH₃COO⁻ undergoes anion hydrolysis:



① The **initial** pH is fairly high (pH 3)
 \Rightarrow weak acid is used.

② Acidic buffer (*buffering region indicated by box*)

- As NaOH (aq) is added, some of the acid gets neutralised, leading to an increase in pH:



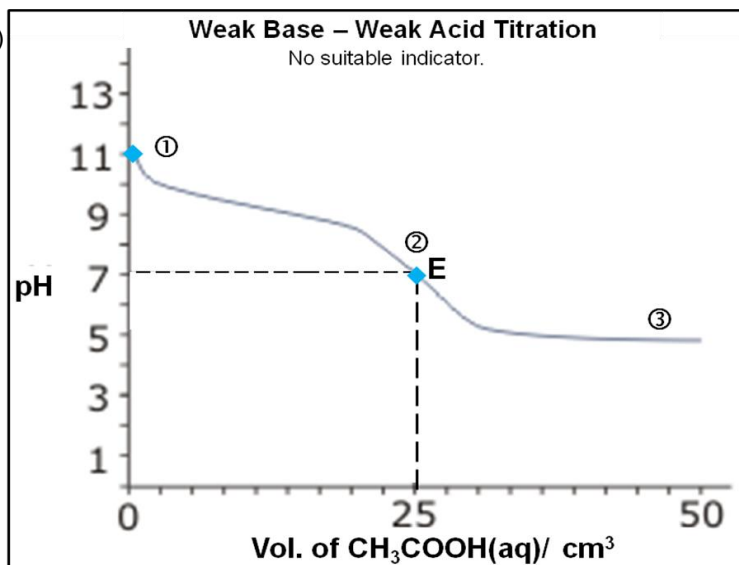
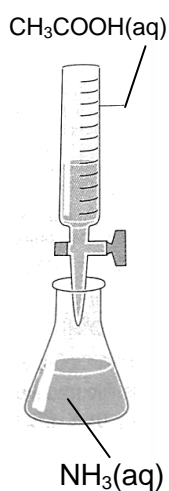
- Change in pH is fairly constant due to the formation of an effective buffer when large amounts of the weak acid and its salt are present.

➤ At **half-equivalence point**, $[\text{HA}]_{\text{remaining}} = [\text{A}^-]_{\text{formed}}$

$\Rightarrow \text{pH} = \text{pK}_a$ (**maximum buffering capacity**).

Type 4: Titration curve of a Weak Base – Weak Acid titration (WB – WA)

- E.g. 25.0 cm^3 of $0.100 \text{ mol dm}^{-3} \text{ NH}_3(\text{aq})$ titrated against $0.100 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH}(\text{aq})$



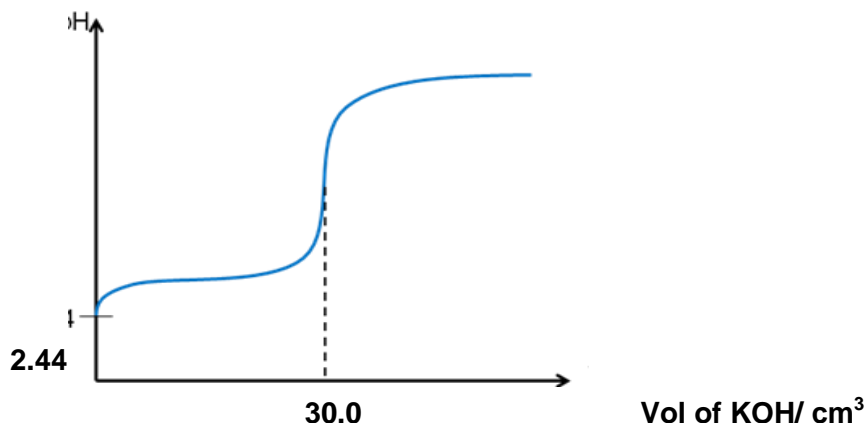
- ① Since base is weak, starting pH is quite low (pH 11).
- ② There is no straight, vertical section on the graph. Change in pH at equivalence point (E) is much less sharp.
 - pH at E < 7, if K_a of WA > K_b of WB
 - pH at E > 7, if K_a of WA < K_b of WB
- ③ Soon after E has passed, titration curve flattens out at a fairly high pH value (e.g. pH 3)

Note: There is no suitable indicator for this titration:

⇒ Region of rapid pH change is absent in the case of a WB–WA titration.

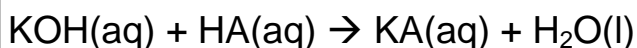
[HCl Prelim 2008/ P3/ Q1(part)]

Lecture E.g. 16: Ethanoic acid is the main component in vinegar. When a 25.0 cm³ sample of vinegar was titrated against 0.6 mol dm⁻³ aqueous potassium hydroxide using a pH meter, the following graph was obtained.



(a) Using the information provided, show by calculations that the acid dissociation constant, K_a , of ethanoic acid has a numerical value of $1.84 \times 10^{-5} \text{ mol dm}^{-3}$.

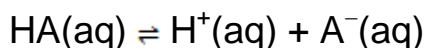
At equivalence point,



$$n(\text{KOH}) = (30.0 / 1000) \times 0.6 = 0.018 \text{ mol}$$

$$n(\text{HA}) \text{ reacted} = 0.018 \text{ mol}$$

$$\text{original } [\text{HA}] = 0.018 / (25/1000) = 0.72 \text{ mol dm}^{-3}$$



Initial []	0.72	-	-
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Change []	- x	+x	+x
------------	-----	----	----

Eqm []	$0.72 - x$	x	x
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$$K_a = \frac{[\text{H}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA(aq)}]} = \frac{x^2}{0.72 - x}$$

Initial pH = 2.44

$-\log [\text{H}^+] = 2.44$, thus $[\text{H}^+] = 10^{-2.44}$

$$K_a = \frac{(10^{-2.44})^2}{0.72 - (10^{-2.44})}$$

$K_a = \underline{1.84 \times 10^{-5} \text{ mol dm}^{-3}}$ (3sf) [shown]

(b) Solution A was prepared by adding 10.0 cm³ of the KOH solution to the 25.0 cm³ vinegar sample. Calculate the pH of Solution A.

Upon addition of KOH to CH₃COOH,

$$n(\text{KOH}) = (10/1000) \times 0.6 = 6 \times 10^{-3} \text{ mol}$$

$$n(\text{acid}) = (25/1000) \times 0.72 = 0.018 \text{ mol}$$

$$n(\text{acid}) \text{ remaining} = 0.018 - (6 \times 10^{-3}) = 0.012 \text{ mol}$$

$$n(\text{salt}) \text{ formed} = 6 \times 10^{-3} \text{ mol}$$

	$\text{CH}_3\text{COOH}(\text{aq})$	$+$	$\text{KOH}(\text{aq})$	\rightarrow	$\text{CH}_3\text{COO}^-\text{K}^+(\text{aq})$	$+$	$\text{H}_2\text{O}(\text{l})$
Initial amount/ mol	0.018		6×10^{-3}		-		-
Change in amount	-6×10^{-3}		-6×10^{-3}		$+6 \times 10^{-3}$		
Final amount	0.012		0		6×10^{-3}		

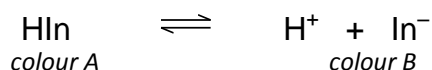
Since for buffer, $pH = pK_a + \lg \frac{[\text{salt}]}{[\text{acid}]}$

$$pH = -\lg(1.84 \times 10^{-5}) + \lg \frac{(\frac{6 \times 10^{-3}}{V})}{(\frac{0.012}{V})}$$

$$pH = \underline{4.43} \text{ (3sf)}$$

Choice of indicators

- **Acid-base indicators** such as phenolphthalein and methyl orange are substances which change colour according to the hydrogen ion concentration of the solution to which they are added.
 \Rightarrow Can be used to **detect the end-point** in acid-base titrations.
- Acid-base indicators are usually **weak acids or weak bases**. When dissolved in water, they dissociate slightly forming ions.
 - Consider an indicator HIn:



$$pH = pK_a + \lg \frac{[\text{In}^-]}{[\text{HIn}]}$$

At low pH, we observe <i>colour A</i> of HIn	At high pH, we observe <i>colour B</i> of In ⁻
<ul style="list-style-type: none"> ○ When acid is added, [H⁺] increases. ○ By Le Chatelier's Principle, the equilibrium position shifts to the left, \Rightarrow Proportion of HIn increases ([HIn] / [In⁻] \geq 10) \Rightarrow Intensity of <i>colour A</i> increases. 	<ul style="list-style-type: none"> ○ When a base is added, [OH⁻] increases. \Rightarrow H⁺ is removed by the OH⁻ added. ○ By Le Chatelier's Principle, the equilibrium position shifts to the right, \Rightarrow Proportion of In⁻ increases ([In⁻] / [HIn] \geq 10) \Rightarrow intensity of <i>colour B</i> increases.

- **Working range of an indicator** (i.e. pH range when colour change is observed) = $pK_{\text{In}} \pm 1$.
- Essential characteristics of a good indicator:
 - ① A suitable indicator is one where its **working range** **coincides** with the region of **rapid pH range** in the titration curve.
 - ② Upon adding one drop of the titrant from the burette, the indicator should give a **sharp** colour change in the titration.
 - It would be useless if the indicator will change colour well before or only after equivalence point \rightarrow titre would not correctly reflect the volume of acid/ base required.
 - ③ Indicator gives a **distinct** colour change.
 - Only 2-3 drops of indicator is required to observe colour change.

Indicator	pK _{Ind}	pH range	Colour change	
			Colour in acid	Colour in alkali
Methyl orange	3.7	3.2 – 4.2	Red	Yellow
Methyl red	5.1	4.2 – 6.3	Red	Yellow
Bromothymol blue	7.0	6.0 – 7.6	Yellow	Blue
Phenol red	7.9	6.8 – 8.4	Yellow	Red
Phenolphthalein	9.3	8.2 – 10.0	Colourless	Red

The rest of the notes will be covered in Term 3 during tutorial.