Anglo-Chinese School (Independent)



Year 6 (2023 ) IBDP HL Chemistry



# **TOPIC 8 ACIDS BASES & SALTS**

# (IBDP syllabus Topic 8)

- 8.1 Theories of acids and bases
  - Essential Idea: Many reactions involve the transfer of a proton from an acid to a base.

# 8.2 Properties of acids and bases

- Essential Idea: The characterisation of an acid depends on empirical evidence such as the production of gases in reactions with metals, the colour changes of indicators or the release of heat in reactions with metal oxides and hydroxides.

# 8.3 The pH scale

- Essential Idea: The pH scale is an artificial scale used to distinguish between acid, neutral and basic/alkaline solutions.

# 8.4 Strong and weak acids and bases

Essential Idea: The pH depends on the concentration of the solution. The strength of acids or bases depends on the extent to which they dissociate in aqueous solution.

# 8.5 Acid deposition

- Essential Idea: Increased industrialisation has led to greater production of nitrogen and sulfur oxides leading to acid rain, which is damaging our environment. These problems can be reduced through collaboration with national and intergovernmental organizations.

# (IBDP syllabus Topic 18)

# 18.1 Lewis acids and bases

- Essential Idea: The acid–base concept can be extended to reactions that do not involve proton transfer.

# 18.2 Calculations involving acids and bases

Essential Idea: The equilibrium law can be applied to acid–base reactions. Numerical problems can be simplified by making assumptions about the relative concentrations of the species involved. The use of logarithms is also significant here.

# 18.3 pH curves

Essential Idea: pH curves can be investigated experimentally but are mathematically determined by the dissociation constants of the acid and base. An indicator with an appropriate end point can be used to determine the equivalence point of the reaction.

## 8.1 Theories of acids and bases

#### ØNature of science:

Falsification of theories—HCN altering the theory that oxygen was the element which gave a compound its acidic properties allowed for other acid–base theories to develop. (2.5)

Theories being superseded—one early theory of acidity derived from the sensation of a sour taste, but this had been proven false. (1.9)

Public understanding of science—outside of the arena of chemistry, decisions are sometimes referred to as "acid test" or "litmus test". (5.5)

#### Understandings:

- A Brønsted–Lowry acid is a proton/H+ donor and a Brønsted–Lowry base is a proton / H<sup>+</sup> acceptor.
- Amphiprotic species can act as both Brønsted–Lowry acids and bases.
- A pair of species differing by a single proton is called a conjugate acid–base pair.

#### Applications and skills:

- Deduction of the Brønsted–Lowry acid and base in a chemical reaction.
- Deduction of the conjugate acid or conjugate base in a chemical reaction.

#### Guidance:

- Lewis theory is not required here.
- The location of the proton transferred should be clearly indicated. For example, CH<sub>3</sub>COOH / CH<sub>3</sub>COO<sup>-</sup> rather than C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> / C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>.
- Students should know the representation of a proton in aqueous solution as both H<sup>+</sup> (aq) and H<sub>3</sub>O<sup>+</sup> (aq).
- The difference between the terms amphoteric and amphiprotic should be covered.

## 8.2 Properties of acids and bases

#### Solution Nature of science:

Obtaining evidence for theories—observable properties of acids and bases have led to the modification of acid–base theories. (1.9)

#### Understandings:

- Most acids have observable characteristic chemical reactions with reactive metals, metal oxides, metal hydroxides, hydrogen carbonates and carbonates.
- Salt and water are produced in exothermic neutralization reactions.

#### Applications and skills:

- Balancing chemical equations for the reaction of acids.
- Identification of the acid and base needed to make different salts.
- Candidates should have experience of acid-base titrations with different indicators.

#### Guidance:

- Bases which are not hydroxides, such as ammonia, soluble carbonates and hydrogen carbonates should be covered.
- The colour changes of different indicators are given in the data booklet in section 22.

## 8.3 The pH scale

#### ØNature of science:

Occam's razor—the pH scale is an attempt to scale the relative acidity over a wide range of H+ concentrations into a very simple number. (2.7)

#### Understandings:

- $pH = -\log[H^+(aq)]$  and  $[H^+] = 10^{-pH}$ .
- A change of one pH unit represents a 10-fold change in the hydrogen ion concentration [H<sup>+</sup>].
- pH values distinguish between acidic, neutral and alkaline solutions.
- The ionic product constant,  $K_w = [H^+] [OH^-] = 10^{-14}$  at 298 K.

#### Applications and skills:

- Solving problems involving pH, [H<sup>+</sup>] and [OH<sup>-</sup>].
- Students should be familiar with the use of a pH meter and universal indicator.

#### Guidance:

- Students will not be assessed on pOH values.
- Students should be concerned only with strong acids and bases in this subtopic.
- Knowing the temperature dependence of K<sub>w</sub> is not required.
- Equations involving H<sub>3</sub>O<sup>+</sup> instead of H<sup>+</sup> may be applied.

#### 8.4 Strong and weak acids and bases

#### ØNature of science:

Improved instrumentation—the use of advanced analytical techniques has allowed the relative strength of different acids and bases to be quantified. (1.8)

Looking for trends and discrepancies—patterns and anomalies in relative strengths of acids and bases can be explained at the molecular level. (3.1)

The outcomes of experiments or models may be used as further evidence for a claim—data for a particular type of reaction supports the idea that weak acids exist in equilibrium. (1.9)

#### Understandings:

- Strong and weak acids and bases differ in the extent of ionization.
- Strong acids and bases of equal concentrations have higher conductivities than weak acids and bases.
- A strong acid is a good proton donor and has a weak conjugate base.
- A strong base is a good proton acceptor and has a weak conjugate acid.

#### Applications and skills:

• Distinction between strong and weak acids and bases in terms of the rates of their reactions with metals, metal oxides, metal hydroxides, metal hydrogen carbonates and metal carbonates and their electrical conductivities for solutions of equal concentrations.

#### Guidance:

- The terms ionization and dissociation can be used interchangeably.
- See section 21 in the data booklet for a list of weak acids and bases.

## 8.5 Acid deposition

#### ØNature of science:

Risks and problems—oxides of metals and non-metals can be characterized by their acid–base properties. Acid deposition is a topic that can be discussed from different perspectives. Chemistry allows us to understand and to reduce the environmental impact of human activities. (4.8)

#### Understandings:

- Rain is naturally acidic because of dissolved CO<sub>2</sub> and has a pH of 5.6. Acid deposition has a pH below 5.6.
- Acid deposition is formed when nitrogen or sulfur oxides dissolve in water to form HNO<sub>3</sub>, HNO<sub>2</sub>,  $H_2SO_4$  and  $H_2SO_3$ .
- Sources of the oxides of sulfur and nitrogen and the effects of acid deposition should be covered.

#### Applications and skills:

- Balancing the equations that describe the combustion of sulfur and nitrogen to their oxides and the subsequent formation of H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>2</sub> and HNO<sub>3</sub>.
- Distinction between the pre-combustion and post-combustion methods of reducing sulfur oxides emissions.
- Deduction of acid deposition equations for acid deposition with reactive metals and carbonates.

## 18.1 Lewis acids and bases

#### Solution Nature of science:

Theories can be supported, falsified or replaced by new theories—acid–base theories can be extended to a wider field of applications by considering lone pairs of electrons. Lewis theory doesn't falsify Brønsted–Lowry but extends it. (2.5)

#### Understandings:

- A Lewis acid is a lone pair acceptor and a Lewis base is a lone pair donor.
- When a Lewis base reacts with a Lewis acid a coordinate bond is formed.
- A nucleophile is a Lewis base and an electrophile is a Lewis acid.

#### Applications and skills:

• Application of Lewis' acid-base theory to inorganic and organic chemistry to identify the role of the reacting species.

#### Guidance:

- Both organic and inorganic examples should be studied.
- Relations between Brønsted–Lowry and Lewis acids and bases should be discussed.

## 18.2 Calculations involving acids and bases

#### ØNature of science:

Obtaining evidence for scientific theories—application of the equilibrium law allows strengths of acids and bases to be determined and related to their molecular structure. (1.9)

#### Understandings:

- The expression for the dissociation constant of a weak acid (Ka) and a weak base (Kb).
- For a conjugate acid base pair,  $K_a \times K_b = K_w$ .
- The relationship between Ka and pKa is (pKa = -log Ka), and between Kb and pKb is  $(pK_b = -log K_b)$ .

#### Applications and skills:

- Solution of problems involving [H<sup>+</sup> (aq)], [OH<sup>-</sup>(aq)], pH, pOH, K<sub>a</sub>, pK<sub>a</sub>, K<sub>b</sub> and pK<sub>b</sub>.
- Discussion of the relative strengths of acids and bases using values of Ka, pKa, Kb and pKb.

## Guidance:

- The value K<sub>w</sub> depends on the temperature.
- The calculation of pH in buffer solutions will only be assessed in options B.7 and D.4.
- Only examples involving the transfer of one proton will be assessed.
- Calculations of pH at temperatures other than 298 K can be assessed.
- Students should state when approximations are used in equilibrium calculations.
- The use of quadratic equations will not be assessed.

#### 18.3 pH curves

#### ØNature of science:

Increased power of instrumentation and advances in available techniques—development in pH meter technology has allowed for more reliable and ready measurement of pH. (3.7)

#### Understandings:

- The characteristics of the pH curves produced by the different combinations of strong and weak acids and bases.
- An acid–base indicator is a weak acid or a weak base where the components of the conjugate acid–base pair have different colours.
- The relationship between the pH range of an acid–base indicator, which is a weak acid, and its  $pK_a$  value.
- The buffer region on the pH curve represents the region where small additions of acid or base result in little or no change in pH.
- The composition and action of a buffer solution.

#### Applications and skills:

- The general shapes of graphs of pH against volume for titrations involving strong and weak acids and bases with an explanation of their important features.
- Selection of an appropriate indicator for a titration, given the equivalence point of the titration and the end point of the indicator.
- While the nature of the acid-base buffer always remains the same, buffer solutions can be prepared by either mixing a weak acid/base with a solution of a salt containing its conjugate, or by partial neutralization of a weak acid/base with a strong acid/base.

• Prediction of the relative pH of aqueous salt solutions formed by the different combinations of strong and weak acid and base.

#### Guidance:

•

- Only examples involving the transfer of one proton will be assessed. Important features are:
   intercept with pH axis
  - equivalence point
  - buffer region
  - points where  $pK_a = pH$  or  $pK_b = pOH$ .
  - For an indicator which is a weak acid:
  - HIn (aq)  $\implies$  H<sup>+</sup> (aq) + In<sup>-</sup> (aq) Colour A Colour B
  - The colour change can be considered to take place over a range of  $pK_a \pm 1$ .
- For an indicator which is a weak base: - BOH (aq)  $\implies$  B<sup>+</sup> (aq) + OH<sup>-</sup> (aq)
  - Colour A Colour B
- Examples of indicators are listed in the data booklet in section 22.
- Salts formed from the four possible combinations of strong and weak acids and bases should be considered. Calculations are not required.
- The acidity of hydrated transition metal ions is covered in topic 13. The treatment of other hydrated metal ions is not required.

## 8.1 Theories of Acids and Bases

## 8.1.1 Arrhenius' theory of acids and bases

- An acid is a substance that has H in its formula and releases H<sup>+</sup> ions when dissolved in water.
- A base is a substance that has OH in its formula and releases OH<sup>-</sup> ions when dissolved in water.
- Examples

 $HNO_3 (aq) \rightarrow H^+ (aq) + NO_3^- (aq)$  acid

NaOH (s)  $\rightarrow$  Na<sup>+</sup> (aq)+ OH<sup>-</sup> (aq) base

- Limitations
  - The definition of Arrhenius acids and bases is confined to those acid–base reactions that occur in aqueous solutions.
  - However there are many reactions which appear to be acid-base reactions that occur in other mediums. For example, the reaction between gaseous hydrogen chloride and ammonia gas can be considered as an acid-base reaction (as it produces a salt).
  - A major shortcoming of the Arrhenius acid–base definition: many substances that releases OH<sup>-</sup> ions when they dissolve in water do not contain OH in their formulas. This theory did not account for the basic properties of ammonia and some organic substances (such as amine) that do not contain the OH group.

Searly theories about acids (Refer to pg 192 of Chemistry Course Companion)

# 8.1.2 Bronsted–Lowry theory of acids and bases

- An acid is a substance that can **donate a proton (H<sup>+</sup>) to another substance**.
- A base is a substance that can accept a proton (H<sup>+</sup>) from another substance.
- A Bronsted–Lowry reaction involves the transfer of a proton from the acid (proton donor) to the base (proton acceptor). An acid and a base always work together in the transfer of a proton. In other words, one species behaves as an acid and the other species behaves as a base simultaneously.

 $\begin{array}{l} HNO_3 \mbox{ (aq) } + \mbox{ } H_2O \mbox{ (l) } \rightarrow \mbox{ } H_3O^+ \mbox{ (aq) } + \mbox{ } NO_3^- \mbox{ (aq) } \\ acid & base \end{array}$ 

Note: Hydronium ions (i.e. H<sub>3</sub>O<sup>+</sup>) are hydrated protons (i.e. H<sup>+</sup>) in solution

- In the above example, HNO<sub>3</sub> (proton donor) is behaving as a Bronsted–Lowry acid while H<sub>2</sub>O (proton acceptor) is behaving as a Bronsted–Lowry base.
- Examples

 $\begin{array}{ll} HNO_3 \mbox{ (aq) + NaOH (aq)} \rightarrow NaNO_3 \mbox{ (aq) + H}_2O \mbox{ (l)} \\ acid & base \end{array}$ 

 $\begin{array}{l} HNO_3 \ (aq) + H_2SO_4 \ (aq) \rightarrow H_2NO_3^+ \ (aq) + HSO_4 \ (aq) \\ base \qquad acid \end{array}$ 

- Using Bronsted–Lowry Theory, nitric acid, HNO<sub>3</sub> can be either Bronsted–Lowry acid or base. It depends on what nitric acid reacts with.
  - If nitric acid reacts with an alkali such as sodium hydroxide, it acts as a Bronsted–Lowry acid.
  - If nitric acid reacts with a stronger acid such as sulfuric acid, it behaves like a Bronsted–Lowry base.
- Using the Bronsted–Lowry Theory, the basic properties of substances that do not contain the OH group in its formula such as NH<sub>3</sub> can be accounted for: NH<sub>3</sub> is a base which accepts a proton from HCl to form NH<sub>4</sub><sup>+</sup> in the acid–base reaction.

NH<sub>3</sub> (aq) + H<sub>2</sub>O (I) → NH<sub>4</sub><sup>+</sup> (aq) + OH<sup>-</sup> (aq) base acid NH<sub>3</sub> (aq) + HCI (aq) → NH<sub>4</sub><sup>+</sup>CI<sup>-</sup> (aq)

base acid

#### 8.1.3 Conjugate acid-base pairs

• Upon losing a proton, an **acid** will become its **conjugate base**:

acid +  $H_2O \implies$  conjugate base +  $H_3O^+$ 

 $\begin{array}{c} & \\ \mathsf{CH}_3\mathsf{COOH}\ (\mathsf{aq}) + \mathsf{H}_2\mathsf{O}\ (\mathsf{I}) \Longrightarrow \mathsf{CH}_3\mathsf{COO^-}\ (\mathsf{aq}) + \mathsf{H}_3\mathsf{O^+}\ (\mathsf{aq}) \\ & \\ \mathsf{acid} & \\ & \\ \mathsf{base} \end{array}$ 

• Upon accepting a proton, a **base** will become its **conjugate acid**:

**base** +  $H_2O \implies$  conjugate acid +  $OH^-$ 

 $VH_{3} (aq) + H_{2}O (I) \implies VH_{4^{+}} (aq) + OH^{-} (aq)$ base conjugate acid

• In other words, the Bronsted–Lowry reaction between an acid and a base is as follows:

Donated a proton to the base acid + base ⇒ conjugate base + conjugate acid Accepted a proton from the acid

 $HCO_3^-(aq) + H_2O(l) \Longrightarrow CO_3^{2-}(aq) + H_3O^+(aq)$ acid base conjugate conjugate base acid

## 8.1.4 Amphiprotic species

- Amphiprotic species are substances that can act both as a Bronsted–Lowry acid and as a Bronsted–Lowry base.
- Example H<sub>2</sub>O
  - Water accepts a proton from ethanoic acid and acts as Bronsted–Lowry base.

$$CH_3COOH (aq) + H_2O (I) \implies CH_3COO^- (aq) + H_3O^+ (aq)$$
  
base

• Water donates a proton to ammonia and acts as Bronsted–Lowry acid.

 $NH_3 (aq) + H_2O (I) \Longrightarrow NH_4^+ (aq) + OH^- (aq)$ acid

- Example H<sub>2</sub>PO<sub>4</sub><sup>-</sup>
  - Polyprotic species like  $H_2PO_4^-$  are frequently involved in reactions in which they behave amphiprotically.

 $H_2PO_4^{-} (aq) + OH^{-} (aq) \Longrightarrow HPO_4^{2-} (aq) + H_2O (I)$ acid  $H_2PO_4^{-} (aq) + H_3O^{+} (aq) \Longrightarrow H_3PO_4 (aq) + H_2O (I)$ 

base

# 8.1.5 Lewis theory of acids and bases

- An acid is a substance that can accept a pair of electrons from a base to form a dative covalent bond i.e. **an acid is an electron–pair acceptor**.
- A base is a substance that can donate a pair of electrons to an acid to form a dative covalent bond i.e. **a base is an electron–pair donor**.
- The product of any Lewis acid–base reaction is called an adduct, a single species that contains a new dative covalent bond.



- In the reaction between BF<sub>3</sub> and NH<sub>3</sub> to form an adduct BF<sub>3</sub>.NH<sub>3</sub>. The reaction occurs because B in BF<sub>3</sub> is electron deficient (Lewis acid) and the nitrogen atom on NH<sub>3</sub> possess a lone pair of electron (Lewis base). In the adduct BF<sub>3</sub>.NH<sub>3</sub>, all the atoms in the molecule possess an octet electron configuration.
- The Lewis definition greatly expands the classes of acids. Many species that do not contain H in their formula (and thus cannot be Bronsted–Lowry acids by donating proton) can function as Lewis acids by accepting an electron pair in their reactions.
- The Lewis definition also includes complex formation such as:

 $[Fe(H_2O)_6]^{3+} (aq) + 6CN^- (aq) \Longrightarrow [Fe(CN)_6]^{3-} (aq) + 6H_2O (I)$ 

- Fe<sup>3+</sup> is behaving as the Lewis acid and the ligand  $CN^-$  as the Lewis base.
- The lone pair on  $CN^{-}$  forms a dative bond with the vacant d orbitals of Fe<sup>3+</sup>.

Sextending our understanding (Refer to pg 396 of Chemistry Course Companion)

# 8.1.6 Comparison of the three theories of acids and bases

## Arrhenius theory of acids and bases

- First attempt at describing acids and bases at the molecular level; most limited and narrowest of the three definitions; applies only to species with an H or an OH group that is released as an ion when the species dissolves in water.
  - An Arrhenius acid is a substance that has H in its formula and releases H<sup>+</sup> ions when dissolved in water.
  - An Arrhenius base is a substance that has OH in its formula and releases OH<sup>-</sup> ions when dissolved in water.
- Relatively few species have these structural prerequisites, Arrhenius acid–base reactions are relatively few in number. All such reactions occur in aqueous medium and hence result in the formation of H<sub>2</sub>O.

## Bronsted–Lowry theory of acids and bases

- Acid–base reactions viewed as proton–transfer process and eliminating the requirement that the reaction must occur in water.
  - A Bronsted–Lowry acid is a proton donor. Like an Arrhenius acid, a Bronsted– Lowry acid still must have a H.
  - A Bronsted–Lowry base is a proton acceptor and can be any species with an electron pair available to accept a proton. This definition includes more species as bases.
- Defines the acid-base reaction in terms of conjugate acid-base pairs, with an acid and a base on both sides of the reaction. The system reaches a state of equilibrium based on the relative strengths of the acid, the base, and their conjugates.

#### Lewis theory of acids and bases

- Widest scope of the three definition
- Acid–base reaction viewed as the donation and acceptance of an electron pair to form a new covalent bond.
  - A Lewis base is an electron pair donor and is similar to a Brønsted–Lowry base in terms of having an electron pair on the donor atom.
  - A Lewis acid is an electron pair acceptor and include many species not encompassed by the former two definitions, including molecules with electron– deficient atoms, metal ions, and the proton itself.

#### Exercise 1

- 1. Which one of the following species can act as both a Bronsted-Lowry acid and base in aqueous solution?
- A. CH<sub>3</sub>COOH
- B. NO<sub>3</sub><sup>-</sup>
- $C. \quad H_2PO_4^-$
- D. OH-
- 2. Which equation represents an acid–base reaction according to the Lewis theory but not the Bronsted–Lowry theory?
- A.  $NH_3 + HCI \Longrightarrow NH_4CI$
- B.  $2H_2O \Longrightarrow H_3O^+ + OH^-$
- C. NaOH + HCl  $\rightarrow$  NaCl + H<sub>2</sub>O
- $\mathsf{D}. \qquad \mathsf{Cr}\mathsf{Cl}_3 + \mathsf{6NH}_3 \Longleftrightarrow [\mathsf{Cr}(\mathsf{NH}_3)_6]^{3+} + \mathsf{3Cl}^-$
- **3.** Outline the Bronsted–Lowry theory of acids and bases.
- 4. The following is a list of compounds that react with or dissolve in water:

sodium chloride, hydrogen chloride, silicon tetrachloride, ammonia, methanol

Water can react as either an acid or base. Choose a compound from the above list with which water acts as

(a) a Bronsted base,

(b) a Bronsted acid.

Construct a balanced equation for each reaction.

- **5.** From the following acid–base reactions, identify which among the reactants is the acid and base according to the Arrhenius theory, Bronsted–Lowry theory and Lewis acid–base theory.
  - (a) NaOH (aq) + HCl (aq)  $\rightarrow$  NaCl (aq) + H<sub>2</sub>O (I)

<u> Acid–Base Pair</u>	<u> Arrhenius Acid /</u>	Bronsted-Lowry	Lewis Acid / Base
	Base	Acid / Base	
HC <i>l</i>			
NaOH			

(b)  $H_2SO_4$  (aq) + 2NH<sub>3</sub> (l)  $\rightarrow$  (NH<sub>4</sub><sup>+</sup>)<sub>2</sub>SO<sub>4</sub><sup>2-</sup> (aq)

Acid–Base Pair	<u>Arrhenius Acid /</u> Base	<u>Bronsted–Lowry</u> Acid / Base	<u>Lewis Acid / Base</u>
$H_2SO_4$		<u></u>	

(c)  $B(OH)_3 (aq) + H_2O (I) \Longrightarrow B(OH)_4^- (aq) + H^+ (aq)$ 

<u>Acid–Base Pair</u>	<u>Arrhenius Acid /</u>	Bronsted–Lowry	<u>Lewis Acid / Base</u>
	Base	Acia / Base	
H₂O			

(d)  $CO_2$  (aq) +  $H_2O$  (l)  $\Longrightarrow$   $H_2CO_3$  (aq)

Acid–Base Pair	<u> Arrhenius Acid /</u>	Bronsted-Lowry	Lewis Acid / Base
	<u>Base</u>	Acid / Base	
CO <sub>2</sub>			
H <sub>2</sub> O			

(e)  $Ag^{+}(aq) + 2NH_{3}(l) \Longrightarrow [Ag(NH_{3})_{2}]^{+}(aq)$ 

<u>Acid–Base Pair</u>	<u>Arrhenius Acid /</u> <u>Base</u>	<u>Bronsted–Lowry</u> <u>Acid / Base</u>	<u>Lewis Acid / Base</u>
Ag⁺ NH₃			

# 8.2 Properties of Acids and Bases

## 8.2.1 Acids

- An acid is defined as a chemical substance with the following properties in aqueous solution:
  - o sour
  - have a pH of 1 to 7 (only at 25 °C)
  - o reacts with bases to form salt and water
  - o reacts with carbonates to form salt, carbon dioxide and water
  - o reacts with metals to form salt and hydrogen
  - releases hydrogen ions (H<sup>+</sup>) when dissolved in water.

## 8.2.2 Chemical reactions of acids

• Acids react with reactive metals e.g. magnesium and iron, to form salts and hydrogen.

Acid + Metal  $\rightarrow$  Salt + Hydrogen gas

 $\begin{array}{l} 2\text{HCl} + \text{Mg} \rightarrow \text{MgCl}_2 + \text{H}_2 \\ \text{CH}_3\text{COOH} + \text{Na} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2 \end{array}$ 

Ionic equation:  $2H^+$  (aq) + Mg (s)  $\rightarrow$  Mg<sup>2+</sup> (aq) + H<sub>2</sub> (g)

• Acids react with carbonates to form salts, water and carbon dioxide.

 $\begin{array}{l} \mbox{Acid} + \mbox{Carbonate} \rightarrow \mbox{Salt} + \mbox{Water} + \mbox{Carbon dioxide} \\ \mbox{2HCl} + \mbox{CaCO}_3 \rightarrow \mbox{CaCl}_2 + \mbox{H}_2 \mbox{O} + \mbox{CO}_2 \end{array}$ 

Ionic equation:  $2H^+$  (aq) +  $CO_3^{2-}$  (aq)  $\rightarrow H_2O$  (I) +  $CO_2$  (g)

• Acids react with bases to form salts and water only. The reaction is called neutralisation.

Acid + Base  $\rightarrow$  Salt + Water HNO<sub>3</sub> + KOH  $\rightarrow$  KNO<sub>3</sub> + H<sub>2</sub>O 2HCl + CaO  $\rightarrow$  CaCl<sub>2</sub> + H<sub>2</sub>O

Ionic equation:  $H^+$  (aq) +  $OH^-$  (aq)  $\rightarrow H_2O$  (I)

## 8.2.3 Bases

- Alkalis (which in effect are bases which are soluble in water) have the following properties in aqueous solution:
  - o bitter
  - have a pH of >7 (only at 25 °C)
  - o reacts with acids to form salt and water
  - releases hydroxide ions (OH<sup>-</sup>) when dissolved in water.



## 8.3 The pH Scale

## 8.3.1 Ionisation and ionic product constant of water, $K_w$

• The electrical conductivity of even the purest form of water never falls to zero. During electrolysis, water is known to dissociate as follows:

$$H_2O(I) \Longrightarrow H^+(aq) + OH^-(aq)$$

• The above representation is again an oversimplification because water molecules dissociate by reacting with one another. This process known as the self-dissociation or auto-ionisation of water can be represented by the following:

 $H_2O(I) + H_2O(I) \Longrightarrow H_3O^+(aq) + OH^-(aq)$ acid base

• In this reaction, one water molecule acts as an acid by donating a proton to the other which acts as a base. Since the above is a reversible reaction, we can write the equilibrium constant as follows:

$$\mathsf{K} = \frac{[\mathsf{H}^+][\mathsf{O}\mathsf{H}^-]}{[\mathsf{H}_2\mathsf{O}]}$$

If the density of water is taken as 1000 kg m<sup>-3</sup> (or 1000 g dm<sup>-3</sup>); and since only a very small quantity of water undergoes dissociation, 1 dm<sup>3</sup> of water will contain 1000 g of H<sub>2</sub>O molecules. The concentration of water [H<sub>2</sub>O (I)] will be (1000/18) mol dm<sup>-3</sup> = 56 mol dm<sup>-3</sup>. Therefore, the concentration of water can be taken as a constant. As such, we can absorb this constant into the equilibrium constant, so that

- The K<sub>w</sub> is known as the **ionic product constant of water**.
- Its units is **mol**<sup>2</sup> dm<sup>-6</sup>
- In pure water, [H<sup>+</sup>] = [OH<sup>-</sup>]
- At the temperature of 25 °C,

$$K_w = [H^+] [OH^-] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

# 8.3.2 Effect of temperature on ionic product constant of water, K<sub>w</sub>

Temperature / °C	K <sub>w</sub> / mol <sup>2</sup> dm <sup>-6</sup>
10.0	0.29 x 10 <sup>-14</sup>
20.0	0.68 x 10 <sup>-14</sup>
25.0	1.00 x 10 <sup>-14</sup>
30.0	1.47 x 10 <sup>-14</sup>
40.0	2.92 x 10 <sup>-14</sup>

• Like all equilibrium constants, the value of K<sub>w</sub> is temperature dependant

- At 25 °C,  $K_w$  value is 1.00 x 10<sup>-14</sup> mol<sup>2</sup> dm<sup>-6</sup>. This value is often assumed in many calculations.
- From the above values, it can be seen that K<sub>w</sub> increases as temperature rises. By applying Le Chatelier's Principle, the self–ionisation of water must be an endothermic process. This is because as the temperature rises, more water molecules will dissociate so as to take in the excess heat supplied.
- It is important to recognise the meaning of K<sub>w</sub>. In aqueous solution at 25 °C, no matter what it contains, the product of [H<sup>+</sup>] and [OH<sup>-</sup>] must always be equal to 1.00 x 10<sup>-14</sup> mol<sup>2</sup> dm<sup>-6</sup>. There are three possible situations:

0	Neutral solution:	[H⁺] = [OH⁻]	; pH = 7
0	Acidic solution:	[H⁺] > [OH⁻]	; pH < 7
0	Alkaline solution:	[H⁺] < [OH⁻]	; pH > 7

• Assuming a temperature of 40.0 °C, where  $K_w$  of water = 2.92 x 10<sup>-14</sup> mol<sup>2</sup> dm<sup>-6</sup>

$$H_2O(I) \Longrightarrow H^+(aq) + OH^-(aq)$$

• Let the concentration of H<sup>+</sup> at equilibrium be x mol<sup>2</sup> dm<sup>-3</sup>

 $[H^+] [OH^-] = 2.92 \text{ x } 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ 

 $x^2$  = 2.92 x 10<sup>-14</sup> x = 1.71 x 10<sup>-7</sup> mol dm<sup>-3</sup>

pH = 6.76

- **pH of pure water at 40.0** °C is obviously not 7. Students should not confuse neutrality and pH = 7.
- A neutral solution is a solution where [H<sup>+</sup>] = [OH<sup>-</sup>]
- A neutral solution only has a pH of 7 at 25 °C. At a higher temperature, a neutral solution may have pH of lower than 7. It is therefore important to quote temperatures in answers.

#### 8.3.3 pH measurement

- The acidity of a substance can be expressed in terms of its H<sup>+</sup> (aq) concentration. However, the H<sup>+</sup> (aq) concentration of solutions commonly dealt with lies in the range of 10<sup>-14</sup> mol dm<sup>-3</sup> to 10<sup>-1</sup> mol dm<sup>-3</sup>. In order to avoid the inconvenience of negative indices, a pH scale is devised.
- The pH of a solution is defined as the negative logarithm to the base 10 of the concentration of hydrogen ions in solution in mol dm<sup>-3</sup>.

$$pH = -log_{10} [H^+]$$

Hence,

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

- The larger the pH value, the smaller the [H<sup>+</sup>].
- Likewise, we can define pOH to be

$$pOH = -log_{10} [OH^-]$$

Hence,

- The larger the pOH value, the smaller the [OH<sup>-</sup>].
- Relationship between pH and pOH in aqueous solutions:



Hence at all temperatures,

$$pK_w = pH + pOH$$

And at 25 °C,

• At the temperature of 25 °C,

0	Neutral solution:	[H⁺] = [OH⁻]	; pH = 7
0	Acidic solution:	[H⁺] > [OH⁻]	; pH < 7
0	Alkaline solution:	[H⁺] < [OH⁻]	; pH > 7

# Method for solving pH / pOH problems involving strong acids / bases:

Step 1:	Identify type of solution
Step 2:	Write down full dissociation equation
Step 3:	Consider water dissociation equilibrium for very dilute solution (when concentration of strong acid / base < $1 \times 10^{-7}$ mol dm <sup>-3</sup> )
Step 4:	Determine [H+] / [OH-] concentration using mole ratio
Step 5:	Determine pH / pOH using formula

## Exercise 2

- 1. Calculate the pH of the following aqueous solutions at 298 K,
  - (a) 0.1 mol dm<sup>-3</sup> HCl

(b) 0.1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>

<sup>(</sup>c) 1.0 x 10<sup>-8</sup> mol dm<sup>-3</sup> HCl

(d) 0.01 mol dm<sup>-3</sup> NaOH

# 8.4 Strong and Weak Acids and Bases

# 8.4.1 Strong acids and strong bases

- Strong acids and strong bases undergo complete dissociation in water and thus have a high concentration of H<sub>3</sub>O<sup>+</sup> ions or OH<sup>-</sup> ions, respectively. To show complete dissociation, the symbol "→" must be used.
- Examples of strong acids are HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl, HBr, HI, HClO<sub>4</sub>.
- Examples of strong bases are
  - Alkali metal hydroxides, e.g. NaOH (caustic soda), KOH (caustic potash), RbOH and CsOH.
  - Alkaline earth metal hydroxides, e.g. Mg(OH)<sub>2</sub>, Ca(OH)<sub>2</sub>, Sr(OH)<sub>2</sub>, and Ba(OH)<sub>2</sub>.

## 8.4.2 Weak acids and weak bases

- Weak acids and bases have very low degree of dissociation. For example, at 25 °C, only about 0.4% of 1.0 mol dm<sup>-3</sup> ethanoic acid, CH<sub>3</sub>COOH dissociates.

$$CH_{3}COOH (aq) + H_{2}O (I) \iff CH_{3}COO^{-} (aq) + H_{3}O^{+} (aq)$$
  
stronger conjugate  
base

- Since the equilibrium lies very much to the left, the CH<sub>3</sub>COO<sup>-</sup> is sometimes referred to as a strong conjugate base i.e. the CH<sub>3</sub>COO<sup>-</sup> (aq) have a high tendency to accept a proton to form the undissociated CH<sub>3</sub>COOH.
- Likewise, weak bases like ammonia have very low degree of dissociation.

 Since the equilibrium lies very much to the left, the NH<sub>4</sub><sup>+</sup> is sometimes referred to as a strong conjugate acid i.e. the NH<sub>4</sub><sup>+</sup> (aq) have a high tendency to donate a proton to form the undissociated NH<sub>3</sub>.

Therefore, the weaker the acid, the stronger is its conjugate base and the weaker the base, the stronger is its conjugate acid.

• The definition of strong and weak acid is independent of concentration.

Will a beaker of 10 mol dm<sup>-3</sup> ethanoic acid (CH<sub>3</sub>COOH) be stronger or weaker than a beaker of 0.5 mol dm<sup>-3</sup> hydrochloric acid (HCl)? The terms "strong" and "weak" when applied to acids and bases are quite distinct from "concentrated" and "dilute", as illustrated in the table below:

	Concentrated	Dilute
Strong	6 mol dm⁻³ HCl	0.5 mol dm <sup>-3</sup> H <sub>2</sub> SO <sub>4</sub>
Weak	10 mol dm⁻³ CH₃COOH	0.1 mol dm <sup>-3</sup> H <sub>2</sub> CO <sub>3</sub>

## 8.4.3 Experimental determination of acid and base strengths

- As weak acids and weak bases are only partially dissociated in aqueous solution, thus the enthalpy change of neutralisation for strong acid–weak base and weak acid–strong base will be less exothermic than the strong acid–strong base reaction. (Recall Topic 5 Energetics)
- Examples of enthalpy changes of neutralisation

	Equation	ΔH <sup>θ</sup> <sub>neu</sub> / kJ mol <sup>−1</sup>
Strong acid– strong base	HCl (aq) + NaOH (aq) $\rightarrow$ NaCl (aq) + H <sub>2</sub> O (I)	-57.3
Strong acid– weak base	HCl (aq) + NH <sub>3</sub> (aq) $\rightarrow$ NH <sub>4</sub> Cl (aq)	-56.1
Weak acid– strong base	CH <sub>3</sub> COOH (aq) + NaOH (aq) $\rightarrow$ CH <sub>3</sub> COONa (aq) + H <sub>2</sub> O (I)	-53.4

# 8.5 Acid Deposition

- Acid deposition is the process by which acid–forming pollutants are deposited on the earth's surface. These acid–forming pollutants come from emissions of the sulfur dioxide and nitrogen oxides, NO and NO<sub>2</sub> that cause acid rain.
- Acid deposition causes deforestation, leaching of minerals from soils leading to elevated acid levels in lakes and rivers, the uptake of toxic materials from soil by plants, reduction in the pH of lake and river systems, increased uptake of toxic metals by shellfish and other marine life, corrosion of limestone buildings.
- Rainwater is naturally acidic (pH  $\approx$  5.6) due to the presence of dissolved carbon dioxide which forms weak carbonic acid, H<sub>2</sub>CO<sub>3</sub>.

 $\circ \qquad \mathsf{CO}_2 \ (\mathsf{g}) + \mathsf{H}_2\mathsf{O} \ (\mathsf{I}) \Longrightarrow \mathsf{H}_2\mathsf{CO}_3 \ (\mathsf{aq})$ 

 $\circ \qquad \mathsf{H}_2\mathsf{CO}_3 \,(\mathsf{aq}) \Longrightarrow \mathsf{H}^+ \,(\mathsf{aq}) + \mathsf{HCO}_3^- \,(\mathsf{aq})$ 

$$\circ \qquad \mathsf{HCO}_{3^{-}}(\mathsf{aq}) \Longrightarrow \mathsf{H}^{+}(\mathsf{aq}) + \mathsf{CO}_{3^{2^{-}}}(\mathsf{aq})$$

# 8.5.1 Oxides of nitrogen (NO<sub>x</sub>)

• At high temperatures of internal combustion engine of a car or a jet engine, nitrogen and oxygen from air react to form nitrogen(II) oxide (nitrogen monoxide) which further reacts with atmospheric oxygen to form nitrogen(IV) oxide (nitrogen dioxide):

 $\circ \qquad \mathsf{N}_2 \ (\mathsf{g}) + \mathsf{O}_2 \ (\mathsf{g}) \to \mathsf{2NO} \ (\mathsf{g})$ 

- $\circ \qquad 2NO\left(g\right)+O_{2}\left(g\right)\rightarrow 2NO_{2}\left(g\right)$
- Nitrogen(IV) oxide causes the brown colour of the smog often observed in cities. The reaction between water and nitrogen(IV) oxide produces nitric acid (HNO<sub>3</sub>) and nitrous acid (HNO<sub>2</sub>):

 $\circ$  2NO<sub>2</sub> (g) + H<sub>2</sub>O (l)  $\rightarrow$  HNO<sub>3</sub> (aq) + HNO<sub>2</sub> (aq)

• Nitrous acid can be oxidised by atmospheric oxygen to nitric acid:

 $\circ$  2HNO<sub>2</sub> (aq) + O<sub>2</sub> (g)  $\rightarrow$  2HNO<sub>3</sub> (aq)

## 8.5.2 Sulfur dioxide (SO<sub>2</sub>)

 Sulfur dioxide is produced from volcanic eruptions and combustion of fossil fuels containing high level of sulfur impurities e.g. coal. Sulfur dioxide reacts with water to form sulfurous acid (H<sub>2</sub>SO<sub>3</sub>):

$$\circ \qquad \mathsf{S}(\mathsf{s}) + \mathsf{O}_2(\mathsf{g}) \to \mathsf{2}\mathsf{S}\mathsf{O}_2(\mathsf{g})$$

- $\circ \qquad \mathsf{SO}_2(\mathsf{g}) + \mathsf{H}_2\mathsf{O}(\mathsf{I}) \Longrightarrow \mathsf{H}_2\mathsf{SO}_3(\mathsf{aq})$
- Sulfur dioxide further reacts with atmospheric oxygen to form sulfur trioxide which then reacts with rainwater to form sulfuric acid:
  - $\circ \qquad \mathsf{SO}_2(\mathsf{g}) + \mathsf{O}_2(\mathsf{g}) \Longrightarrow \mathsf{2SO}_3(\mathsf{g})$
  - $\circ \qquad SO_3 (g) + H_2O (I) \rightarrow H_2SO_4 (aq)$

**G** The role of chemists in studying acid deposition (Refer to pg 206 of Chemistry Course Companion)

## 8.5.3 Methods of dealing with acid deposition

• Pre-combustion method of reducing sulfur dioxide emission

To produce a more environmentally friendly fuel, sulfur can be removed before the fuel is burned. This involves heating crude oil fractions with hydrogen in the presence of a catalyst to convert the sulfur to hydrogen sulfide ( $H_2S$ ), a process known as hydrodesulfurisation. Hydrogen sulfide can be removed from the reaction mixture by bubbling it through an alkaline solution.

• Post–combustion method of reducing sulfur dioxide emission

In coal-fired power stations, the exhaust gases from the furnace can be passed through a vessel to allow sulfur dioxide to react with bases such as calcium oxide, calcium carbonate or calcium hydroxide.

 $\begin{array}{c} \text{CaCO}_3\left(s\right) + \text{SO}_2\left(g\right) \rightarrow \text{CaSO}_3\left(s\right) + \text{CO}_2\left(g\right) \\ \text{calcium sulfite} \end{array}$ 

# 18.2 Calculations Involving Acids and Bases

# 18.2.1 Weak acid and acid dissociation constant (K<sub>a</sub>)

• Weak acid (HA) dissociates partially in solution to give protons (H<sup>+</sup>).

```
HA (aq) + H<sub>2</sub>O (I) \implies A<sup>-</sup> (aq) + H<sub>3</sub>O<sup>+</sup> (aq)
acid conjugate
base
```

Definition of acid dissociation constant, Ka:

- It is a measure of the strength of a weak acid.
- The larger the K<sub>a</sub> value, the stronger the weak acid.
- K<sub>a</sub> is an equilibrium constant so it is **constant at constant temperature**
- Derivation of acid dissociation constant (K<sub>a</sub>)

HA (aq) + H<sub>2</sub>O (I)  $\implies$  A<sup>-</sup> (aq) + H<sub>3</sub>O<sup>+</sup> (aq)

$$K_{c} = \frac{[H_{3}O^{+}][A^{-}]}{[HA][H_{2}O]}$$

For weak acid, the degree of dissociation of water is extremely small, hence  $[H_2O]$  is constant.

$$K_{c}[H_{2}O] = \frac{[H_{3}O^{+}][A^{-}]}{[HA]}$$

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

## K<sub>a</sub> is known as the acid dissociation constant.

Units: mol dm-3

• The pK<sub>a</sub> of a weak acid is defined as

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

Hence,

- The larger the pK<sub>a</sub> value, the weaker the acid.
- Values of K<sub>a</sub> for some common monobasic weak acids:

Weak Acid	Chemical Name	K <sub>a</sub> value / mol dm⁻³	pKa
HCIO <sub>2</sub>	Chlorous acid	1 × 10 <sup>-2</sup>	2.00
HF	Hydrofluoric acid	$7  imes 10^{-4}$	3.15
HNO <sub>2</sub>	Nitrous acid	$4 \times 10^{-4}$	3.39
CH₃COOH	Acetic acid	$2 \times 10^{-5}$	4.70
HOCI	Hypochlorous acid	4 × 10 <sup>-8</sup>	7.40
HCN	Hydrocyanic acid	$7 \times 10^{-10}$	9.15
NH <sub>4</sub> +	Ammonium ion	6 × 10 <sup>-10</sup>	9.22
C <sub>6</sub> H₅OH	Phenol	$2 \times 10^{-10}$	9.70

## 18.2.2 Calculations involving pH of weak acids

- In general, for a monobasic weak acid, of a concentration **C** mol dm<sup>-3</sup>, it will dissociate partially in solution as shown in the table below.
- Let the equilibrium concentration of H<sup>+</sup> be **x** mol dm<sup>-3</sup>.

	HA (aq)	H <sub>2</sub> O (I)	A⁻ (aq)	H <sub>3</sub> O <sup>+</sup> (aq)
Initial / mol dm <sup>-3</sup>	С	—	0	0
Change / mol dm-3	- <b>x</b>	—	+ <b>X</b>	+ <b>X</b>
Equilibrium / mol dm <sup>-3</sup>	<b>C</b> – <b>x</b>	_	x	x

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

$$K_{a} = \frac{\mathbf{x}^{2}}{\mathbf{C} - \mathbf{x}}$$

Using the approximation method If HA is a very weak acid, the [H<sup>+</sup>] at equilibrium or **x** is very small. i.e. Assume **x** is so small that: [HA] at equilibrium  $\approx$  initial [HA]  $\Rightarrow$  **C** – **x**  $\approx$  **C** 

$$K_a = \frac{\mathbf{x}^2}{\mathbf{C}}$$

 $\mathbf{x} = \sqrt{\mathbf{C} \times \mathbf{K}_{\mathbf{a}}}$ 

Since  $\mathbf{x} = [H^+]$ ,

$$[\mathsf{H}^+] = \sqrt{\mathbf{C} \times \mathbf{K}_{\mathbf{a}}}$$

18.2.3 Weak base and base dissociation constant (K<sub>b</sub>)

• Weak base (B) dissociates partially in solution to give hydroxide ions (H<sup>+</sup>).

B (aq) + H<sub>2</sub>O (I)  $\implies$  HB<sup>+</sup> (aq) + OH<sup>-</sup> (aq) base conjugate acid

Definition of acid dissociation constant, K<sub>b</sub>:

- It is a measure of the strength of a weak base.
- The larger the K<sub>b</sub> value, the stronger the weak base.
- K<sub>b</sub> is an equilibrium constant so it is **constant at constant temperature**
- Derivation of base dissociation constant (K<sub>b</sub>)

 $B(aq) + H_2O(I) \implies HB^+(aq) + OH^-(aq)$ 

$$K_{c} = \frac{[HB^{+}][OH^{-}]}{[B][H_{2}O]}$$

For weak base, the degree of dissociation of water is extremely small, hence  $[H_2O]$  is constant.

$$K_{c}[H_{2}O] = \frac{[HB^{+}][OH^{-}]}{[B]}$$

$$K_{b} = \frac{[HB^{+}][OH^{-}]}{[B]}$$

K<sub>b</sub> is known as the base dissociation constant.

Units: mol dm<sup>-3</sup>

• The pK<sub>b</sub> of a weak base is defined as

$$pK_b = -log_{10} K_b$$

Hence,

$$K_b = 10^{-pKb}$$

• The larger the pK<sub>b</sub> value, the weaker the base.

18.2.4 Calculations involving pH of weak bases

- In general, for a monoacidic weak base, of a concentration **C** mol dm<sup>-3</sup>, it will dissociate partially in solution as shown in the table below.
- Let the equilibrium concentration of OH<sup>-</sup> be **x** mol dm<sup>-3</sup>.

	B (aq)	H <sub>2</sub> O (I)	HB⁺ (aq)	OH⁻ (aq)
Initial / mol dm <sup>-3</sup>	С	—	0	0
Change / mol dm-3	- <b>x</b>	—	+ <b>X</b>	+ <b>x</b>
Equilibrium / mol dm <sup>-3</sup>	<b>C</b> – <b>x</b>	_	x	x

$$K_{b} = \frac{[HB^{+}][OH^{-}]}{[B]}$$

$$K_{b} = \frac{\mathbf{x}^{2}}{\mathbf{C} - \mathbf{x}}$$

Using the approximation method If B is a very weak base, the [OH<sup>-</sup>] at equilibrium or **x** is very small. i.e. Assume **x** is so small that: [B] at equilibrium  $\approx$  initial [B]  $\Rightarrow$  **C** – **x**  $\approx$  **C** 

$$K_b = \frac{\mathbf{x}^2}{\mathbf{C}}$$

$$\mathbf{x} = \sqrt{\mathbf{C} \times \mathbf{K}_{\mathbf{b}}}$$

Since  $\mathbf{x} = [OH^{-}]$ ,

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

# Method for solving pH / pOH problems involving weak acids / bases:

Step 1: Identify type of solution

Step 2: Apply formula to determine the [H<sup>+</sup>] or [OH<sup>-</sup>]

For weak acids:  $[H^+] = \sqrt{\mathbf{C} \times \mathbf{K}_a}$ 

For weak bases:  $[OH^-] = \sqrt{\mathbf{C} \times \mathbf{K}_{\mathbf{b}}}$ 

Step 3: Determine pH / pOH using formula

# Example 1

Given 0.1 mol dm<sup>-3</sup> aqueous ethanoic acid CH<sub>3</sub>COOH, with  $K_a = 1.80 \times 10^{-5}$  mol dm<sup>-3</sup>, calculate its pH.

Step 1:	Identify type of solution
	Weak acid
Step 2:	Apply formula to determine the [H <sup>+</sup> ]
	For weak acids: [H <sup>+</sup> ] = $\sqrt{\mathbf{C} \times \mathbf{K}_{a}}$
	$[H^+] = \sqrt{0.1 \times (1.80 \times 10^{-5})} = 1.34 \times 10^{-3} \text{ mol dm}^{-3}$
Step 3:	Determine pH using formula
	pH = −log <sub>10</sub> [H <sup>+</sup> ] = −log <sub>10</sub> [1.34 x 10 <sup>-3</sup> ] = <u>2.87</u>

# Example 2

Given 0.010 mol dm<sup>-3</sup> aqueous propanoic acid CH<sub>3</sub>CH<sub>2</sub>COOH with pH of 3.43, calculate its K<sub>a</sub>.

# Example 3

Calculate the pH of 0.50 mol dm<sup>-3</sup> ethylamine  $C_2H_5NH_2$  (K<sub>b</sub> = 4.3 x 10<sup>-4</sup> mol dm<sup>-3</sup>)

Step 1:	Identify type of solution
	Weak base
Step 2:	Apply formula to determine the [OH <sup>-</sup> ]
	For weak bases: $[OH^-] = \sqrt{C \times K_b}$
	$[OH^{-}] = \sqrt{0.50 \times (4.3 \times 10^{-4})} = 1.47 \times 10^{-2} \text{ mol dm}^{-3}$
Step 3:	Determine pH using formula
	pOH = −log <sub>10</sub> [OH <sup>-</sup> ] = −log <sub>10</sub> [1.47 x 10 <sup>-2</sup> ] = 1.83
Example 4	pH = 14 – 1.83 = <u>12.2</u>

Calculate the base dissociation constant of 0.0010 mol dm<sup>-3</sup> of 1–phenylmethanamine,  $C_6H_5CH_2NH_2$ , given that the pH of the solution is 10.17.

# Exercise 3

- 1. Calculate the pH of the following aqueous solutions at 298 K,
  - (a) 0.2 mol dm<sup>-3</sup> CH<sub>3</sub>COOH (K<sub>a</sub> =  $1.80 \times 10^{-5}$  mol dm<sup>-3</sup>)

(b) 0.0002 mol dm<sup>-3</sup> HCl

**2.** Propanoic acid,  $CH_3CH_2COOH$  is a weak acid.

- (a) Give the equation for the ionisation of propanoic acid in water and deduce the expression for the ionisation constant,  $K_a$ , of propanoic acid.
- (b) Calculate the  $K_a$  value of propanoic acid using the  $pK_a$  value in the Data Booklet.

(c) Use your answer from (b) to calculate the  $[H^+]$  in an aqueous solution of propanoic acid of concentration 0.0500 mol dm<sup>-3</sup>, and hence the pH of this solution.

18.2.5 Relationship between  $K_a$  ,  $K_b$  and  $K_w$ 

• Consider the ionisation of ethanoic acid:

 $CH_3COOH$  (aq) +  $H_2O$  (I)  $\implies CH_3COO^-$  (aq) +  $H_3O^+$  (aq)

$$K_{a} = \frac{[H_{3}O^{+}][CH_{3}COO^{-}]}{[CH_{3}COOH]} - (1)$$

We now know that the above position of equilibrium lies very much to the left (for concentrations other than infinite dilution). CH<sub>3</sub>COO<sup>-</sup>, the ethanoate ion, is often referred to as a strong conjugate base. A solution of CH<sub>3</sub>COO<sup>-</sup> will be expected to undergo hydrolysis (reaction with water):

 $CH_3COO^-$  (aq) +  $H_2O$  (I)  $\iff$   $CH_3COOH$  (aq) +  $OH^-$  (aq)

- The reaction occurs because CH<sub>3</sub>COO<sup>-</sup> prefers to abstract a proton to become the undissociated form CH<sub>3</sub>COOH.
- Because the reaction produces  $OH^-$  (aq), we can write a  $K_b$  expression for the hydrolysis:

$$K_{b} = \frac{[CH_{3}COOH][OH^{-}]}{[CH_{3}COO^{-}]}$$
 (2)

• Taking equation (1) x (2):

 $K_a \mathrel{x} K_b$ 

$$= \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} \times \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$
$$= [H_3O^+] [OH^-]$$
$$= [H^+] [OH^-]$$
$$= K_w$$

•  $K_b$  of the conjugate base of an acid (A<sup>-</sup>) is related to the  $K_a$  of the same acid (HA) by the relationship:

```
K_a \ge K_b = K_w = 1.00 \ge 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 25 \text{ }^{\circ}\text{C}
```

# Example 5

Calculate the K<sub>b</sub> of the ethanoate ion at 25 °C given the K<sub>a</sub> of ethanoic acid at 25 °C is 1.80 x  $10^{-5}$  mol dm<sup>-3</sup>.

 $K_{a} \times K_{b} = 1.00 \times 10^{-14}$  $K_{b} = \frac{1.00 \times 10^{-14}}{K_{a}} = \frac{1.00 \times 10^{-14}}{1.80 \times 10^{-5}} = 5.56 \times 10^{-10} \text{ mol dm}^{-3}$ 

• The larger the  $K_a$  of an acid, the smaller is the  $K_b$  of its conjugate base.

- The stronger the acid, the weaker is its conjugate base and conversely.
- The weaker the acid, the stronger is its conjugate base. This is in agreement with the definition of weak acid as defined earlier. The degree of dissociation of a weak acid is low (< 5 %) so its conjugate base has a high tendency to gain a proton to become the undissociated form.
- However, it must be noted that the word "strong" in strong conjugate base is relative (in comparison with the conjugate bases of strong acids). As can be seen in the example above, the K<sub>b</sub> value of 5.56 x 10<sup>-10</sup> mol dm<sup>-3</sup> is very small.

[Note: Hydrolysis of the conjugate bases will be considered in the section on salt hydrolysis.]

- To derive a similar relationship between NH<sub>3</sub> and its conjugate acid NH<sub>4</sub>+:
- Consider the ionisation of ammonia in water

 $NH_3$  (aq) +  $H_2O$  (I)  $\implies NH_4^+$  (aq) +  $OH^-$  (aq)

$$K_{b} = \frac{[NH_{4}^{+}][OH^{-}]}{[NH_{3}]} - (1)$$

• The conjugate acid of ammonia,  $NH_4^+$  (aq) hydrolyses in water according to the equation:

 $NH_4^+$  (aq) +  $H_2O$  (I)  $\implies$   $NH_3$  (aq) +  $H_3O^+$  (aq)

$$K_{a} = \frac{[H_{3}O^{+}][NH_{3}]}{[NH_{4}^{+}]} - (2)$$

• Taking equation (1) x (2):

K<sub>b</sub> x K<sub>a</sub>

$$= \frac{[NH_4^+][OH^-]}{[NH_3]} \times \frac{[H_3O^+][NH_3]}{[NH_4^+]}$$
$$= [H_3O^+] [OH^-]$$
$$= [H^+] [OH^-]$$
$$= K_w$$

 Hence, K<sub>a</sub> of the conjugate acid of a base (HB<sup>+</sup>) is related to the K<sub>b</sub> of the same base (B) by the relationship:

$$K_a \times K_b = K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 25 \text{ }^{\circ}\text{C}$$

• The same principle applies here, i.e. the weaker the base, the stronger is its conjugate acid. This can be illustrated using the following two bases:

 $\begin{array}{ll} \mathsf{NH}_3 \mbox{ (aq) } + \mbox{ H}_2 O \mbox{ (l) } & \longrightarrow \mbox{ NH}_4^+ \mbox{ (aq) } + \mbox{ OH}^- \mbox{ (aq) } & K_b = 1.8 \ x \ 10^{-5} \ \text{mol } dm^{-3} \\ \mathsf{C}_2 \mathsf{H}_5 \mathsf{NH}_2 \mbox{ (aq) } + \mbox{ H}_2 O \mbox{ (l) } & \longleftarrow \mbox{ C}_2 \mathsf{H}_5 \mathsf{NH}_3^+ \mbox{ (aq) } + \mbox{ OH}^- \mbox{ (aq) } & K_b = 4.47 \ x \ 10^{-4} \ \text{mol } dm^{-3} \\ \end{array}$ 

- From the K<sub>b</sub> values, it can be concluded that C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> is a stronger base (higher tendency to abstract a proton from water to form OH<sup>-</sup>) than NH<sub>3</sub>.
- The corresponding K<sub>a</sub> values of the conjugate acids are:

 $\begin{array}{ll} \mathsf{NH}_{4^+} \left( aq \right) + \mathsf{H}_2 \mathsf{O} \left( \mathsf{I} \right) & \Longrightarrow & \mathsf{NH}_3 \left( aq \right) + \mathsf{H}_3 \mathsf{O}^+ \left( aq \right) \\ \mathsf{C}_2 \mathsf{H}_5 \mathsf{NH}_3^+ \left( aq \right) + \mathsf{H}_2 \mathsf{O} \left( \mathsf{I} \right) & \rightleftharpoons & \mathsf{C}_2 \mathsf{H}_5 \mathsf{NH}_2 \left( aq \right) + \mathsf{OH}^- \left( aq \right) \\ \mathsf{K}_a = 2.24 \times 10^{-11} \text{ mol } dm^{-3} \\ \mathsf{K}_a = 2.24 \times 10^{-11} \text{ mol } dm^{-3} \\ \end{array}$ 

• The ammonium ion (NH<sub>4</sub><sup>+</sup>) is a stronger conjugate acid than the conjugate acid of ethylamine (C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>), ethylammonium ion (C<sub>2</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup>).

## Exercise 4

- **1.** The  $K_a$  value for an acid is  $1.0 \times 10^{-2}$ . What is the  $K_b$  value for its conjugate base?
- A. 1.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>
- B. 1.0 x 10<sup>-6</sup> mol dm<sup>-3</sup>
- C.  $1.0 \times 10^{-10} \text{ mol dm}^{-3}$
- D. 1.0 x 10<sup>-12</sup> mol dm<sup>-3</sup>

## 18.3 pH Curves

#### 18.3.1 Salt solutions

- Weak acid (HA) dissociates partially in solution to give protons (H<sup>+</sup>). Salt is an ionic compound. When a salt dissolves in water, it dissociates fully in solution to give free aqueous ions. For example, when NaCl (s) dissolves in water, it forms Na<sup>+</sup> and Cl<sup>-</sup>. The solution of NaCl is neutral, with a pH of 7 at 25 °C.
- However, not all salts interact with water like NaCl does. Some salts, when dissolved in water, undergo further reaction with water to produce either H<sub>3</sub>O<sup>+</sup> ions or OH<sup>-</sup> ions, resulting in an acidic or alkaline solution respectively. Such reactions are known as salt hydrolysis.
- Salt hydrolysis, a reversible reaction, occurs for salts containing one or more of the following species:
  - o an anion that is a conjugate base of a weak acid
  - o a cation that is a conjugate acid of a weak base
  - $\circ$  a cation of high charge density such as Al<sup>3+</sup>, Cr<sup>3+</sup>, and Fe<sup>3+</sup>.
- The pH of an aqueous salt solution can be predicted on the basis of the strength of the acid and base from which the salt is derived.
- Strong acid + strong base  $\rightarrow$  neutral salt

HCl (aq) + NaOH (aq)  $\rightarrow$  NaCl (aq) + H<sub>2</sub>O (l)

Both Na<sup>+</sup> and Cl<sup>-</sup> ions do not undergo hydrolysis in aqueous solution. This is because both Na<sup>+</sup>) and Cl<sup>-</sup> do not react with water since they are very weak conjugate acids/bases from strong acids / bases.

Hence, the pH of the salt solution = 7.

• Strong acid + weak base  $\rightarrow$  acidic salt

HCl (aq) + NH<sub>3</sub> (aq)  $\rightarrow$  NH<sub>4</sub><sup>+</sup> (aq) + Cl<sup>-</sup> (aq)

 $CI^{-}$  (aq) ions do not undergo hydrolysis in aqueous solution.  $CI^{-}$  (aq) does not react with water since it is a very weak conjugate base from strong acid HCI (aq).

 $NH_4^+$  (aq), a conjugate acid of the weak base  $NH_3$  (aq), undergoes hydrolysis to form  $H_3O^+$  (aq).

 $NH_4^+$  (aq) +  $H_2O$  (I)  $\implies$   $NH_3$  (aq) +  $H_3O^+$  (aq)

 $[H_3O^+]_{total} = [H_3O^+]_{from water} + [H_3O^+]_{from hydrolysis} > 10^{-7} \text{ mol } dm^{-3}$ 

Hence, pH of the salt solution is < 7.

• Weak acid + strong base  $\rightarrow$  basic salt

 $\begin{array}{l} CH_{3}COOH \ (aq) + NaOH \ (aq) \rightarrow CH_{3}COONa \ (aq) + H_{2}O \ (l) \\ CH_{3}COONa \ (aq) \rightarrow CH_{3}COO^{-} \ (aq) + Na^{+} \ (aq) \end{array}$ 

Na<sup>+</sup> (aq) ions do not undergo hydrolysis in aqueous solution. Na<sup>+</sup> (aq) does not react with water since it is a very weak conjugate acid from strong base NaOH (aq).

 $CH_3COO^-$  (aq), a conjugate base of the weak acid  $CH_3COOH$  (aq), undergoes hydrolysis to form  $OH^-$  (aq).

 $CH_3COO^-$  (aq) +  $H_2O$  (I)  $\iff CH_3COOH$  (aq) +  $OH^-$  (aq)

 $[OH^{-}]_{total} = [OH^{-}]_{from water} + [OH^{-}]_{from hydrolysis} > 10^{-7} \text{ mol } dm^{-3}$ 

Hence, pH of the salt solution is > 7.

## Enrichment: Calculation of pH for salt solutions

**Example 6:** Calculate the pH of a 0.2 mol dm<sup>-3</sup> aqueous ammonium chloride at room temperature. The K<sub>b</sub> of ammonia at room temperature is  $1.78 \times 10^{-5}$  mol dm<sup>-3</sup>.

Analysis: NH<sub>4</sub>Cl completely dissociates to give its ions, NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup>

 $NH_4Cl (s) \rightarrow NH_4^+ (aq) + Cl^- (aq)$ 

Only the cation (conjugate acid of weak base)  $NH_4^+$  undergoes hydrolysis to form an acidic solution due to the  $H_3O^+$  formed.

 $NH_{4^{+}}(aq) + H_2O(I) \Longrightarrow NH_3(aq) + H_3O^{+}(aq)$ 

# Step 1: Identify type of solution

Weak acid (due to conjugate acid NH<sub>4</sub><sup>+</sup>)

# Step 2: Apply formula to determine the [H<sup>+</sup>]

For weak acids:  $[H^+] = \sqrt{C \times K_a}$ 

 $K_a \times K_b = 1.00 \times 10^{-14}$ 

$$K_{a} = \frac{1.00 \times 10^{-14}}{K_{b}} = \frac{1.00 \times 10^{-14}}{1.78 \times 10^{-5}} = 5.62 \times 10^{-10} \text{ mol dm}^{-3}$$

$$[H^+] = \sqrt{0.2 \times (5.62 \times 10^{-10})} = 1.06 \times 10^{-5} \text{ mol dm}^{-3}$$

Step 3: Determine pH using formula

 $pH = -log_{10} [H^+] = -log_{10} [1.06 \times 10^{-5}] = 4.97$ 

**Example 7:** Calculate the pH of a 0.1 mol dm<sup>-3</sup> aqueous sodium ethanoate CH<sub>3</sub>COONa at room temperature. The pK<sub>a</sub> of ethanoic acid CH<sub>3</sub>COOH at room temperature is 4.76.

**Exercise 5** 

- 1. Which compound will dissolve in water to give a solution with a pH smaller than 7?
- A. sodium chloride
- B. potassium carbonate
- C. ammonium nitrate
- D. lithium sulfate
- **2.** When the following 1.0 mol dm<sup>-3</sup> aqueous solutions are arranged in order of increasing pH, which is the correct order?
  - I. Ammonium chloride
  - II. Ammonium ethanoate
  - III. Sodium ethanoate
- A. I, II, III
- B. II, I, III
- C. III, I, II
- D. III, II, I
- **3.** Predict and explain, using equations where appropriate, whether the following solutions are acidic, alkaline or neutral.
  - (a) 0.1 mol  $dm^{-3}$  NaNO<sub>3</sub> (aq)

(b)  $0.1 \text{ mol } dm^{-3} \text{ Na}_2 \text{CO}_3$  (aq)

## 18.3.2 Buffer solutions

- Buffer solutions are solutions that **maintain an approximately constant pH** when **small amounts of either acid or base are added** or when the solution is diluted.
- A buffer solution has two components one component (basic component) to neutralise any acids that is added and the other component (acidic component) to neutralise any bases added.

Buffer	Acidic component	Basic component
Acidic	Weak acid e.g. CH₃COOH	Salt of its conjugate base e.g. CH₃COO⁻Na⁺
Basic	Salt of its conjugate acid e.g. NH₄⁺Cl⁻	Weak base e.g. NH₃

• There are two kinds of buffer: acidic buffers and basic buffers.

## 18.3.2.1 Acidic buffer

 In a buffer system made up of a weak acid (for example ethanoic acid) and its salt with a strong base (such as sodium ethanoate), the large amount of ethanoate ions contributed by the fully dissociated salt tends to suppress the dissociation of the weak acid (in accordance with Le Chatelier's Principle):

 $CH_3COOH (aq) + H_2O (I) \Longrightarrow CH_3COO^- (aq) + H_3O^+ (aq)$ 

 $CH_3COO^-Na^+$  (aq)  $\rightarrow CH_3COO^-$  (aq) +  $Na^+$  (aq)

- Sodium ethanoate, being a soluble salt will dissociate completely. Since the dissociation constant of the weak acid is very small, this results in a CH<sub>3</sub>COOH / CH<sub>3</sub>COONa buffer system consisting of an abundant supply of the undissociated acid and its conjugate base.
- How does an acidic buffer work?
  - When a small amount of acid, H<sup>+</sup> is added:

 $CH_3COO^-$  (aq) + H<sup>+</sup> (aq)  $\rightarrow CH_3COOH$  (aq)

The added  $H^+$  (aq) is removed as  $CH_3COOH$  (aq).

[H<sup>+</sup>] is slightly changed hence pH remains fairly constant.

 $\circ$  When a small amount of base, OH<sup>-</sup> is added:

 $CH_3COOH (aq) + OH^- (aq) \rightarrow CH_3COO^- + H_2O (I)$ 

The added  $OH^{-}$  (aq) is removed as  $CH_{3}COO^{-}$  (aq).

[OH<sup>-</sup>] is slightly changed hence pH remains fairly constant.

## 18.3.2.2 Basic buffer

• In a buffer system made up of a weak base (for example ammonia) and its salt with a strong acid (such as ammonium chloride), the large amount of ammonium ions contributed by the fully dissociated salt tends to suppress the dissociation of the weak base (in accordance with Le Chatelier's Principle):

 $NH_3$  (aq) +  $H_2O$  (I)  $\implies NH_4^+$  (aq) +  $OH^-$  (aq)

 $NH_4Cl (s) \rightarrow NH_4^+ (aq) + Cl^- (aq)$ 

- Ammonium chloride, being a soluble salt will dissociate completely. Since the dissociation constant of the weak base is very small, this results in a NH<sub>3</sub> / NH<sub>4</sub>Cl buffer system consisting of an abundant supply of the undissociated base and its conjugate acid.
- How does a basic buffer work?
  - $\circ$  When a small amount of acid, H<sup>+</sup> is added:

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

The added  $H^+$  (aq) is removed as  $NH_{4^+}$  (aq).

[H<sup>+</sup>] is slightly changed hence pH remains fairly constant.

• When a small amount of base,  $OH^-$  is added:

 $NH_4^+$  (aq) +  $OH^-$  (aq)  $\rightarrow NH_3$  +  $H_2O$  (I)

The added  $OH^{-}$  (aq) is removed as  $NH_{3}$  (aq).

[OH<sup>-</sup>] is slightly changed hence pH remains fairly constant.

# 18.3.2.3 pH calculations involving buffer solutions

• For an acidic buffer:

• For a basic buffer:

$$pOH = pK_b + log_{10} \frac{[salt]}{[base]}$$

# **18.3.2.4 Preparation of buffer solutions**

- There are two ways to prepare a buffer solution:
  - To directly mix a salt of a weak acid ( $CH_3COONa$ ) to a solution of weak acid ( $CH_3COOH$ ); or salt of a weak base ( $NH_4CI$ ) to a solution of weak base ( $NH_3$ ).
  - Another way is to neutralise excess weak acid with a strong alkali; or excess weak base with a strong acid.

Example:

An acidic buffer solution is prepared by adding 10 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> NaOH (strong base) and 20 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> CH<sub>3</sub>COOH (excess weak acid).

After neutralisation, the solution contains the salt and the unreacted weak acid.

NaOH (aq) + CH<sub>3</sub>COOH (aq)  $\rightarrow$  CH<sub>3</sub>COONa (aq) + H<sub>2</sub>O (l)

	NaOH (aq)	CH <sub>3</sub> COOH (aq)	CH <sub>3</sub> COONa (aq)
Initial / mol	0.001	0.002	0.000
Change / mol	-0.001	-0.001	+0.001
Final / mol	0.000	0.001	0.001

# Method for solving pH / pOH problems involving acidic / basic buffers:

- Step 1: Identify type of solution
- Step 2: Write down the pH formula for acidic buffer / Write down the pOH formula for basic buffer
- Step 3: Identify the weak acid and salt for acidic buffer / Identify the weak base and salt for basic buffer
- Step 4: Calculate the new concentrations of buffer components (note: need to calculate new concentration of buffer components if total volume changes)
- Step 5: Substitute new concentrations into pH expression and solve

Example 8

(a) Calculate the pH of a buffer solution made by mixing 500 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> CH<sub>3</sub>COOH and 500 cm<sup>3</sup> of 0.2 mol dm<sup>-3</sup> CH<sub>3</sub>COONa, given that the K<sub>a</sub> of CH<sub>3</sub>COOH is 1.8 x 10<sup>-5</sup> mol dm<sup>-3</sup> at 25 °C.

# Step 1: Identify type of solution

Acidic buffer (due to weak acid CH<sub>3</sub>COOH and conjugate base CH<sub>3</sub>COO<sup>-</sup>)

## Step 2: Write down the pH formula for acidic buffer

For acidic buffer:  $pH = pK_a + \log_{10} \frac{[salt]}{[acid]}$ 

Step 4: Calculate the new concentrations of buffer components (note: need to calculate new concentration of buffer components if total volume changes)

Total volume of mixture =  $0.500 + 0.500 = 1.00 \text{ dm}^3$ 

New [CH<sub>3</sub>COO<sup>-</sup>] after mixing =  $\frac{0.2 \times 0.5}{0.5 + 0.5}$  = 0.100 mol dm<sup>-3</sup>

New [CH<sub>3</sub>COOH] after mixing =  $\frac{0.1 \times 0.5}{0.5 + 0.5}$  = 0.0500 mol dm<sup>-3</sup>

## Step 5: Substitute new concentrations into pH expression and solve

$$pH = pK_a + \log_{10} \frac{[salt]}{[acid]} = -\log_{10} (1.8 \times 10^{-5}) + \log_{10} \frac{0.100}{0.0500} = \frac{5.05}{0.0500}$$

- (b) Using 1 dm<sup>3</sup> of the buffer solution prepared, calculate the change of pH in each case when the following has been added:
  - (i) 1.0 g of potassium hydroxide

 $CH_{3}COOH (aq) + OH^{-} (aq) \rightarrow CH_{3}COO^{-} + H_{2}O (I)$ 

Hence, [CH<sub>3</sub>COO<sup>-</sup>] (salt) increases but [CH<sub>3</sub>COOH] (weak acid) decreases

No. of moles of KOH added =  $\frac{1.0}{39.10 + 16.00 + 1.01}$  = 0.0178 mol Since KOH = OH-No. of moles of OH- added = 0.0178 mol  $[OH^{-}] added = \frac{0.0178}{1} = 0.0178 \text{ mol dm}^{-3}$ New  $[CH_3COO^{-}] = 0.100 + 0.0178 = 0.1178 \text{ mol dm}^{-3}$ New  $[CH_3COOH] = 0.05 - 0.0178 = 0.0322 \text{ mol dm}^{-3}$ New  $pH = -\log_{10}(1.8 \times 10^{-5}) + \log_{10}\frac{0.1178}{0.0322} = 5.31$  Change in pH = New pH - Original pH = 5.31 - 5.05 = 0.26

(ii) 1.0 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> hydrochloric acid (Assume no change in total volume).

 $CH_3COO^-$  (aq) + H<sup>+</sup> (aq)  $\rightarrow CH_3COOH$  (aq)

Hence, [CH<sub>3</sub>COO<sup>-</sup>] (salt) decreases but [CH<sub>3</sub>COOH] (weak acid) increases

No. of moles of HCl added =  $0.1 \times \frac{0.1}{1000} = 1.00 \times 10^{-3} \text{ mol}$ 

Since  $HCI \equiv H^+$ 

No. of moles of H<sup>+</sup> added =  $1.00 \times 10^{-3}$  mol

 $[H^+] \text{ added} = \frac{1.0 \times 10^{-3}}{1.0} = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$ 

New [CH<sub>3</sub>COO<sup>-</sup>] =  $0.100 - (1.00 \times 10^{-3}) = 0.0990 \text{ mol dm}^{-3}$ 

New [CH<sub>3</sub>COOH] =  $0.05 + (1.00 \times 10^{-3}) = 0.0510 \text{ mol dm}^{-3}$ 

New pH =  $-\log_{10} (1.8 \times 10^{-5}) + \log_{10} \frac{0.0990}{0.0510} = 5.03$ 

Change in pH = New pH – Original pH = 5.03 - 5.05 = -0.02

## 18.3.2.5 Maximum buffer capacity

- Maximum buffer capacity occurs when the solution contains equal concentration of weak acid / base and its salt.
- For an acidic buffer:

$$pH = pK_a + log_{10} \frac{[salt]}{[acid]} = pK_a + log_{10} \frac{1}{1} = pK_a$$

Hence,

$$pH = pK_a$$
 at maximum buffering capacity

• For a basic buffer:

$$pOH = pK_b + log_{10} \frac{[salt]}{[base]} = pK_b + log_{10} \frac{1}{1} = pK_b$$

Hence,

 $pOH = pK_b$  at maximum buffering capacity

**Exercise 6** 

- 1. Which mixture would produce a buffer solution when dissolved in 1.0 dm<sup>3</sup> of water?
- A. 0.30 mol of  $NH_3$  (aq) and 0.30 mol of HCl (aq)
- B. 0.30 mol of  $NH_3$  (aq) and 0.15 mol of HCl (aq)
- C. 0.30 mol of  $NH_3$  (aq) and 0.60 mol of HCl (aq)
- D. 0.30 mol of  $NH_3$  (aq) and 0.15 mol of  $H_2SO_4$  (aq)
- 2. What is the value of [H<sup>+</sup>] in a buffer solution in which [CH<sub>3</sub>COOH] = 2.0 mol dm<sup>-3</sup> and [CH<sub>3</sub>COO<sup>-</sup>] 1.0 mol dm<sup>-3</sup>? For CH<sub>3</sub>COOH, K<sub>a</sub> = 1.80 × 10<sup>-5</sup> mol dm<sup>-3</sup>.
- A. 6.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>
- B. 3.6 x 10<sup>-5</sup> mol dm<sup>-3</sup>
- C. 1.8 x 10<sup>-5</sup> mol dm<sup>-3</sup>
- D. 9.1 x 10<sup>-6</sup> mol dm<sup>-3</sup>
- 3. (a) Calculate the pH of a 1 dm<sup>3</sup> buffer solution containing 0.100 mol dm<sup>-3</sup> aqueous ammonia and 0.100 mol dm<sup>-3</sup> ammonium nitrate, given that the K<sub>b</sub> of aqueous ammonia is  $1.6 \times 10^{-5}$  mol dm<sup>-3</sup> at 25 °C.

(b) the new pH of the solution after 0.10 g of NaOH has been added.

(c) the new pH of the solution after 0.10 g of  $H_2SO_4$  has been added

18.3.2 pH Titration Curves

- Equivalence point
  - Corresponds to the theoretical point when equivalent (or stoichiometric) amounts of the acid and base have been reacted
  - Generally involves a rapid pH change over the equivalence point
- End–point (equivalence point)
  - The point in a titration where an indicator changes colour is called the end-point
  - End–point pH is given by the mid–point of the vertical (or rapid pH change)
- Choice of indicator
  - Each indicator changes colour over its characteristic pH transition range in solution
  - Selection of an appropriate indicator to mark the end–point depends on the range of rapid pH change over the equivalence point
  - The pH transition range of the indicator should lie within the rapid pH change over the equivalence point in the titration
- Types of acid–base titration
  - Strong acid strong base
  - Strong acid weak base
  - Weak acid strong base
  - Weak acid weak base

## 18.3.2.1 Strong acid – strong base titrations

 Consider the titration of 0.10 mol dm<sup>-3</sup> of 50.0 cm<sup>3</sup> hydrochloric acid in the conical flask against 0.10 mol dm<sup>-3</sup> of sodium hydroxide solution.

HCl (aq) + NaOH (aq)  $\rightarrow$  NaCl (aq) + H<sub>2</sub>O (l)



Point	Titration Curve	pH for Strong Acid – Strong Base Titration
1	Start of titration:	Species present in conical flask: HCI (aq)
	0 cm <sup>3</sup> of NaOH added from burette	Type of solution: Strong acid
		HCl (aq) $\rightarrow$ H <sup>+</sup> (aq) + Cl <sup>-</sup> (aq)
		[H <sup>+</sup> ] = [HCI] = 0.10 mol dm <sup>-3</sup>
		$pH = -log_{10} [H^+] = -log_{10} (0.10) = \underline{1.0}$
2	25 cm <sup>3</sup> of NaOH added from burette	Species present in conical flask: HCI (aq) and NaCI (aq)
		Type of solution: Strong acid
		Amount of unreacted HCI
		$= (0.10 \times \frac{50}{1000}) - (0.10 \times \frac{25}{1000}) = 2.5 \times 10^{-3} \text{ mol}$
		HCI (aq) $\rightarrow$ H <sup>+</sup> (aq) + CI <sup>-</sup> (aq)
		$[H^+] = [HCI] = \frac{2.5 \times 10^{-3}}{\frac{50 + 25}{1000}} = 0.033 \text{ mol } dm^{-3}$
		$pH = -log_{10} [H^+] = -log_{10} (0.033) = \underline{1.5}$
3	Equivalence point of titration:	pH = 7

	50 cm <sup>3</sup> of NaOH added from burette	The ions Na⁺ and Cl⁻ do not undergo hydrolysis in water.
4	Excess titrant added: 75 cm <sup>3</sup> of NaOH added from burette	Species present in conical flask: NaOH (aq) and NaCl (aq) Type of solution: Strong base Amount of unreacted NaOH = $(0.10 \times \frac{75}{1000}) - (0.10 \times \frac{50}{1000}) = 2.5 \times 10^{-3}$ mol
		NaOH (aq) → Na <sup>+</sup> (aq) + OH <sup>-</sup> (aq) $[OH-] = [NaOH] = \frac{2.5 \times 10^{-3}}{\frac{75 + 50}{1000}} = 0.020 \text{ mol dm}^{-3}$ $pOH = -\log_{10} [OH-] = -\log_{10} (0.020) = 1.7$ $pH = 14 - pOH = 14 - 1.7 = 12.3$

- Characteristics of a strong acid strong base titration curve: •
  - 1. Low initial pH due to strong acid
  - pH changes only gradually until equivalence point is reached 2.
  - 3.
  - Very sharp jump in pH at equivalence point from pH 3 to pH 11 After equivalence point the curve flattens out at a high value due to strong base 4.
  - 5. pH at equivalence point = 7

## 18.3.2.2 Strong acid – weak base titrations

• Consider the titration of 0.10 mol dm<sup>-3</sup> of 50.0 cm<sup>3</sup> hydrochloric acid in the conical flask against 0.10 mol dm<sup>-3</sup> of ammonia solution.

HCl (aq) + NH<sub>3</sub> (aq)  $\rightarrow$  NH<sub>4</sub>Cl (aq)



Point	Titration Curve Start of titration:	pH for Strong Acid – Weak Base Titration Species present in conical flask: HCI (aq)
	0 cm <sup>3</sup> of NH <sub>3</sub> added	Type of solution: Strong acid
		HCI (aq) $\rightarrow$ H <sup>+</sup> (aq) + CI <sup>-</sup> (aq)
		$[H^+] = [HCI] = 0.10 \text{ mol } dm^{-3}$
		$pH = -log_{10} [H^+] = -log_{10} (0.10) = \underline{1.0}$
2	25 cm <sup>3</sup> of NH <sub>3</sub> added from burette	Species present in conical flask: HCI (aq) and NH <sub>4</sub> CI (aq)
		Type of solution: Strong acid
		Amount of unreacted HCl = $(0.10 \times \frac{50}{1000}) - (0.10 \times \frac{25}{1000}) = 2.5 \times 10^{-3} \text{ mol}$
		HCI (aq) $\rightarrow$ H <sup>+</sup> (aq) + CI <sup>-</sup> (aq)
		$[H^+] = [HCI] = \frac{2.5 \times 10^{-3}}{\frac{50 + 25}{1000}} = 0.033 \text{ mol dm}^{-3}$
		$pH = -log_{10} [H^+] = -log_{10} (0.033) = \underline{1.5}$
3	Equivalence point of titration:	Species present in conical flask: NH <sub>4</sub> Cl (aq)

	50 cm <sup>3</sup> of NH <sub>3</sub> added from burette	Type of solution: Salt of strong acid and weak base $NH_{4^{+}}$ (aq), a conjugate acid of the weak base $NH_{3}$ (aq), undergoes hydrolysis to form $H_{3}O^{+}$ (aq). $NH_{4^{+}}$ (aq) + $H_{2}O$ (I) $\implies NH_{3}$ (aq) + $H_{3}O^{+}$ (aq) $K_{a} \times K_{b} = 1.00 \times 10^{-14}$ $K_{a}$ $= \frac{1.00 \times 10^{-14}}{K_{b}} = \frac{1.00 \times 10^{-14}}{10^{-4.75}} = 5.62 \times 10^{-10} \text{ mol dm}^{-3}$ $[NH_{4^{+}}] = [NH_{4}CI] = \frac{0.10 \times \frac{50}{1000}}{\frac{50 + 50}{1000}} = 0.050 \text{ mol dm}^{-3}$
		$[H^+] = \sqrt{0.050 \times (5.62 \times 10^{-10})} = 5.30 \times 10^{-6} \text{ mol dm}^{-3}$ $pH = -\log_{10} [H^+] = -\log_{10} [5.30 \times 10^{-6}] = 5.28$
4a	Excess titrant added: 75 cm <sup>3</sup> of NH <sub>3</sub> added from burette	Species present in conical flask: NH <sub>3</sub> (aq) and NH <sub>4</sub> CI (aq) Type of solution: Basic buffer Amount of unreacted NH <sub>3</sub> = $(0.10 \times \frac{75}{1000}) - (0.10 \times \frac{50}{1000}) = 2.5 \times 10^{-3} \text{ mol}$ $[NH_3] = \frac{2.5 \times 10^{-3}}{\frac{75 + 50}{1000}} = 0.020 \text{ mol dm}^{-3}$ $[NH_4^+] = [NH_4CI] = \frac{0.10 \times \frac{50}{1000}}{\frac{75 + 50}{1000}} = 0.040 \text{ mol dm}^{-3}$ pOH = $pK_b + log_{10} \frac{[salt]}{[base]}$ = $-log_{10} (10^{-4.75}) + log_{10} \frac{(0.020)}{(0.040)}$ = 4.85 pH = 14 - pOH = 14 - 4.85 = <u>9.15</u>

4b	Excess titrant added:	Species present in conical flask: NH <sub>3</sub> (aq) and NH <sub>4</sub> Cl (aq)

100 cm	<sup>3</sup> of	NH <sub>3</sub>	Type of solution: Basic buffer (maximum buffer capacity)
added fro	om bure	ette	Amount of unreacted NH <sub>3</sub> = $(0.10 \times \frac{100}{1000}) - (0.10 \times \frac{50}{1000}) = 5.0 \times 10^{-3} \text{ mol}$
			$[NH_3] = \frac{5.0 \times 10^{-3}}{\frac{100 + 50}{1000}} = 0.033 \text{ mol } dm^{-3}$
			$[NH_4^+] = [NH_4CI] = \frac{0.10 \times \frac{50}{1000}}{\frac{100 + 50}{1000}} = 0.033 \text{ mol } dm^{-3}$
			Since $[NH_3] = [NH_4^+]$
			$pOH = pK_b = 4.75$
			pH = 14 - pOH = 14 - 4.75 = <u><b>9.25</b></u>

- Characteristics of a strong acid weak base titration curve:
  - 1. Low initial pH due to strong acid
  - 2. pH changes until equivalence point is reached
  - 3. Very sharp jump in pH at equivalence point from pH 3 to pH 7
  - 4. After equivalence point the curve flattens out and increases gradually after equivalence point due to presence of basic buffer (maximum buffer capacity occurs at 2 x equivalence volume, i.e.  $100 \text{ cm}^3$  of NH<sub>3</sub> added)
  - 5. pH at equivalence point < 7

#### 18.3.2.3 Weak acid – strong base titrations

• Consider the titration of 0.10 mol dm<sup>-3</sup> of 50.0 cm<sup>3</sup> ethanoic acid in the conical flask against 0.10 mol dm<sup>-3</sup> of sodium hydroxide solution.

14 4 13 -12 11 10 3 equivalence (5) 9 point > 78 buffer 표 7 region 6 5  $pH = pK_a$ 2 4 3 2  $(\mathbf{1})$ 1 0 50 25 75 half-equivalence volume of 0.10 mol dm<sup>-3</sup> NaOH/cm<sup>3</sup> point

 $CH_3COOH (aq) + NaOH (aq) \rightarrow CH_3COONa (aq) + H_2O (I)$ 

Point	Titration Curve	pH for Weak Acid – Strong Base Titration
1	Start of titration:	Species present in conical flask: CH <sub>3</sub> COOH (aq)
	0 cm <sup>3</sup> of NaOH added from burette	Type of solution: Weak acid
		$[H^+] = \sqrt{0.10 \times (10^{-4.76})} = 1.32 \times 10^{-3} \text{ mol dm}^{-3}$
		pH = −log <sub>10</sub> [H <sup>+</sup> ] = −log <sub>10</sub> [1.32 x 10 <sup>-3</sup> ] = <u>2.88</u>
2	25 cm <sup>3</sup> of NaOH added from burette	Species present in conical flask: CH <sub>3</sub> COOH (aq) and CH <sub>3</sub> COONa (aq)
		Type of solution: Acidic buffer (maximum buffer capacity)
		Amount of unreacted CH <sub>3</sub> COOH = $(0.10 \times \frac{50}{1000}) - (0.10 \times \frac{25}{1000}) = 2.5 \times 10^{-3} \text{ mol}$
		$[CH_3COOH] = \frac{2.5 \times 10^{-3}}{\frac{50 + 25}{1000}} = 0.033 \text{ mol dm}^{-3}$
		Amount of CH <sub>3</sub> COONa formed
		$= (0.10 \text{ x} \frac{1000}{1000}) = 2.5 \text{ x} 10^{-3} \text{ mol}$

		$[CH_{3}COONa] = \frac{2.5 \times 10^{-3}}{\frac{50 + 25}{1000}} = 0.033 \text{ mol dm}^{-3}$	
		$pH = pK_a + \log_{10} \frac{[salt]}{[acid]}$	
		Since [CH <sub>3</sub> COOH] = [CH <sub>3</sub> COONa]	
		pH = pK <sub>a</sub> = <u>4.76</u>	
3	Equivalence point of titration:	Species present in conical flask: CH <sub>3</sub> COONa (aq)	
	50 cm <sup>3</sup> of NaOH added from burette	Type of solution: Salt of weak acid and strong base	
		$CH_3COO^-$ (aq), a conjugate base of the weak acid $CH_3COOH$ (aq), undergoes hydrolysis to form $OH^-$ (aq).	
		$CH_3COO^-$ (aq) + $H_2O$ (I) $\implies$ $CH_3COOH$ (aq) + $OH^-$ (aq)	
		$K_a \times K_b = 1.00 \times 10^{-14}$	
		$K_{b} = \frac{1.00 \times 10^{-14}}{K_{a}} = \frac{1.00 \times 10^{-14}}{10^{-4.76}} = 5.75 \times 10^{-10} \text{ mol dm}^{-3}$	
		$[CH_{3}COO^{-}] = [CH_{3}COONa] = \frac{0.10 \times \frac{50}{1000}}{\frac{50 + 50}{1000}} = 0.050 \text{ mol } dm^{-3}$	
		$[OH^{-}] = \sqrt{0.050 \times (5.75 \times 10^{-10})} = 5.36 \times 10^{-6} \text{ mol dm}^{-3}$	
		pOH = −log <sub>10</sub> [OH <sup>-</sup> ] = −log <sub>10</sub> [5.36 x 10 <sup>-6</sup> ] = 5.27	
		pH = 14 – pOH = 14 – 5.27 = <b><u>8.73</u></b>	
4	Excess titrant added:	Species present in conical flask: NaOH (aq) and CH <sub>2</sub> COONa (aq)	
	75 cm <sup>3</sup> of NaOH added from burette	Type of solution: Strong base	
		Amount of unreacted NaOH	
		$= (0.10 \times \frac{75}{1000}) - (0.10 \times \frac{50}{1000}) = 2.5 \times 10^{-3} \text{ mol}$	
		$[OH^{-}] = [NaOH] = \frac{2.5 \times 10^{-3}}{\frac{75 + 50}{1000}} = 0.020 \text{ mol } dm^{-3}$	

	$pOH = -log_{10} [OH^-] = -log_{10} [0.020] = 1.70$
	pH = 14 – pOH = 14 – 1.70 = <u>12.3</u>

- Characteristics of a weak acid strong base titration curve:
  - 1. Fairly high initial pH due to weak acid
  - pH changes gradually until equivalence point is reached due to presence of acidic buffer (maximum buffer capacity occurs at half equivalence volume, i.e. 25 cm<sup>3</sup> of NaOH added)
  - 3. Very sharp jump in pH at equivalence point from pH 7 to pH 11
  - 4. After equivalence point the curve flattens out at a high value due to strong base
  - 5. pH at equivalence point > 7

## 18.3.2.3 Weak acid – weak base titrations

• Consider the titration of 0.10 mol dm<sup>-3</sup> of 50.0 cm<sup>3</sup> ethanoic acid in the conical flask against 0.10 mol dm<sup>-3</sup> of ammonia solution.

 $CH_3COOH (aq) + NH_3 (aq) \rightarrow CH_3COONH_4 (aq)$ 



- Characteristics of a weak acid weak base titration curve:
  - 1. Fairly high initial pH due to weak acid
  - 2. Addition of base causes pH to rise steadily
  - 3. Change in pH at the equivalence point is much less sharp than in the other titrations
  - 4. After equivalence point the curve flattens out at a fairly low pH (pH of weak base)
  - 5. pH at equivalence point is difficult to determine

## 18.3.3 Indicators

- An indicator is a substance used in a titration to signal the end point at which reaction is complete.
- Most indicators used for acid-base titrations are weak organic acids with complex structures represented by HIn. The molecules of indicators, HIn, are one colour and the conjugate bases, In-, are another colour.
- Phenolphthalein, for example, is a commonly used indicator that is colourless in its HIn form and pink in its In<sup>-</sup> or basic form.
  - Acid MEINTE Alkali
- Consider another indicator: Methyl orange

 Its molecules (HIn) are red and the anions (In<sup>-</sup>) that are the conjugate base of methyl orange are yellow. In aqueous solution, indicator molecules are in equilibrium with hydrogen ions and indicator ions:

$$Hln (aq) \Longrightarrow H^+ (aq) + ln^- (aq)$$

- By applying Le Chatelier's Principle, we can predict how this equilibrium will respond to a change in pH of the solution:
  - Low pH, hence increase in [H<sup>+</sup>]: Position of equilibrium shifts to the left to remove the excess H<sup>+</sup> ions. Colour of methyl orange changes to red.
  - High pH, hence increase in [OH<sup>-</sup>]: Position of equilibrium shifts to the right to remove the excess OH<sup>-</sup> ions. Colour of methyl orange changes to yellow.

- To see how an indicator works, consider the following equilibrium for an indicator HIn (methyl orange), a weak acid with  $K_a = 2.00 \times 10^{-4}$  mol dm<sup>-3</sup>.
- Using the dissociation expression for indicators,

 $Hln (aq) \Longrightarrow H^+ (aq) + ln^- (aq)$ 

we can write an acid dissociation constant for the indicator as

$$K_{a} = \frac{[H^{+}][In^{-}]}{[HIn]}$$

• At acid pH (say pH = 1),

$$\frac{K_a}{[H^+]} = \frac{[2.0 \times 10^{-4}]}{[1.0 \times 10^{-1}]} = 2.0 \times 10^{-3}$$
$$\frac{[ln^-]}{[Hln]} = 2.0 \times 10^{-3} = \frac{1}{500}$$

- This ratio shows that the predominant form of the indicator in this solution is HIn, and the colour of the solution will be red. If OH<sup>-</sup> is added to this solution, H<sup>+</sup> ions are removed and according to Le Chatelier's principle, the above position of equilibrium shifts to the right, changing HIn to In<sup>-</sup>.
- For most indicators, the ratio of the minor form (i.e.  $In^-$ ) to the major form (i.e. HIn) must be  $\frac{1}{10}$  before a colour change is apparent to the human eyes:

 $\frac{[\text{ln}^-]}{[\text{Hln}]} = \frac{1}{10}$ 

• Assuming this ratio and applying the Henderson–Hasselbach equation to the above equilibrium we have the following equation for determining the pH at which colour change occurs when an acid solution is being titrated:

 $pH = pK_a + log_{10} \frac{[salt]}{[acid]}$ 

$$pH = pK_a + \log_{10} \frac{[In^-]}{[HIn]} = pK_a + \log_{10} \frac{1}{10} = pK_a - 1$$

• On the other hand, when a basic solution is titrated, the indicator HIn will initially exist as In<sup>-</sup> in solution. As acid is added, HIn will form. The colour change in this case will be apparent when there is a mixture of 10 parts In<sup>-</sup> and 1 part HIn, i.e.

 $\frac{[\text{ln}^-]}{[\text{Hln}]} = \frac{10}{1}$ 

which is just the reciprocal of the ratio for the titration of an acid. Substituting this ratio into the Henderson–Hasselbach equation gives:

$$pH = pK_{a} + \log_{10} \frac{[salt]}{[acid]}$$
$$pH = pK_{a} + \log_{10} \frac{[ln^{-}]}{[Hln]} = pK_{a} + \log_{10} \frac{10}{1} = pK_{a} + 1$$

Thus the useful pH range for colour change of an indicator is  $pK_a$  (indicator) ± 1.

- The precise range over which an indicator changes predominantly from one form to another therefore depends very much on the pK<sub>a</sub> of the (indicator).
- To determine the pH range over which an indicator changes colour, one can add an alkali or an acid, 1.0 cm<sup>3</sup> at a time, to a solution containing this indicator and a buffer, and measure the pH by a pH meter at each addition. The pH values at which a colour change begins and ends define the pH range.
- The indicator range must be measured in a buffer solution (as opposed to a water solution) to ensure that the pH does not change too rapidly on the addition of acid/alkali. It would almost be impossible to change the pH of the solution in a controlled way without using a buffer.



- An indicator will be effective in signaling the equivalence point of a titration when its endpoint coincides with the pH at equivalence point. This means that different indicators must be used for different titrations, depending on the pH at the equivalence point.
- Steps to choose an appropriate indicator for a particular titration:
  - Determine what combination of weak or strong acid or base are reacting together.
  - Deduce the pH of the salt solution at equivalence point:
    - Strong acid–strong base: pH = 7
    - Strong acid–weak base: pH < 7</li>
    - Weak acid–strong base: pH > 7
  - Choose an indicator whose **pH transition range lies within the rapid pH change over the equivalence point in the titration**
- List of acid–base indicators (Table 22 of IB Data Booklet)

			Colour change	
Indicator	рКа	pH range	Acid	Alkali
Methyl orange	3.7	3.1 – 4.4	Red	Yellow
Bromophenol blue	4.2	3.0 - 4.6	Yellow	Blue
Bromocresol green	4.7	3.8 - 5.4	Yellow	Blue
Methyl red	5.1	4.4 - 6.2	Red	Yellow
Bromothymol blue	7.0	6.0 - 7.6	Yellow	Blue
Phenol red	7.9	6.8 - 8.4	Yellow	Red
Phenolphthalein	9.6	8.3 - 10.0	Colourless	Pink