ACIDS AND BASES

Topics covered in this chapter:

2.1 Electrolytes

Strong Electrolytes

- Are good conductors of electricity in aqueous solution because they completely ionise (covalent molecular substances) or dissociate (ionic substances).

- Ionic substances are all strong electrolytes even if only slightly soluble since any amount dissolved completely breaks up into ions.

- Strong acids are also strong electrolytes as they completely ionise in solution

$$HCl_{(g)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$
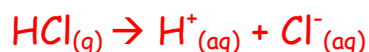
Weak Electrolytes

- Are poor conductors of electricity in aqueous solution.

- Only a small percentage of molecules ionise when dissolved in water and so only a small concentration of ions are produced to conduct charge.

- Weak acids, and weak covalent molecular bases (such as NH_3), tend to be weak electrolytes.

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

The double headed arrow ($\rightleftharpoons$) is used to indicate only a small percentage of molecules ionise.

Non Electrolytes

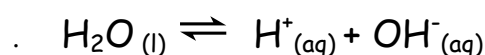Are non-conductors of electricity because no ions are produced when they dissolve in water.

$$C_6H_{12}O_{6\ (s)} \rightarrow C_6H_{12}O_{6\ (aq)}$$
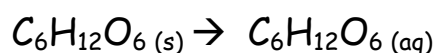
- Glucose molecules dissolve but no ions are formed.

Self-Ionisation of Water

Water, no matter how pure, is always a very weak conductor of electricity. This is due to the self ionisation of water.

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant for the self-ionisation of water is given the symbol K_W.

$$K_W = [H^+][OH^-] = 1.00 \times 10^{-14} \text{ at } 25\ ^OC$$

ACIDIC SOLUTIONS

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

- $[H^+] > 1.00 \times 10^{-7}$ at 25 ^{O}C

- $[OH^-] < 1.00 \times 10^{-7}$ at 25 ^{O}C

BASIC SOLUTIONS

- $[H^+] < [OH^-]$

- $[H^+] < 1.00 \times 10^{-7}$ at 25 ^{O}C

- $[OH^-] > 1.00 \times 10^{-7}$ at 25 ^{O}C

NEUTRAL SOLUTIONS

- $[H^+] < [OH^-]$

- $[H^+] < 1.00 \times 10^{-7}$ at 25 ^{O}C

- $[OH^-] > 1.00 \times 10^{-7}$ at 25 ^{O}C

2.2 The pH scale

- The pH of a solution is a measure of its acidity. It depends on the hydrogen ion concentration.

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

Where pH < 7 acidic

pH = 7 neutral

pH > 7 basic

Worked Examples

2.1 Calculate the $[OH^-]$ of a 2.00×10^{-2} mol L^{-1} solution of HCl.

2.2 Calculate the $[H^+]$ of a 0.350 mol L^{-1} solution of $Ba(OH)_2$.

2.3 Calculate the final pH of a solution made by mixing 25.0 mL of 0.0750 mol/L HCl with 32.5 mL of 0.0675 mol/L KOH

2.1 Summary Questions

1. Calculate the pH of a 1.00 L of an antacid solution that contained 50.0 mg of $Mg(OH)_2$ as its main ingredient.

2. Determine the $[H^+]$ and the $[OH^-]$ of a sample of orange juice that had a pH of 3.60

3. At 50.0 °C, pure water was found to have a K_w of 5.48×10^{-14}. Determine the pH of the water at 50.0 °C

4. A sample of sulfuric acid was found to have a pH of 2.5 at 50.0 °C. Determine the $[OH^-]$ of this sample.

5. Calculate the final pH of a solution when 47.5 mL of 0.540 mol L^{-1} HNO_3 is mixed with 55.5 mL of 0.444 mol L^{-1} NaOH.
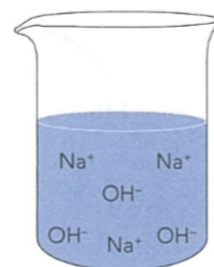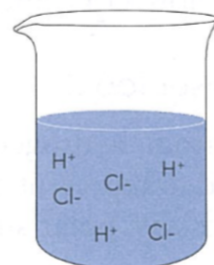
2.3 Theories on Acids and Bases

Arrhenius Theory

- Acids produce hydrogen ions in aqueous solutions

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$
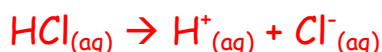
- Bases provide hydrogen ions in aqueous solutions

$$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

The Arrhenius model is restricted to aqueous solutions and so a more general theory with wider application was proposed known as the Brønsted-Lowry Theory.

Brønsted-Lowry Theory

- Acids act as a proton (H^+) donors
- Bases act as a proton (H^+) acceptors.

<u>Example 1</u>

$$HCl_{(aq)} + NH_{3(aq)} \rightleftharpoons NH_4^+_{(aq)} + Cl^-_{(aq)}$$

HCl is acting as an acid by donating a proton (H^+) to NH_3 and NH_3 is acting as a base as it accepting a proton.

Example 2

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

H_2O is acting as an acid (proton donor). NH_3 is acting as a base (proton acceptor).

Example 3

$$H_2PO_4^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HPO_4^{2-}{}_{(aq)} + H_3O^+{}_{(aq)}$$

$H_2PO_4^-{}_{(aq)}$ is acting as an acid (donating a proton). $H_2O_{(l)}$ is acting as a base (accepting a proton).

Conjugated acids and bases

When an acid loses (donates) a proton, what is left behind is its conjugated base. Similarly, when a base accepts a proton, the substance formed is its conjugated acid.

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

i.e. the conjugated pairs are CH_3COOH/ CH_3COO^- and H_2O/ H_3O^+

2.3 Summary Questions

1. Complete the following equations so as to show HCO_3^- acting as (a) an acid, (b) a base.

$$HCO_3^-\,_{(aq)} + H_2O \rightleftharpoons$$

$$HCO_3^-\,_{(aq)} + H_2O \rightleftharpoons$$

2. Complete the following tables.

a.

Acid	Conjugated base
HCl	
H_2SO_4	
HF	
H_2S	
HCO_3^-	

b.

Base	Conjugated acid
CO_3^{2-}	
NH_3	
$H_2PO_4^-$	
F^-	
HSO_4^-	

3. Identify and list the conjugated acid/base pairs in each of the following

    a. $NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + NH_{3(aq)}$

    b. $NH_{3(aq)} + PO_4^{3-}{}_{(aq)} \rightleftharpoons NH_2^-{}_{(aq)} + HPO_4^{2-}{}_{(aq)}$

2.4 Strength of acids and bases

- **Strong acids** completely ionise in water. For example, hydrogen chloride molecules in solution exist essentially as hydrogen ions, H^+ and Chloride ions Cl^-.

  ○ e.g. $HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

- **Weak acids** only partly ionise in water. For example, an ethanoic acid solution contains mostly CH_3COOH molecules.

  ○ e.g. $CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$

- **Strong bases** completely *dissociate* in water to produce hydroxide (OH^-) ions (the dissociation is simply the break up of ions that already exist within the ionic compound.

  e.g. $NaOH_{(s)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

- **Weak bases** only partly react with water in forming hydroxide (OH^-) ions. Apart from ammonia (NH_3), most bases are anions such as CO_3^{2-} and CH_3COO^- which react with water to produce OH^- ions.

  ○ e.g. $NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$

  ○ $CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$

Hydrolysis of Salts

Hydrolysis is the process in which an ion reacts with water to produce H_3O^+ ions or OH^- ions. Ions that produce H_3O^+ are said to be acidic while ions that produce OH^- are said to be basic.
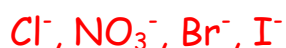
Acidic Anions:

HSO_4^- and $H_2PO_4^-$

(i.e. anion from a polyprotic acid)

Basic Anions:

CH_3COO^-, HPO_4^{2-}, PO_4^{3-}, SO_4^{2-}, F^-, HCO_3^{2-}, ClO^-, HS^-, CN^-

Neutral Anions:

Cl^-, NO_3^-, Br^-, I^-

Acidic Cations:

NH_4^+, Al^{3+}, Fe^{3+}

Basic Cations

There are no basic cations covered in this course.

Neutral Cations

Na^+, K^+, Ca^{2+}, Mg^{2+}, Li^+, Ba^{2+}

(Group 1 and 2 metal cations)

Worked Example:

1. Determine whether the hydrolysis of the following salts will result in an acid or basic solution.

    a. Na_2SO_4

    b. NH_4Cl

2.4   Summary Questions

- Determine whether the following hydrolysis reaction will become acidic, basic or neutral.

    a. $NH_4^+{}_{(aq)}$

    b. CO_3^{2-}

    c. F^-

    d. HSO_4^-

    e. ClO^-

- Complete the following table and predict the nature of each salt solution as being acidic, basic or neutral.

Salt Solution	Constituents	Nature
$NH_4NO_{3(aq)}$		
$NaCl_{(aq)}$		
$Na_2NO_{3(aq)}$		
$KH_2PO_{4\ (aq)}$		
$MgF_{2\ (aq)}$		
$Ca(ClO)_{2\ (aq)}$		
$K_2SO_{4(aq)}$		

2.5 Buffer Solutions

- Buffer solutions are mixtures of a weak acid and its conjugate base or of a weak base and its conjugated acid.

- The advantage of buffer solutions is that they can maintain a relatively constant pH when small quantities of acidic or basic materials are added to them.

- For a buffer to work, the amount of weak acid and its conjugated base must be large compared to the amount of H^+ and OH^- being added or removed.

Buffer Capacity

- Buffer capacity is the ability of the buffer to resist changes in pH.
- It refers to the amount of H^+ or OH^- that can be added without causing a change to the pH of the buffer solution.

- The buffering capacity increases as the concentration of the acid/conjugated base pair increase.
- The greater the concentration of the acid/conjugated base pair, the greater the amount of H^+ or OH^- that can be added without overwhelming the buffer's capacity to maintain a constant pH.

- Exercise tends to increase the acidity (reduce the pH) of the blood. The presence of H_2CO_3 and its conjugated base, HCO_3^- helps to maintain the bloods pH at 7.4

$$H_2CO_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCO_3^-_{(aq)}$$

    Acid   Conjugate Base

  - During exercise, more H_3O^+ is released into the blood from the muscles.
  - Le Châtelier's Principle predicts that the reverse reaction would be favoured to partially counteract the increase in $[H_3O^+]$ and effectively maintain a relatively constant pH.

2.5   Summary Questions

1. Another buffer solution in blood is the $H_2PO_4^-/HPO_4^{2-}$ combination.

    a. Write the equation for the reaction of the acidic ion, $H_2PO_4^-{}_{(aq)}$ with water.

    b. Identify the acid/base conjugated pairs in the equation.

    c. Use Le Châtelier's Principle to predict how this combination would respond to the addition of OH^- to the blood.

2. A 50, 000 L swimming pool had a pH of 7.6

    a. What would be the expected new pH if 100 mL of 12.0 mol/L of HCl was added to the pool?

b. After adding the 100mL of 12.0 mol/L HCl to the pool, the owner measured the pH and found it to be 7.2. Account for the difference between the pH calculated in part (a) and the value obtained by the owner.

c. Suggest what chemicals could be added to the pool to form a buffer solution. Write the equilibrium equation for this buffering solution and suggest two points to consider when choosing a suitable buffer for a swimming pool.

2.6 Volumetric Analysis

- Volumetric analysis is a quantitative method of chemical analysis.
- In a titration, a solution of an accurately known concentration is reacted with a solution of unknown concentration.

- By comparing the reacting volumes, we can determine the concentration of the unknown. This is known as **titration.**

- The two types are:
    - o Acid-base titration
    - o Redox titration

Acid-base Titrations

- These involves reactions between solutions of acids and bases.

- The point at which the reaction is complete is referred to as the equivalence point when reactants are in stoichiometric proportions.

- This is often not visible, as acids and bases are colourless, and so an indicator or a pH meter is required.

- Since the products of an acid-base reactions may acidic, basic or neutral, it is important to choose an indicator so that the end point matches the equivalence point.

- An appropriately chosen indicator will show a colour change (end point) when the reaction is complete (equivalence point).

Indicator	pH range	Colour change acid/base	Suitable for
Methyl orange	3.1 – 4.4	Red → yellow	Strong acid + weak base e.g. $HCl + NH_3$
Methyl red	4.2 – 6.3	Red → yellow	Strong acid + strong base e.g. $HCl + NaOH$
Phenolphthalein	8.3 – 10.0	Colourless → pink	Weak acid + strong base e.g. $CH_3COOH + NaOH$

Changes in pH during acid-base Titrations

(i)   Strong acid – strong base
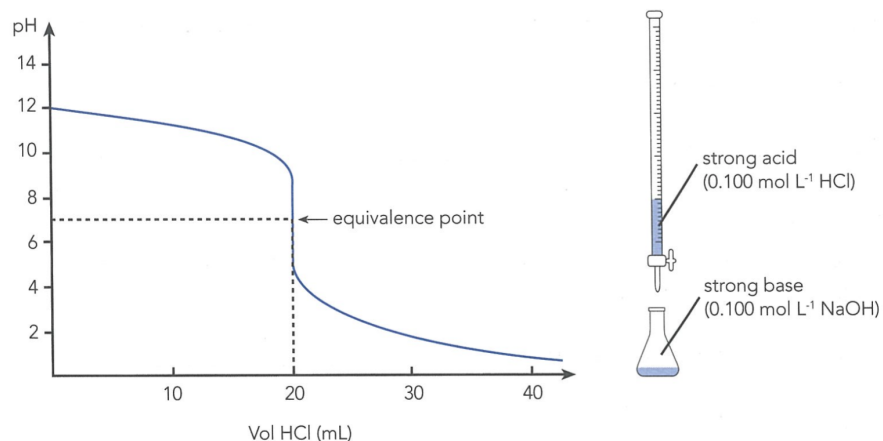
- Equivalence point pH = 7.

- Suitable indicator: Methyl red or phenolphthalein. Methyl red often preferred.

(ii)   Strong acid – weak base
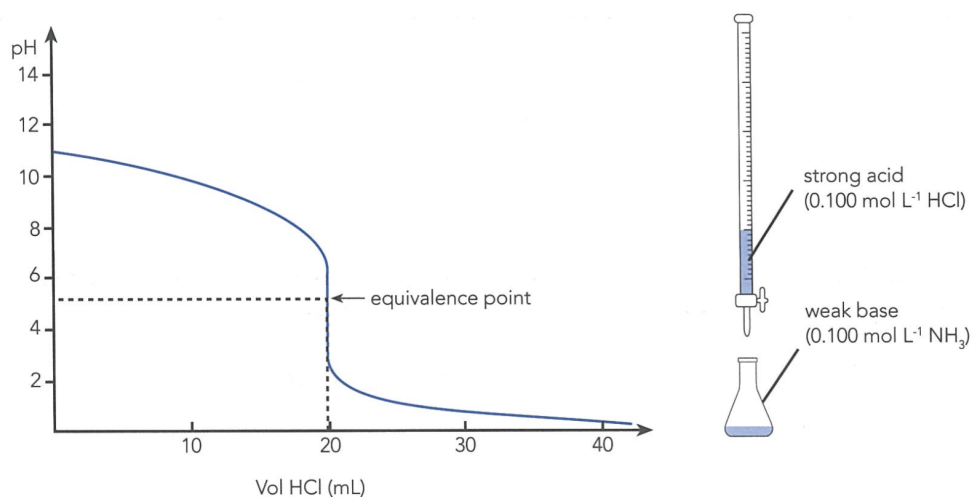
- Equivalence point pH ≈ 5.5

- Suitable indicator: Methyl orange

(iii) Strong acid – weak base

pH axis with values 14, 12, 10, 8, 6, 4, 2; horizontal axis Vol CH_3COOH (mL) with values 10, 20, 30, 40. Curve with equivalence point marked.

weak acid (0.100 mol L^{-1} CH_3COOH)

strong base (0.100 mol L^{-1} NaOH)
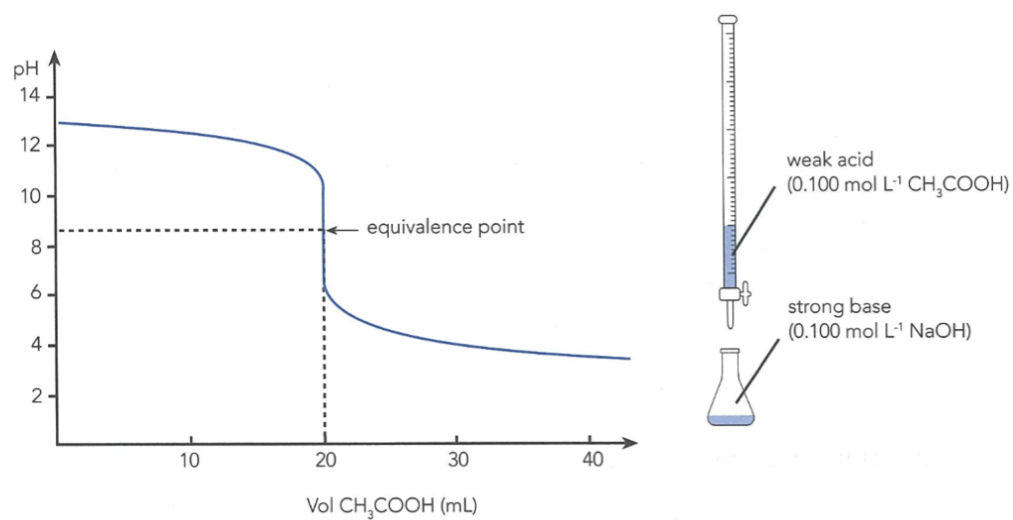
- Equivalence point pH ≈ 9

- Suitable indicator: phenolphthalein.

2.6A Summary Questions

1. A student carrying out a titration between HCl acid and ammonia solution used phenolphthalein as an indicator.

(a). Is this an appropriate indicator?

(b). Explain clearly why/why not

Primary Standards

- A primary standard is required to establish the concentration of unknown solutions.

- Some characteristics of a good primary standards are:
    - High purity and known formula
    - Does not react with water
    - Reasonably high molar mass
    - Soluble in water.

Two commonly used primary standards are anhydrous sodium carbonate (Na_2CO_3) and hydrated oxalic acid ($H_2C_2O_4.2H_2O$).

<u>Worked Example</u>

1. A student prepared a primary standard of Na_2CO_3 by dissolving 1.320g of pure anhydrous sodium carbonate and making it up to 250.0 mL in a volumetric flask.

   This solution was used to standardise some HCl acid. A 20.00 mL aliquot of Na_2CO_3 solution required on average 21.20 mL of the acid for a complete reaction.

   Calculate:

   a. The concentration of the Na_2CO_3 solution
   b. The concentration of the HCl solution.

(b)   the concentration of the HCl solution.

(a) $n = \dfrac{m}{M}$

(b) $Na_2CO_{3(aq)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$

 20.00 mL   21.20 mL

$M(Na_2CO_3)$ = 22.99 × 2
 + 12.01
 + 48.00
 $\overline{105.99}$ g mol^{-1}

0.0498 mol L^{-1}

$n(Na_2CO_3)_{(aq)}$ used in the titration

$= cV = (4.98 \times 10^{-2})(0.0200) = 9.9616 \times 10^{-4}$ mol

$n = (Na_2CO_3) = \dfrac{1.320}{105.99}$

∴ $n(HCl)$ in 21.20 mL $= (2)(9.9616 \times 10^{-4})$

$ = 0.012454$ mol

from equation $= 1.992 \times 10^{-3}$ mol

$c = \dfrac{n}{V}$

∴ $c(HCl) = \dfrac{n}{V} = \dfrac{1.992 \times 10^{-3}}{0.02120}$

∴ $c(Na_2CO_3) = \dfrac{0.012454}{0.2500}$

$\phantom{∴ c(HCl) = \dfrac{n}{V}} = 9.40 \times 10^{-2}$ mol L^{-1}

$ = 4.98 \times 10^{-2}$ mol L^{-1}

2. A 1.252g sample of an oven cleaner containing mostly sodium hydroxide was dissolved and made up to 250.0 mL using a volumetric flask. A 20.00 mL aliquot of this solution was titrated against 0.0950 mol L –1 HCl and required 23.85 mL of this acid to reach the end point. Calculate the percentage (by mass) of NaOH in the oven cleaner.

Hint: the 1.252g is the mass of the oven cleaner and not the mass of NaOH. In this problem we work backwards from the titration to find out how much NaOH was actually in the sample.

2.6B Summary Questions

Question 1

1. A 15.50 g sample of commercial vinegar was diluted and made up to 250.0 mL in a volumetric flask. A 20.00 mL aliquot of this diluted vinegar required 17.75 mL of a 0.05050 mol L^{-1} NaOH solution for complete neutralisation.

    a. What indicator would have been suitable for this titration?

    b. Determine the % by mass of ethanoic acid in the commercial vinegar sample.

    c. Determine also the concentration of ethanoic acid in commercial vinegar (in mol L^{-1} and g L^{-1}). Assume that the density of vinegar is 1.00 g mL^{-1}.

Question 2

a. An oxalic acid solution was prepared by dissolving 0.554 g of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) in distilled water and making it up to 500.0 mL in a volumetric flask. Determine its concentration.

b. The solution was placed in a burette and used to standardise a NaOH solution. A 20.00 mL aliquot required 19.65 mL of the oxalic acid solution to reach the end point.

(i) Name an appropriate indicator for this titration.

(ii) What is the colour change at the end point?

(iii) Calculate the concentration of the NaOH solution.

c. The NaOH solution was used to determine the concentration of a diluted vinegar solution. A 20.00 mL aliquot of NaOH solution required 32.50 mL of diluted vinegar solution to complete the reaction.

        (i) Name an appropriate indicator for this titration?

        (ii)   What is the colour change at the end point?

        (iii)   Calculate the concentration of ethanoic acid (CH_3COOH) in the diluted vinegar solution.