Year 12 Chemistry

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Contents

Chapter 1

Module 5 Equilibrium and Acid Reactions

1.1 Practical Investigation 2.1

Aim: To determine whether chemical reactions are reversible or not

1.1.1 Materials

- 25 mL dropper bottle of $1\,\mathrm{mol\,L^{-1}}$ cobalt(II) chloride hexahydrate
- 25 mL dropper bottle of $0.05\,\mathrm{mol\,L^{-1}}$ potassium chromate
- 25 mL dropper bottle of $0.05\,\mathrm{mol\,L^{-1}}$ potassium dichromate
- 25 mL dropper bottle of $0.1\,\mathrm{mol\,L^{-1}}$ hydrochloric acid
- 25 mL dropper bottle of $0.1\,\mathrm{mol\,L^{-1}}$ sodium hydroxide
- 1 $\times$ 5 cm piece of magnesium ribbon
- Distilled water
- 1 piece of filter paper (55 mm $\times$ 55 mm)
- 3 watch glasses
- 1 drying oven/incubator
- 4 test tubes
- Test-tube rack
- 4 small labels
- 1 pair brass tongs
- 1 $\times$ (5 cm $\times$ 5 cm) piece of sandpaper

- 1 × (5 cm × 5 cm) piece of steel wool
- Gas lighter
- Dropper
- Video camera
- Safety glasses and gloves

1.1.2 Risk Assessment

Hazard	Precaution
Shattering glassware	Keep beakers, test tubes, and watch glasses in centre of table
Exposure to harmful chemicals	Wear gloves and eye glasses. Handle with caution
Burns from Bunsen burner	Keep on safety flame when not in use

1.1.3 Method

Part A

1. Place a piece of filter paper on a watch glass.
2. Add cobalt chloride drop by drop until the filter paper is covered.
3. Observe the colour of the filter paper.
4. Place the watch glass into a drying oven overnight at $35\,^{\circ}\mathrm{C}$.
5. Remove the watch glass and filter paper and observe the colour of the filter paper.
6. Add distilled water drop by drop to the same filter paper until it is covered.
7. Observe the colour of the filter paper.
8. Repeat steps 4 and 5.

Part B

1. Label four test tubes A, B, C and D.
2. Add about 1 mL of potassium chromate to test tubes A and B.
3. Add about 1 mL of potassium dichromate to test tubes C and D.
4. Test tubes A and C are reference solutions.
5. Add hydrochloric acid dropwise to test tube B until a colour change occurs.
6. Record your observations.
7. Add sodium hydroxide dropwise to test tube B until another colour change occurs.
8. Record observations.

9. Add sodium hydroxide dropwise to test tube D until a colour change occurs.
10. Record observations.
11. Add hydrochloric acid dropwise to test tube D until another colour change occurs.
12. Record observations

Part C

1. Clean a 5 cm piece of magnesium with sandpaper.
2. Hold the piece of magnesium ribbon with a pair of brass tongs.
3. Light the magnesium ribbon and hold it over a watch glass. Do not look directly at the magnesium while it is alight.
4. Record observations.

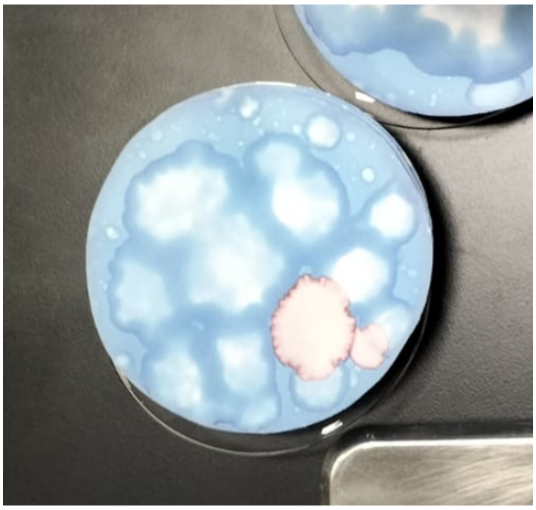
Part D

1. Hold a piece of steel wool with a pair of brass tongs.
2. Light the steel wool and hold it over a watch glass.
3. Record observations

1.1.4 Results

Part A

- When dehydrated, filter paper was blue when saturated with cobalt chloride
- When rehydrated, became pink



Part B

- Potassium chromate → initially bright yellow
- Potassium dichromate → initially orange
  - HCL → greenish-yellow
  - NaOH → darker yellow/orange
- $2\,\mathrm{CrO_4}^{2-} + 2\,\mathrm{H}^+ \rightleftharpoons \mathrm{Cr_2O_{72}}^{2-} + \mathrm{H_2O}$
- $\mathrm{K_2Cr_2O_7} + 2\,\mathrm{KOH} \rightleftharpoons 2\,\mathrm{K_2CrO_4} + \mathrm{H_2O}$

Part C

Part D

1.2 Le Chatelier's Principle

"If a system at equilibrium is subject to a change in conditions, then the system will behave in such a way so as to partially counteract the imposed change"

Haber process:

1.2.1 Effect of Concentration

$$\mathrm{N_{2(g)}} + 3\,\mathrm{H_{2(g)}} \rightleftharpoons 2\,\mathrm{NH_{3(g)}} \quad \Delta\mathrm{H}^{\circ} = -92.5\,\mathrm{kJ\,mol^{-1}} \tag{1.1}$$

1.2.2 Effect of Pressure

1.2.3 Effect of Partial Pressure

1.2.4 Effect of Volume

Decreasing the volume will increase the pressure. (Boyle's Law) This increases the collision rate between the reactants and favours the forward reaction.

1.2.5 Effect of Temperature

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1.2.6 Summary

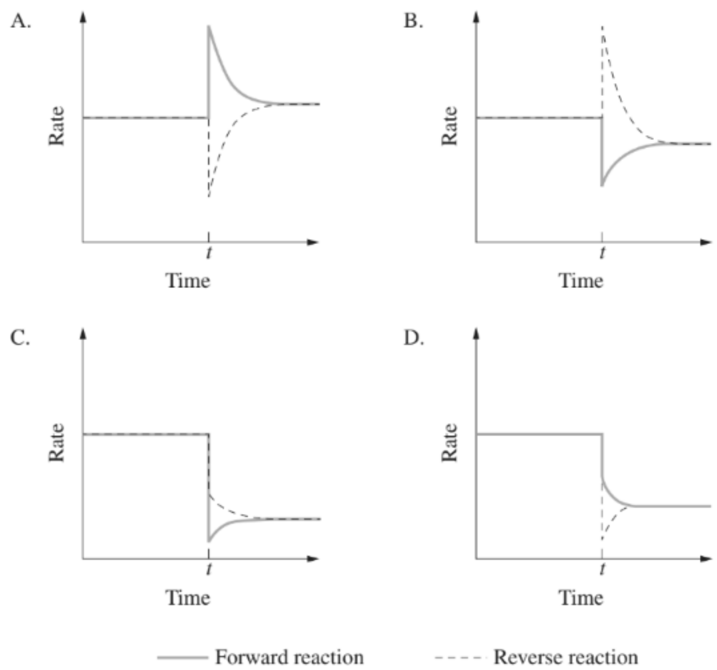
To use Le Chatelier's principle to predict the outcome of a change in conditions, you need to consider the following points.

1. What change is imposed?
2. What is the opposite of the change?
3. Which reaction direction is favoured - the forward or reverse?
4. Does equilibrium shift to the left or right?
5. What happens to the concentrations of each aqueous substance or gas?

19 Nitrogen dioxide reacts to form dinitrogen tetroxide in a sealed flask according to the following equation.

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57.2 \text{ kJ mol}^{-1}$$

Which graph best represents the rates of both the forward and reverse reactions when an equilibrium system containing these gases is cooled at time t?



D When temperature decreases, the rates of both forward and backward reactions will decrease regardless of which way the endothermic or exothermic reaction goes. (A and B can be eliminated)

This is because all the particles in the system lose kinetic energy, decreasing the rate of collisions hence, decreasing the rate of reaction.

However, since there is a decrease in temperature the exothermic reaction will be favoured in order to counteract the change. In this case, the forward reaction being exothermic is affected less by the drop in temperature as shown in D.

1.3 Practical Investigation 2.3 - Effect of changes to concentration on equilibrium

Aim: To observe the effect of a change in concentration on a system at equilibrium

1.3.1 Materials

- 2 mL of 0.1 molL^{-1} iron(III) chloride solution
- 2 mL of 0.1 molL^{-1} ammonium thiocyanate solution
- 1 mL of 0.1 molL^{-1} calcium fluoride solution
- 20 mL distilled water
- 2x 10 mL measuring cylinders
- 25 mL measuring cylinder
- 4 test tubes
- Test-tube rack
- 4 small labels
- Disposable 1 mL droppers
- Waste bottle
- Digital camera
- Safety glasses

1.3.2 Risk Assessment

Hazard	Precaution
Chemicals may splash onto skin or eyes	Wear safety glasses and wash hands
Chemicals may harm aquatic life	Place in inorganic waste container

1.3.3 Method

1. Pour 1 mL of iron(III) chloride solution into a 10 mL measuring cylinder.
2. Pour 1 mL of ammonium thiocyanate into another 10 mL measuring cylinder.
3. Pour both solutions into the 25 mL measuring cylinder.
4. Add 18 mL of distilled water to the 25 mL measuring cylinder so that the total volume is 20 mL.
5. Label four test tubes A, B, C and D.
6. Pour equal volumes of the solution in the 25 mL measuring cylinder into each of the test tubes.

7. Retain test tube A as the reference solution.

8. Add 1 mL of iron(III) chloride to test tube B.

9. Take a photo to record observations for test tube B relative to test tube A.

10. Add 1 mL of ammonium thiocyanate to test tube C.

11. Take a photo to record observations for test tube C relative to test tube A.

12. Add 1 mL of calcium fluoride to test tube D. (Note: This reacts with the iron(III) ion so there is less iron(III) available to react with the thiocyanate ion.)

13. Take a photo to record observations for test tube D relative to test tube A

1.3.4 Results

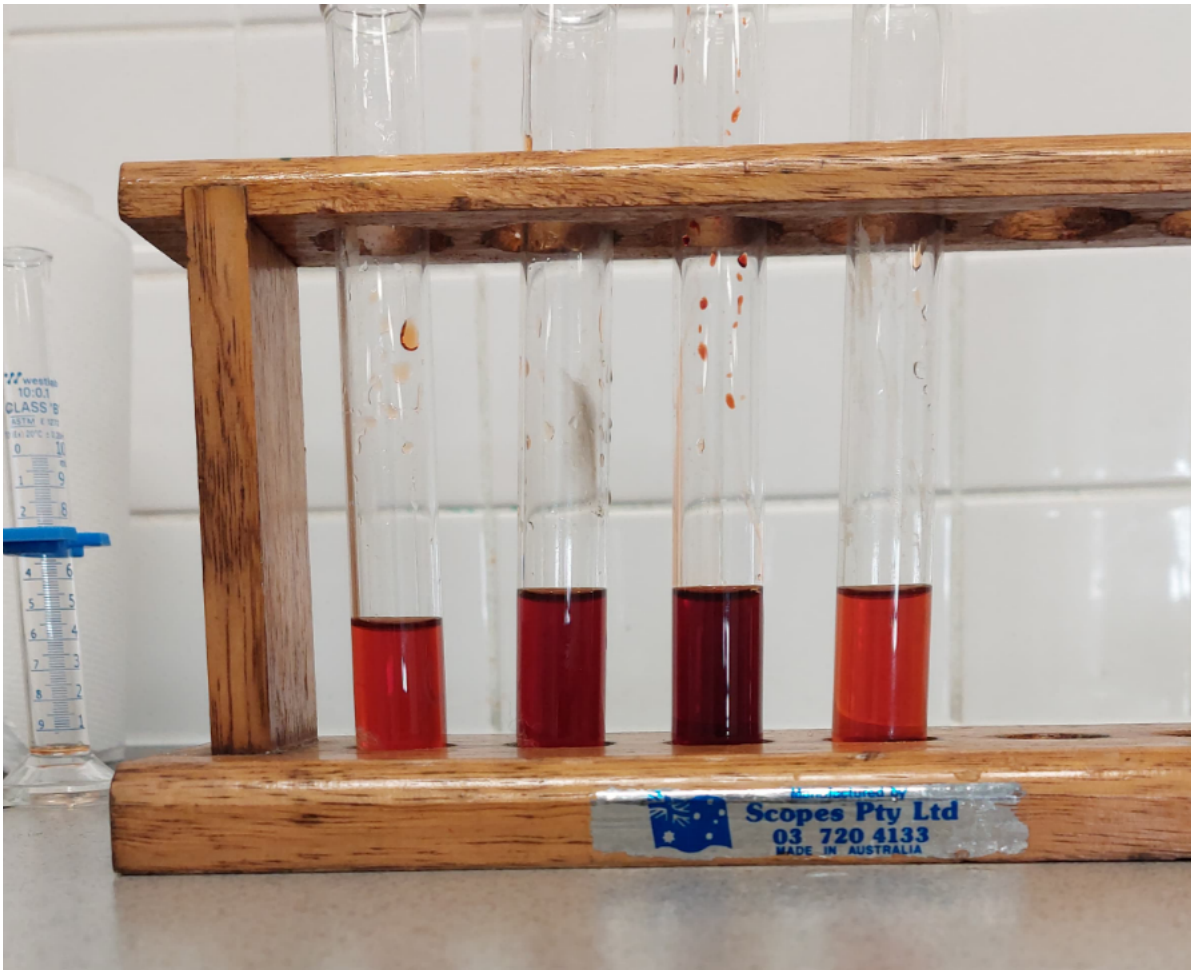


Figure 1.1: Test tubes A, B, C, D

1.3.5 Discussion

Explain each colour change in terms of collision theory.

The test tube B was darker in colour in comparison to test tube A. The increase in moles of reactants allows more successful collisions to occur, increasing the amount of product. The same principle applies to test tube C.

Test tube D was lighter in colour compared to A, due to the calcium fluoride reacting with the iron (III) chloride

1.3.6 Conclusion

Use Le Chatelier's principle to explain what happened in test tubes B, C and D.

Test tube B was darker due to the increase in concentration of the reactant iron (III) chloride causes a shift of the equilibrium towards the products due Le Chatelier's principle

Test tube C was darker due to the increase in concentration of the reactant ammonium thiocyanate causes a shift of the equilibrium towards the products due Le Chatelier's principle

Test tube D was lighter because the calcium fluoride reacted with the iron (III) chloride, lowering the overall concentration of iron (III) chloride. This reduced the amount of reactants available, making the reverse reaction more favourable by Le Chatelier's principle.

1.4 Calculating the Equilibrium Constant

The equilibrium constant can be used to predict the direction of chemical reactions

$$K_{eq} = \frac{[products]}{[reactants]}$$

For reaction:

$$\mathrm{aA + bB \rightleftharpoons cC + dD}$$

the equilibrium expression is:

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The concentration of each chemical species is raised to the power of the number of moles of that species indicated in the chemical equation. (Eg. there are d moles of species D, hence in the equilibrium expression the concentration of species D is raised to the power of d, written as $[D]^d$)

- The value for the equilibrium constant only takes into account the concentration of substances where the concentration can vary
- Solutions and gases can vary in concentration or partial pressure hence are included in K_{eq}
- Solids and pure liquids are NOT included eg. $\mathrm{H_2O}$ isn't required when calculating

1.4.1 Reaction Quotient

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Has the same formula as K_{eq}, however applies to any stage of a reaction

1.4.2 Equilibrium Constant

- Comparing Q to K_{eq} predicts which way the equilibrium will shift
- K_{eq} is where the equilibrium lies
- A large K_{eq} means that there are more products than reactants; ie. equilibrium lies towards completion
- If K_{eq} is close to one, both reactants and products are plentiful at equilibrium

Example Let $Q = 2.1$, $K_{eq} = 0.315$, $\therefore$ products>reactants.

1.4.3 Calculating the equilibrium expression

Consider the reaction between hydrogen and iodine producing hydrogen iodide:

$$\mathrm{H_{2(g)} + I_{2(g)} \rightleftharpoons 2\,HI_{(g)}}$$

1.5 ICE Tables

	[A]	[B]	[C]
Initial concentration			
Change in concentration			
Equilibrium concentration			

$$\Delta c = c_{eq} - c_u$$

Eg. $\mathrm{A + B \rightleftharpoons C + D}$

	[A]	[B]	[C]	[D]
Initial concentration	0.6	0.6	0	0
Change in concentration	-0.5	-0.5	+0.5	+0.5
Equilibrium concentration	0.1	0.1	0.5	0.5

Eg. $\mathrm{2\,X_{(g)} \rightleftharpoons 3\,Y_{(g)} + 4\,Z_{(g)}}$

A sample consisting of 0.500 mol of X is placed into a system with a volume of 0.750 litres.
At equilibrium, the amount of sample X is known to be 0.350 mol.

	X	Y	Z
I	0.5	0	0
C			
E	0.35		

	X	Y	Z
I	0.5	0	0
C	-0.15	-0.225	+0.3
E	0.35	0.225	0.3

$$[X] = \frac{0.35}{0.75} = 0.467$$
$$[Y] = \frac{0.225}{0.75} = 0.3$$
$$[Z] = \frac{0.3}{0.75} = 0.4$$

1.6 Effect of Temperature on the Equilibrium Constant

Although other factors may affect equilibrium, K_{eq} is only affected by temperature. Changing concentration, pressure, or volume will change the concentrations and therefore adjust the reaction point, however the reaction will still equalise to achieve the same K_{eq}

- For a particular reaction, K_{eq} is constant at a given temperature
- Temperature changes the ratio of products and reactants, hence changing K_{eq}
- For $N_2O_{2\,(g)} \rightleftharpoons 2\,NO_{2\,(g)}$, temperature increases the K_{eq} value and favours the formation of products. The forward reaction is endothermic

1.6.1 Example Question

Nitric oxide gas (NO) can be produced from the direct combination of nitrogen gas and oxygen gas in a reversible reaction.

1. **Write a balanced chemical equation for this reaction (1 mark)**

   $N_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2\,NO_{(g)}$

2. **Explain, using collision theory, how an increase in temperature would affect the value for K_{eq} for this system. Refer to the diagram in your answer.**

   An increase in temperature would favour the forward reaction, hence K_{eq} will increase. More energy allows more collisions to occur

$$K_{eq} = \frac{[p_1][p_2]}{[r_1][r_2]}$$
$$1 = \frac{[1][1]}{[1][1]}$$

If p_2 decreases to $[0.5]$, favouring the forward reaction

$$= \frac{[1.15][0.65]}{[0.85][0.85]}$$
$$= K_{eq}$$

1.7 Applications of the Equilibrium Constant

1.7.1 Use of the Equilibrium Constant for the Dissociation of Ionic Solutions

Different ionic compounds have different solubilities

Example reaction

$$AgNO_3\,_{(aq)} + NaCl\,_{(aq)} \longrightarrow AgCl\,_{(s)} + NaNO_3\,_{(aq)}$$

Complete ionic equation: $Ag^+ + NO_3{}^- + Na^+ + Cl^- \longrightarrow AgCl\,_{(s)} + NO_3{}^- + Na^+$

Net ionic equation: $Ag^+\,_{(aq)} + Cl^-\,_{(aq)} \longrightarrow AgCl\,_{(s)}$

Although a precipitate is formed, the reaction rests at a dynamic equilibrium where the rate at which the precipitate is formed is equal to the rate at which the ions are formed.

$$AgCl\,_{(s)} \rightleftharpoons Ag^+\,_{(aq)}\, Cl^-\,_{(aq)}$$

- By general practice, the solid precipitate is written on the left and the ions on the right.
- $K_{sp} = [Ag^+][Cl^-]$
- Since the solid is not included in the equilibrium constant, it is referred to as the **solubility product** (K_{sp})
- If the system is not at equilibrium, it is referred to as the **ionic product**
- If ionic product $= K_{sp}$, then the system is at equilibrium.
- If ionic product $< K_{sp}$, the forward reaction would be favoured and the solid would dissolve for the system to reach equilibrium.
- If ionic product $> K_{sp}$, the reverse reaction would be favoured and more precipitate would form for the system to reach equilibrium.

1.7.2 Use of the Equilibrium Constant for the Dissociation of Acids and Bases

Acids

Strong acids dissociate completely in solution. The reaction goes to completion and is not an equilibrium system

Eg: $HCl_{(l)} \longrightarrow H^+{}_{(aq)} + Cl^-{}_{(aq)}$

Weak acids do not dissociate completely, instead forming an equilibrium system

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

The acid dissociation constant is expressed as $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

Bases

Strong bases dissociate completely in solution.

Eg. $NaOH_{(s)} \longrightarrow Na^+{}_{(aq)} + OH^-{}_{(aq)}$

Weak bases do not dissociate completely, only some of the molecules react with water to form ions, they form an equilibrium system

Eg. $NH_3{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_4{}^+{}_{(aq)} + OH^-{}_{(aq)}$

The base dissociation constant is expressed as $K_b = \frac{[NH_4{}^+][OH^-]}{[NH_3]}$

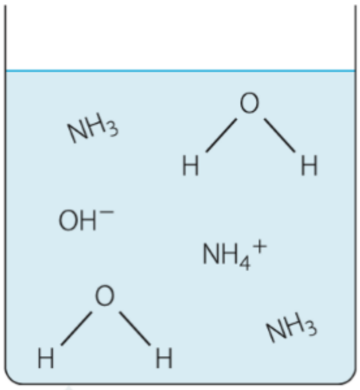


FIGURE 3.3 Some molecules of ammonia react with water to produce ammonium ions and hydroxide ions. This is an example of a dissociation reaction.

Weak Acid

General equation:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + A^-{}_{(aq)}$$

General expression for equilibrium constant:

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

Weak Base

General equation:

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

General expression for equilibrium constant:

$$K_b = \frac{[BH^+][OH-]}{[B]}$$

1.7.3 Use of the Equilibrium Constant for Gaseous Systems

In a gaseous system (where all reactants are gases), the partial pressure of each species is related to its concentration ($c = \frac{n}{V}$)

Pressure is due to the collisions between the gases and the walls of the container, therefore all particles within the system contribute to the pressure.

The **partial pressure** is the proportion of the pressure due to collisions for a particular gas species

For the general equation:

$$\mathrm{aA}_{(g)} + \mathrm{bB}_{(g)} \rightleftharpoons \mathrm{cC}_{(g)} + \mathrm{dD}_{(g)}$$

, where a, b, c and d are the number of moles

$$\text{Mole fraction of gas A} = \frac{\text{Number of moles of gas}}{\text{Total number of moles of gas present}}$$

$$\text{Partial pressure of gas A} = \text{Mole fraction of gas A} \times \text{Total pressure of the system}$$

Expression of equilibrium constant in terms of pressure:

$$K_p = \frac{P_A^a \times P_B^b}{P_C^c \times P_D^d}$$

1.8 Beer Lambert Law

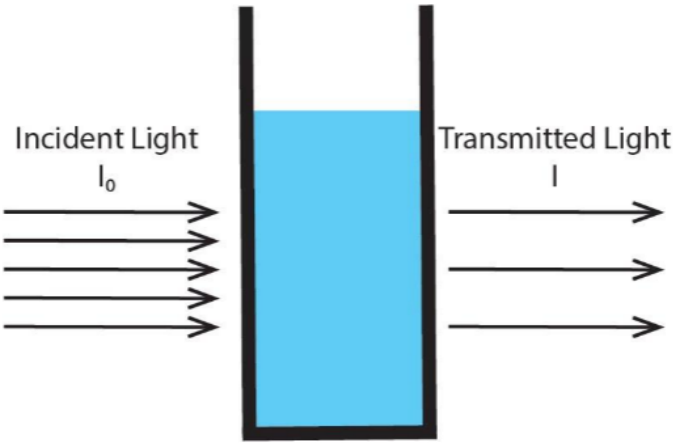
$$\text{Absorbance (for a given wavelength)} = \text{Molar absorbility} \times \text{Path length} \times \text{Concentration}$$
$$A = \varepsilon l c$$

- Absorbance has a direct relationship to concentration
- Greater concentration, greater absorbance

Absorbance can be measured using a spectrophotometer (for all wavelengths) or a colourimeter (for the visible spectrum). Using the formula, the absorbance coefficient (ε) for a given material can be calculated. The coefficient determines how far light can penetrate a material before it is absorbed, depending on the material and the wavelength being absorbed. Measured in $\mathrm{L\,mol^{-1}\,cm^{-1}}$

A filter is applied to the light and must be the complement to the colour of the solution.

Eg: For reaction $\mathrm{Fe_3}^{+}{}_{(aq)} + \mathrm{SCN^-}{}_{(aq)} \rightleftharpoons \mathrm{FeSCN_2}^{+}{}_{(aq)}$ FeSCN is red, $\therefore$ a green filter is needed



$$A = \log_{10} \frac{I_o}{I} = \varepsilon l c$$

1.8.1 Worked Example

A solution thickness of 1 cm transmits 30% incident light.

1. **Calculate the concentration of the solution given the molar absorptivity of the solution being 4000 L mol^{-1} cm^{-1}**

$$A = \log_{10} \frac{100}{30} = 0.523$$
$$\therefore C = \frac{A}{\varepsilon l} = \frac{0.523}{4000 \times 1}$$
$$= 1.31 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$$

2. **Calculate the molar absorptivity of a $1 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ solution which has an absorbance of 0.20, when the path length is 2.5 cm.**

$$A = \varepsilon l c$$
$$0.2 = 1 \times 10^{-4} \times 2.5 \times \varepsilon$$
$$\varepsilon = \frac{0.2}{1 \times 10^{-4} \times 2.5}$$
$$= 800\mathrm{L\,mol^{-1}\,cm^{-1}}$$

3. **Which instrument is used in the verification of Lambert's Beer's law?**

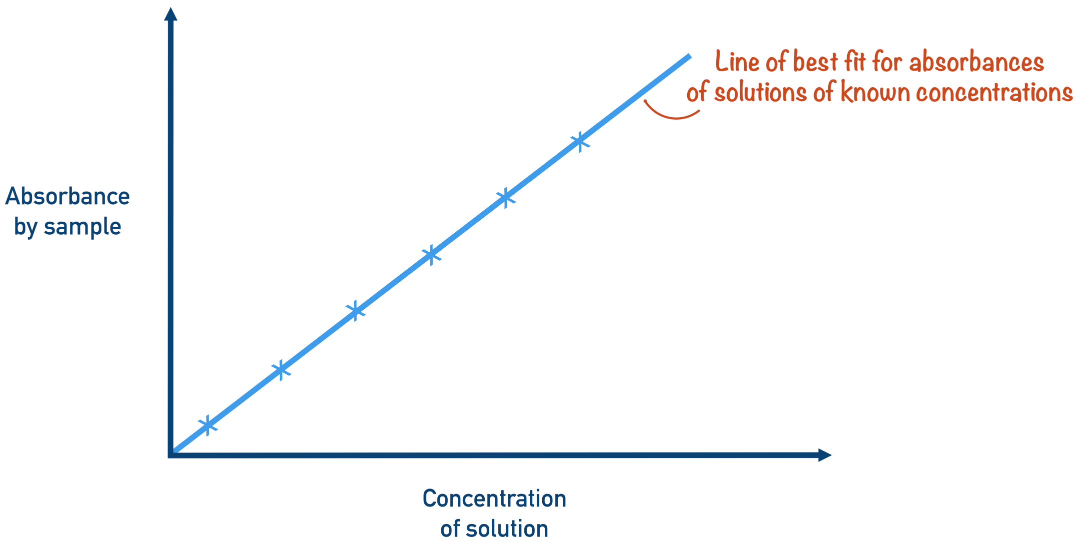
   Colourimeter

4. **Find out the molar absorptivity of a $1 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ solution with an absorbance of 0.30, when the path length is 1.5 cm. (3 marks)**

$$A = \varepsilon l c$$
$$0.3 = \varepsilon \times 1.5 \times 1 \times 10^{-4}$$
$$\varepsilon = 2000\mathrm{L\,mol^{-1}\,cm^{-1}}$$

1.8.2 Colourimeters

In order to determine concentration of a solution from its absorbance, a calibration curve using known concentrations and absorbances must be used to interpolate or extrapolate datapoints corresponding to a desired value.



Beer Lambert's Law collapses at high and low concentrations, where $c < 20\%$, $c > 80\%$

1.9 Practical Investigation 3.2

Aim: To use colourimetry to determine the equilibrium constant for the reaction of iron(III) ions with thiocyanate ions to form the iron(III) thiocyanate ion

1.9.1 Materials

- 200 mL 0.2 $\mathrm{mol\,L^{-1}}$ $Fe(NO_3)_3$
- 100 mL 0.002 $\mathrm{mol\,L^{-1}}$ KSCN
- 500 mL 0.5 $\mathrm{mol\,L^{-1}}$ HNO_3
- 60 mL 0.002 $\mathrm{mol\,L^{-1}}$ $Fe(NO_3)_3$
- 150 mL distilled water
- 6 * 100 mL volumetric flasks
- 5 * 150 mL beakers
- 2 * 100 mL beakers
- 1 * 25 mL bulb pipette
- 2 * 10 mL graduated pipettes
- 1 * 10 mL bulb pipette
- 2 pipette bulbs
- 1 disposable pipette
- Waste bottle

- 14 small labels
- 1 colourimeter and set of cuvettes
- Safety glasses

1.9.2 Risk Assessment

Hazard	Precaution
Breaking glassware	Keep glassware on inside of table, do not run with glassware
Spillage of solutions	Handle with caution, clean any spills immediately
Splashing of solution into eyes	Wear safety goggles

1.9.3 Method

1. Label the six volumetric flasks A-F.
2. Use a 25 mL bulb pipette to transfer 25.00 mL of the 0.200 $\mathrm{mol\,L^{-1}}$ $\mathrm{Fe(NO_3)}$
3. 3 to flask A.
4. Use a graduated 10 mL pipette to transfer 1.00 mL of the 0.002 $\mathrm{mol\,L^{-1}}$
5. KSCN to flask A.
6. Add HNO3 to make a final volume of 100.00 mL.
7. Make solutions with known concentration by pushing equilibrium as far as possible to the products. $\mathrm{HNO_3}$ can be used to reduce the concentration of $\mathrm{H_3O}$
8. Rinse the cuvette with distilled water.
9. $\frac{3}{4}$ fill the cuvette with distilled water and wipe the clear sides.
10. Turn on the colourimeter and turn the light to blue or 470 nm.
11. Use the cuvette with distilled water to calibrate the colourimeter. Note: Orientate the cuvette correctly in the colourimeter so that the light passes through the clear sides of the cuvette.
12. Rinse, a 100 mL beaker with standard solution A - it is easier to pour the solution into the cuvette using a beaker than using a volumetric flask.
13. Rinse, then $\frac{3}{4}$ fill the cuvette with standard solution A and measure the absorbance with the colourimeter.
14. Repeat steps 10 and 11 for the other standard solutions (B-F)

1.10 Solution Equilibria - Dissolution of Ionic Compounds

1.10.1 Solubility Revision

- Ionic compounds consist of a positive cation and negative anion

- Due to the polar nature of water molecules, they can arrange themselves around the ions and overcome the ionic bonding, dissolving the substance into an aqueous solution
- When surrounded by water, the ion becomes a **hydrated ion**
- For an ionic compound to dissolve, the energy required has to be less than or similar to the energy released when hydrated

$$\text{Energy to break lattice} \approx \text{Energy released when ions hydrated}$$

Solubility can be measured in $\mathrm{g\,L^{-1}}$, g/100 g, or g/100 mL

1.10.2 Factors influencing solubility

- Activation energy required to break lattice
- Strength of ionic bonding
- Size of ions
- Charge of ions

1.10.3 Solubility

- The solubility of a solute is the maximum mass in grams that can dissolve in 100 g of the solvent at a given temperature ($\mathrm{g\,L^{-1}}$ can also be used)
- A solution is saturated when no more solute will dissolve at a given temperature
- Heat will increase the solubility of a solute
- Solubility curves show how much of a solute dissolves at a given temperature

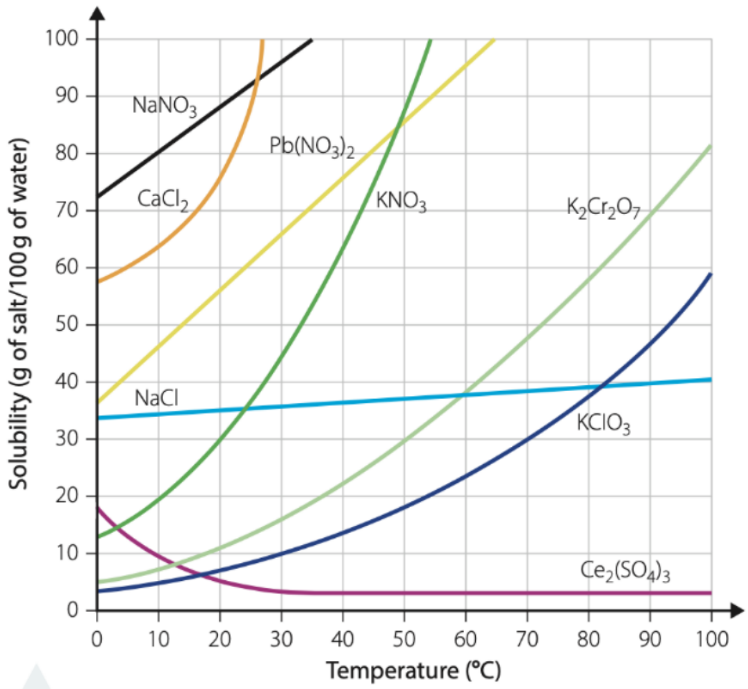


FIGURE 4.8 A selection of solubility curves for various salts

1.10.4 Water of Crystallisation

Water of crystallisation occurs when water molecules are attracted to the ions of a salt

Eg. $CuSO_4 \cdot 5\,H_2O$ is a substance with five water molecules of crystallisation per unit of copper (II) sulphate

Water or other molecules that form dipole bonds to a metal atom are referred to as ligands

The water of crystallisation can be evaporated by heating the hydrated compound and the product is said to be anhydrous

1.10.5 Toxins in Cycad Fruit

Cycad plants are native Australian trees that produce fruits that contain seeds with cone-like structures. There are several types, however most fruits and seeds are poisonous.

They contain two main toxins; cycasin and beta-methylamino-L-alanine (BMAA)

Cycasin and BMAA are types of azoxy glycosides, a group of toxins known to cause severe gastrointestinal issues in humans. These toxins can cause severe liver disorders and impact the functioning of nerves, leading to ataxia.

Cycasin and BMMA are water-soluble and can be dissolved out of the seeds and into the surrounding water.

Leaching involves placing the fruit in water and leaving it to soak, removing the toxins

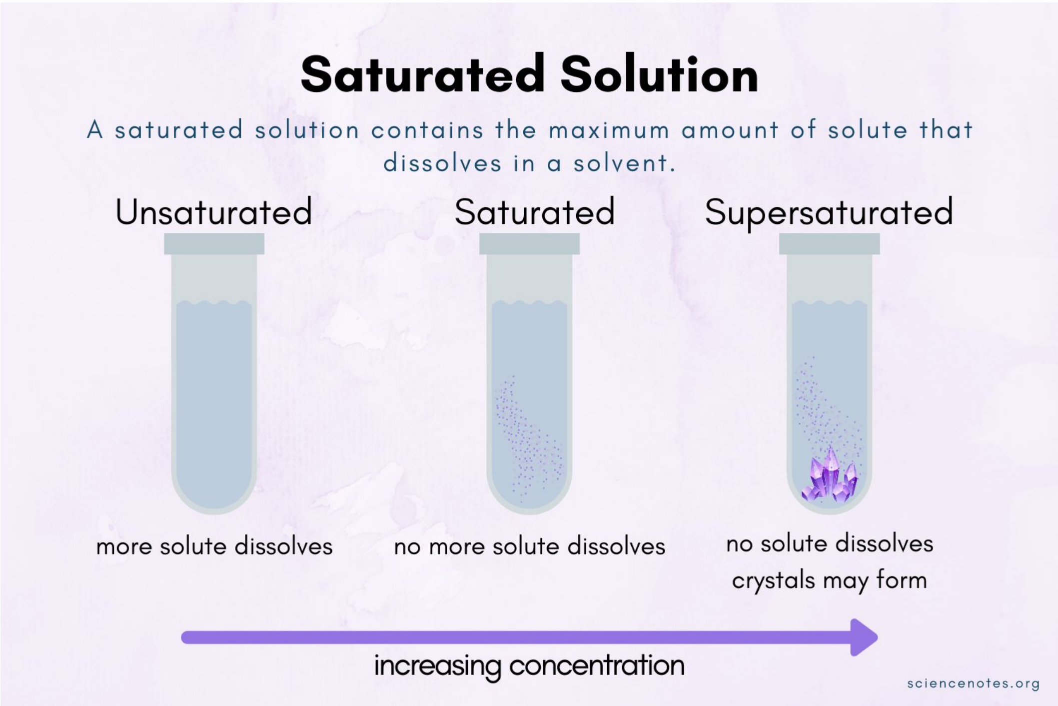
$$\text{Cycasin}_{(s)} \rightleftharpoons \text{Cyasin}_{(aq)}$$

In the above equilibrium, the concentration of toxins in the water is initially zero. By Le Chatelier's Principle, the equilibrium shifts to the right, decreasing the high concentration of solid toxins in the fruit, eventually reaching a dynamic equilibrium. Although some toxins are removed, the system reaches an equilibrium where toxins are still present. To improve the result, running water can be used (ie. an open system) so that the system can never reach an equilibrium. The equilibrium will constantly shift to the right, hence removing most toxins from the seed and fruit.

Other Methods **Cooking** cycad fruit causes the toxins to decompose due to the intense heat. **Fermenting** cycad fruit sees natural processes break toxins down over time.

1.11 Measuring Solubility

- The mass of a substance that dissolves depends upon temperature.
- The solubility of a solute is the maximum mass in grams that can dissolve in 100 g of the solvent at a given temperature.
- Unsaturated solution
- Saturated - solid stays at bottom
- Supersaturated - more solute dissolved than in a saturated solution at the same temperature.
  - If this supersaturated solution is bumped, sugar crystal is added or the side of the glass is scratched, then the extra sugar will precipitate out again.



1.11.1 Solubility Rules

- Solutions of substances dissolved in water are called aqueous solutions. The term "aqueous" comes from the Latin aqua, meaning water.

When ionic substances dissolve in water, they dissociate. This means they separate into their ions, which are then able to move freely and independently of each other through the solution.

Although most ionic compounds are soluble in water, they do not all dissolve to the same extent.

"Soluble" means that a compound dissolves to more than 10 g L-1 (or 1 g/100 mL),

"insoluble" means that it dissolves to less than 1 g L-1, and

"sparingly soluble" means that it dissolves in the range 1 g L-1 to 10 g L-1 .

1.12 Solubility Product

1.13 Practical Investigation 4.2 - Deriving the solubility curve for potassium chloride

Aim: To gather data to draw a solubility curve for potassium chloride

1.13.1 Materials

- Potassium chloride
- Distilled water
- 250 mL
- 10 mL measuring cylinder
- Large test tubes
- Bunsen burner
- Tripod
- Gauze mat
- Boss head and clamp
- Retort stand
- -10-110 °C thermometer
- Stirring rod
- Balance
- Weighing bottle
- Matches
- Test-tube rack
- Wire gauze
- Spatula
- Safety glasses

1.13.2 Risk Assessment

Hazard	Precaution
Burning from Bunsen burner	Do not use the Bunsen burner if the gas tube is damaged.
Poison from chemicals	Do not drink chemicals
Spillage of chemicals	Keep beakers in centre of table. Handle with caution

1.13.3 Scientific Diagram

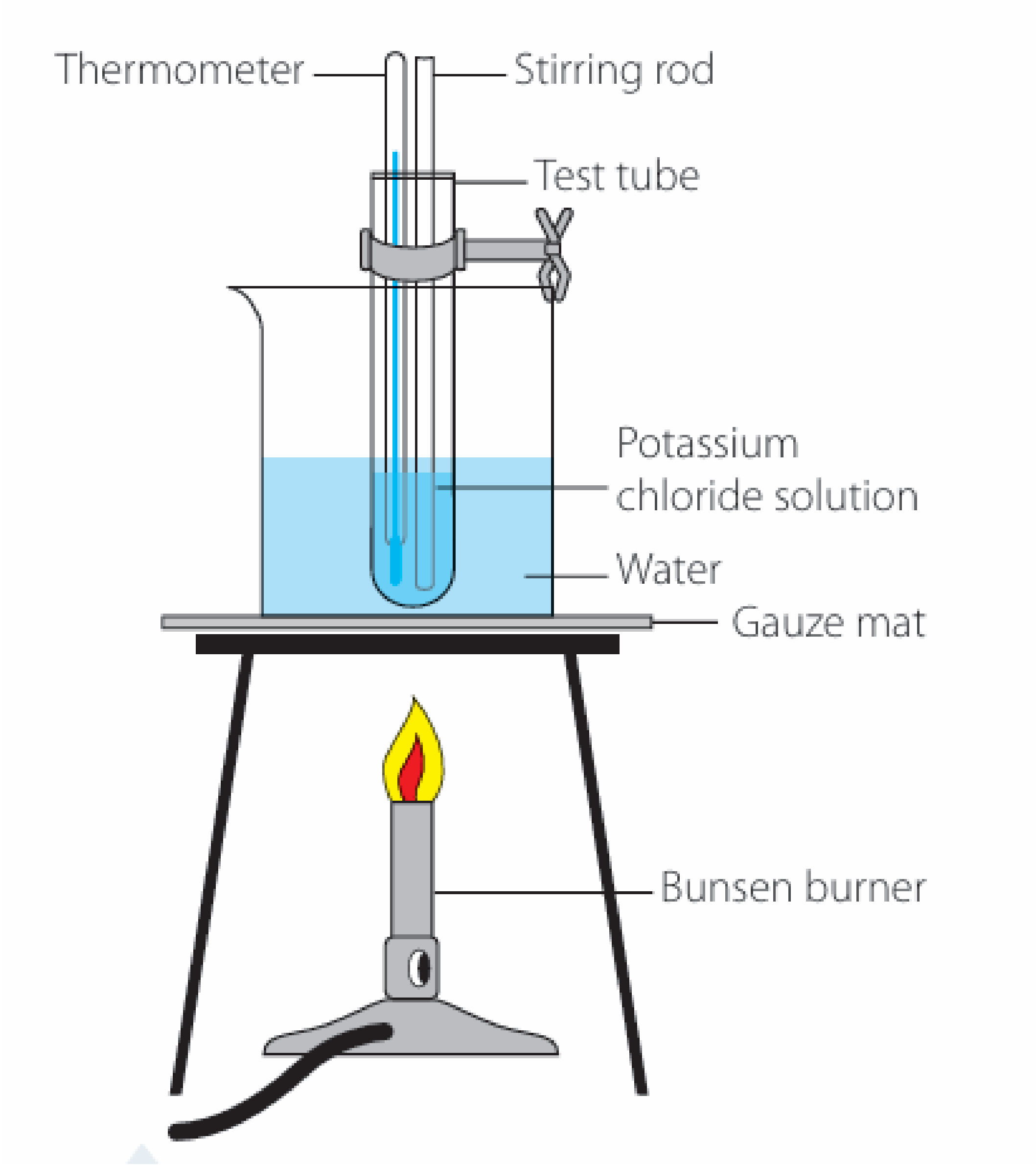


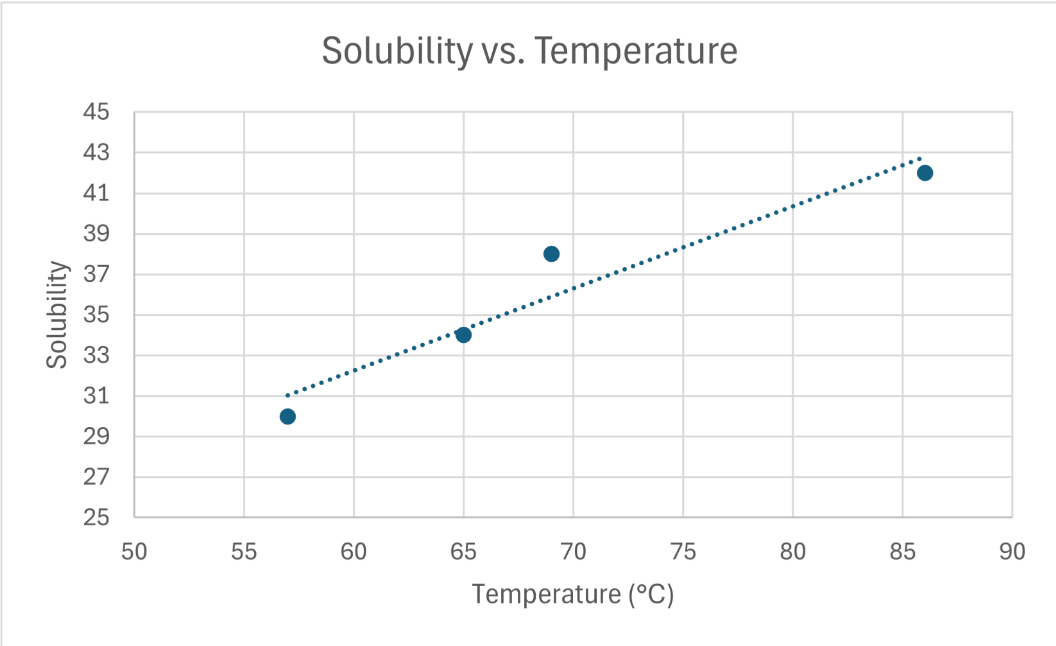
Figure 1.2: Use retort stand instead of beaker clip

1.13.4 Results

Mass of KCl (g)	m_{water} (g)	Temp. recrystallisation (°C)	Solubility (g/100 g H_2O)
3.00	10.00	57	30
3.40	10.00	65	34
3.80	10.00	69	38
4.20	10.00	86	42

1.13.5 Analysis of Results

1. **Use the class results to plot a graph of solubility against temperature. Plot the temperature along the horizontal axis (0-100°C).**



2. **From the graph, predict the solubility of potassium chloride at 20 °C 40 °C, 60 °C and 80 °C.**

   By technology, trendline forms equation Solubility $= 0.4056T + 7.9142$

$$\begin{aligned}\text{Solubility at } 20^\circ\text{C} &= 0.4056(20) + 7.9142\\ &= 16.0262\text{g}/100\,\text{g}\,\text{H}_2\text{O}\end{aligned}$$

$$\begin{aligned}\text{Solubility at } 40^\circ\text{C} &= 0.4056(40) + 7.9142\\ &= 24.1382\end{aligned}$$

$$\begin{aligned}\text{Solubility at } 60^\circ\text{C} &= 0.4056(60) + 7.9142\\ &= 32.2502\end{aligned}$$

$$\text{Solubility at } 80^\circ\mathrm{C} = 0.4056(80) + 7.9142$$
$$= 40.3622$$

1.13.6 Discussion

1. **Describe what happens to the solubility of potassium chloride as temperature increases**

   As temperature increases, solubility of potassium chloride increases, ie. directly proportional relationship

2. **If the theoretical value for the solubility of potassium chloride at $50\,^{\circ}\mathrm{C}$ is $50\,\mathrm{g}/100\,\mathrm{g}\,\mathrm{H_2O}$, what percentage error does your experiment have?**

$$\text{Percentage error} = \frac{\text{Experimental value} - \text{true value}}{\text{True value}} \times 100\%$$

$$\begin{aligned}\text{Solubility at } 50^{\circ}\mathrm{C} &= 0.4056(50) + 7.9142\\ &= 28.1942\end{aligned}$$

$$\begin{aligned}\text{Percentage error} &= \frac{28.1842 - 50}{50} \times 100\\ &= \frac{-21.8158}{50} \times 100\\ &= -43.6316\%\\ &\therefore \text{The experiment had a error value of 43.6316 \%}\end{aligned}$$

3. **List possible sources of errors in your experiment.**

   - Observing the formation of precipitate was subjective as small particles initially formed
   - The water bath helped to regulate the temperature of the test tube, however may not have been fully effective

Chapter 2

Module 6   Acid and Base Reactions

2.1 Introduction to Acid and Bases

General Properties of Acids

- Sour taste
- Low pH
- Turn blue litmus paper red
- Corrosive

General Properties of Bases

- Bitter taste (eg. caffeine)
- High pH
- Turn red litmus paper blue
- Corrosive and caustic

2.2 Indicators

Indicators are substances added to solutions to show their pH. They show the concentration of hydrogen ions in a solution through a colour change.

Most indicators are **weak acids or bases** meaning they exist in equilibrium.acids or

$$\mathrm{HIn} \rightleftharpoons \mathrm{H}^{+} + \mathrm{In}^{-}, \text{ where In stands for indicator}$$

Eg. Added to an acidic solution:

1. Equilibrium is disturbed by the increase of H^+ ions
2. Equilibrium therefore shifts left to decrease this concentration (LCP)
3. As a result, the concentration of HIn Increases, therefore changing the colour

Indicators are more useful in clear, colourless solutions that make it easier to identify the equivalence point.

Example Question

An indicator is usually a solution of a weak acid and its differently coloured conjugate base. Explain this statement. **(4 marks)**

1. Provide an equation

2. Effect of a decrease in pH

3. Effect of an increase in pH

4. Final statement

2.2.1 Common Indicators

Indicator	pH Range	Colour (increasing pH)
Methyl orange	3.1 - 4.4	Red - Orange - Yellow
Liquid litmus	4.5 - 8.3	Red - Purple - Blue
Bromothymol blue	6.0 - 7.6	Yellow - Green - Blue
Phenolphthalein	8.3 - 10.0	Colourless - Pale pink - Bright pink
Universal indicator	All pH	Red - Violet

2.3 Practical Investigation 5.1 - Preparing and using natural indicators

Aim: To prepare and test natural indicators on a range of substances to determine their acidity or alkalinity

2.3.1 Materials

- Plant material that acts as an indicator (Eg. red cabbage, blueberries, turmeric, petals from violets, geranium, petunias)
- Approx. 5mL of:
  - $0.1\,\mathrm{mol\,L^{-1}}$ NaOH
  - $0.1\,\mathrm{mol\,L^{-1}}$ HCl

- white vinegar
- household ammonia
- lemon juice
- lemonade
- bicarbonate of soda
- washing powder
- antacid tablet
- salt water

- Distilled water
- $500\,\mathrm{mL}$ beaker
- $100\,\mathrm{mL}$ beakers
- Test tubes
- Test-tube rack
- $10\,\mathrm{mL}$ measuring cylinder
- Knife
- Cutting board
- Mortar and pestle
- Kettle (for warm water)
- Hotplate
- Spatula
- Droppers
- Stirring rod
- Strainer or filter paper and funnel
- Safety glasses

2.3.2 Risk Assessment

Hazard	Precaution
Acids are corrosive, irritate eyes	Handle with caution
Bases are caustic, irritate eyes	Handle with caution
Ammonia is caustic	Use in well ventilated areas

2.3.3 Method

1. For the red cabbage: Finely shred two leaves of cabbage, place in 500 mL beaker and just cover with distilled water (about 200 mL). Slowly boil the cabbage leaves until the water turns a dark reddish-purple and the leaves lose most of their colour.

2. Allow to cool and pour the liquid off into a clean 100 mL beaker. This is the red cabbage indicator. Note: If the colour of the solution is pale, further boiling may be necessary to concentrate the solution.
3. For other plant material: Cut the material into small pieces and place in a mortar and pestle. Grind the material to a paste, add 5-10 mL of warm water and stir.
4. Strain the solution into a beaker to remove any solids.
5. Place 2 mL of each of NaOH and HCl into clean separate test tubes. Add a few drops of one indicator to each test tube until a definite colour is observed. Record the indicator and its colour in your results table.
6. Repeat step 5 with other indicators and record your results in the table.
7. Repeat steps 5 and 6 with other substances. Classify the substances as acidic, basic or neutral.
8. Place 2 mL of HCl in a clean test tube. Choose an indicator that produced a good colour difference between acid and base and add a few drops to the test tube.
9. Add NaOH a few drops at a time to the HCl test tube until the colour no longer changes. Record any colour changes that occur during the addition of NaOH.
10. To the test tube from step 9 add HCl a few drops at a time until the colour no longer changes. Record any colour changes.

2.3.4 Results

2.3.5 Discussion

1. **Identify which indicators would be most effective in identifying acidic, basic and neutral solutions. Provide a reason for your choice.** Acid Neutral Basic
2. **Which indicators, if any, were not effective in distinguishing between acidic, basic and neutral solutions? Suggest possible reasons for this.**

   The beetroot and blue tea indicators were not as effective compared to the universal indicator. For unknown solutions, universal indicator allows identification of the pH. Blue tea has a lower concentration of anthocyanin compared to the beetroot solution, therefore was less effective as an indicator.
3. **Using your results, justify whether or not indicator colour change is a reversible reaction.**

   It is a reversible reaction

2.3.6 Conclusion

1. **Explain why indicators give a range of colours in different acid and alkaline solutions.**

2.4 History of Acid-Base Models

Lavoisier - Acids contain oxygen

- Correct for some acids, eg. H_2SO_4
- However doesn't apply to all acids, eg. HCl doesn't have oxygen

Davy - Acids contain displaceable hydrogen

- Considered reactions with metals and acid
- H_2 gas produced as metal displaces hydrogen in acid
- $H_2(g) + 2\,HCl(aq) \longrightarrow H_2(g) + MgCl_2(aq)$

Arrhenius - Acids ionise in water to form H+ ions

- $HA\,(aq) \longrightarrow H^+(aq) + A^-(aq)$
- $XOH(aq) \longrightarrow X^+(aq) + OH^-(aq)$
- Couldn't explain why ammonia was a base
- Nature and role of the solvent was not considered
- All salts produced by reactions of an acid and base should be neutral, but acetic acid and sodium hydroxide results in a basic solution

2.5 Ammonia Dilemma

TODO: Ammonia ionises in water and produces OH^- ions, and is therefore classified as an Arrhenius base. However, considering the following reaction:

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$$

The above reaction is an acid (HCl) base (NH_3) reaction, however it doesn't form water.

2.5.1 Bronsted-Lowry Model

Acids are proton donors, bases are proton acceptors $HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$

In the above reaction, HCl accepts a proton from H_2O, $\therefore$ HCl = acid, H_2O = base

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

Water is **amphiprotic**, ie. can act as an acid or a base.

$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$

Limitations:

- Requires a solvent and doesn't explain for non-aqueous solutions
- Cannot explain for acidic oxides, eg. $CaO(s) + SO_3(g) \longrightarrow CaSO_4(s)$
- BF_3, $AlCl_3$ act as acids, however have no H^+ to donate.

2.5.2 Lewis Model

Acid is an electron pair acceptor, base is an electron pair donator

Explains the $BF_3 + NH_3$ reaction:

Boron accepts a pair of electrons from the nitrogen in ammonia. Although no proton is transferred, it is still an acid-base reaction

2.6 Practical Investigation 5.2 - Measuring the enthalpy of neutralisation

Aim: To determine the enthalpy of neutralisation and the effect of the state of the reactants

2.6.1 Materials

- 4g NaOH
- 100mL 1.0 $molL^{-1}$ HCl
- 50mL 2.0 $molL^{-1}$ HCl
- 50mL 2.0 $molL^{-1}$ NaOH
- 100mL measuring cylinder
- -10-110°C thermometer or temperature probe and data logger
- Spatula
- Electronic balance
- 2 polystyrene cups
- Safety glasses

2.6.2 Analysis of Results

Part A

1. Heat of reaction:

2.6.3 Discussion

2.7 pH Scale

- pH scale is a quantitative measurement of the acidity of a solution, generally between 0-14, where 7 is neutral, there are values outside the range
- Lower values are acids, higher values are basic
- Each step on the scale represents a factor of 10, ie. logarithmic scale
- Eg. pH 6 is 10x stronger than pH 5
- The term pH stands for "potential of hydrogen"
- The scale is based on the concentration of hydrogen ions in solution
- Remember that in aqueous solutions, the hydrogen ion attaches to a water molecule to form

The **lower** the pH, the **more acidic** a solution is Therefore, at 25°C, acids have a pH of less than 7 and bases have a pH greater than 7. A substance that has a pH equal to 7 is neutral pH is the concentration of H^+

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

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

2.7.1 Why is pH important?

- Soil has to be in a certain pH range to grow, usually 5-6
- Fish need a specific pH, very particular, slightly acidic

2.7.2 Measuring pH

- Natural indicators
- Universal indicator
- Colour scale
- pH probe

2.7.3 Common thingies

- -1 =¿ concentrated HCl
- 3 =¿ vinegar
- 6 =¿ Rain water
- 8 =¿ Blood

2.7.4 Calculating pH

Eg. Calculate pH, given [H+] = 2.0

$$q = -\Delta H \times n_{water}$$

2.8 Enthalpy of Neutralisation

Neutralisation reactions are typically exothermic with a theoretical value of $-57\,\mathrm{kJ\,mol^{-1}}$

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

Neutralisations involving strong acids and strong bases **have the same molar enthalpy of reaction**

Hydrochloric Acid

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$
$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l),\ \Delta H = -57.1\ kJmol^{-1}$$

Nitric Acid

$$HNO_3(aq) + NaOH(aq) \longrightarrow NaNO_3(aq) + H_2O(l)$$
$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l),\ \Delta H = -57.1\ kJmol^{-1}$$

2.8.1 Neutralisations involving weak acids/bases

Neutralisation requires a H^+ from acid. The ionisation of weak acids/bases have different ΔH values.

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq),\ \Delta H = 1.0\ kJmol^{-1}$$

Net ionic equation of neutralisation is different

$$CH_3COOH(aq) + OH^-(aq) \rightleftharpoons H_2O(aq) + CH_3COO^-(aq),\ \Delta H = -56.1\ kJmol^{-1}$$

2.8.2 Calculating the Enthalpy of Neutralisation

Energy produced/released by neutralisation is absorbed by solution, where the reaction produces a salt solution.

The temperature of the solution increases, where the change in temperature is given by $q = mc\Delta T$, where:
q = amount of energy absorbed by the solution in J., m = the mass of the final solution (unit depends on c), c = the specific heat capacity of the solution, ΔT = change in temperature of the solution in K

2.8.3 Specific heat capacity

c is the amount of energy required to raise the temperature of a substance by 1K per unit mass.

Eg. $c_{water} = 4.18 \times 10^3 \text{ J kg}^{-1}\text{ K}^{-1}$, $c_{\text{NaCl}} = 880 \text{ J kg}^{-1}\text{ K}^{-1}$

It is much easier to raise the temperature of NaCl because it has a much lower specific heat capacity.

c depends on the concentration of NaCl(aq)

2.8.4 Molar Enthalpy of Neutralisation

$\Delta H =$ energy absorbed or produced by a reaction **per mole**

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l),\ \Delta H = -57.1\ kJmol^{-1}$$

57.1 kJ of energy is produced **per mole of water** formed

$$q = -\Delta H \times n_{water}$$

where $q =$ energy absorbed by solution. q depends on the number of moles of water formed

Eg. in the above reaction;

$$\begin{aligned} q &= -\Delta H \times n \\ &= -(-57.1) \times 2 \\ &= 114.2 \text{ kJ of energy absorbed by the solution} \end{aligned}$$

2.9 Concentration vs. Strength of Acids and Bases

2.9.1 Acid reaction with water

The reaction of an acid with water is called an **ionisation reaction** since ions are formed. When an acid ionises, it produces hydronium ions (H_3O^+) in aqueous solution, although this is often simplified to H^+

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

or

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

2.9.2 Base reaction with water

When a base dissolves in water, it forms separate ions. This reaction is called a **dissociation reaction**. A base usually dissociates to produce hydroxide ions in aqueous solution.

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$
$$K_2O(s) + H_2O(l) \longrightarrow 2\,K^+(aq) + 2\,OH^-(aq)$$

Note: Some bases ionise, eg. ammonia

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

2.9.3 Strength of acids and bases

The strength of an acid or base is determined by the ratio of ions to unionised molecules. Strong acids/bases have few molecules and no ions.

Strong acids

A strong acid essentially fully ionises.

Eg. HCl reaction

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

where $[HCl] = [H_3O^+]$, $[Cl^-]$

Weak acids

An example of a weak acid is acetic acid, CH_3COOH

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

where $[CH_3COOH] > [H_3O^+]$, $[CH_3COO]$ with 5% ionisation at 25 °C

Strong bases

A strong base dissociates nearly completely into its ions. All oxides and hydroxides of Group 1 and Group 2 are strong bases, eg. NaOH

$$NaOH(s) + H_2O(l) \longrightarrow Na^+(aq) + OH^-(aq)$$

where $[NaOH] = [Na^+]$, $[OH^-]$

Weak bases

A weak base ionises to a small extent, eg. $NH_3(g)$

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

2.9.4 Acids and bases as electrolytes

Strong acids/bases are strong electrolytes, weak acids/bases are weak electrolytes.

Current is defined as **the flow of charge carriers**, therefore ions are required to form a current. Strong acids/bases are mostly ions and can therefore conduct the most charge.

To experimentally distinguish strong acids from weak acids, the following methods can be used:

- use a conductivity apparatus test (eg. a light bulb will be brighter for a strong acid)
- measure conductivity of solutions (eg. an ammeter will measure a higher current for a strong acid)
- react the two acids with a metal like magnesium (the stronger acid will react faster)
- measure the pH of the solutions using a pH meter or indicators (stronger acid will have a lower pH)

2.9.5 Effect of concentration on pH

If an aqueous solution of a *strong acid* is diluted, the **pH will increase**

Consider the following reaction:

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

The addition of water decreases the concentration of H_3O^+ ions already present. The equilibrium position is already far to the right, therefore there is no HCl to react with the added water and the equilibrium doesn't shift

In an aqueous solution of a *weak acid* is diluted, the **pH will increase**, but the increase will be smaller than that of the dilution of a strong acid

The addiction of water decreases the concentration of H_3O^+ ions, however the equilibrium shifts to the right and puts more H_3O^+ ions into the solution.

2.9.6 Polyprotic Acids

Acids such as HCl, HNO_3, and HF will give up one proton (hydrogen ion) per molecule when they ionise. These are called **monoprotic acids**

Some acids can give up more than one proton. These acids are called **polyprotic acids**. The term "polyprotic" refers to the ability to donate more than one proton, not how readily these protons ionise in water. **Diprotic acids** can donate two protons.

pH of polyprotic acids

The measured pH of a 0.1 molar solution of sulfuric acid (H_2SO_4) is around 0.69, not 1.0. Therefore, it is a more acidic solution than a 0.1 molar solution of monoprotic HCl.

The small pH of the H_2SO_4 indicates that there are more hydronium ions than the HCl equivalent concentration.

The pH value can be used to calculate the concentration of hydronium ions [H_3O^+] as almost 0.2 molar.

This means there are almost twice as many hydronium ions for H_2SO_4 than for HCl when these acids are the same concentration.

Ionisation of sulfuric acid

$$\mathrm{H_2SO_4(l) + H_2O(l) \longrightarrow HSO_4{}^-(aq) + H_3O^+(aq)}$$
$$\mathrm{HSO_4{}^-(aq) + H_2O(l) \rightleftharpoons SO_4{}^{2-}(aq) + H_3O^+(aq)}$$

Other acids, such as phosphoric acid (H_3PO_4), can donate up to three protons and are called **triprotic acids**, with the second and third ionisation steps involving weak acids.

$$\mathrm{H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4{}^-(aq) + H_3O^+(aq)}$$
$$\mathrm{H_2PO_4{}^-(aq) + H_2O(l) \rightleftharpoons HPO_4{}^{2-}(aq) + H_3O^+(aq)}$$
$$\mathrm{HPO_4{}^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4{}^{3-}(aq) + H_3O^+(aq)}$$

2.10 Self-ionisation of Water

Self-ionisation is a reaction in which two like molecules react to form ions.

Water's amphiprotic nature means that it can react with itself to form hydronium and hydroxide ions.

$$\mathrm{H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)}$$

One water molecule acts as an acid, the other as a base

2.10.1 Self ionisation constant

While this is a reversible reaction, the forward reaction only occurs to a very small extent, therefore has a small equilibrium constant.

The concentration of water is very large ($\approx$) 55 M and so does not significantly change the reaction, so H_2O is not included in the equilibrium expression.

To represent this, the **self-ionisation constant** is used:

$$K_w = [\mathrm{OH^-}][\mathrm{H_3O^+}], \text{ where } K_w = 1.0 \times 10^{-14} \mathrm{mol\,L^{-1}}$$

In pure water, the concentration of OH^- is equal to the concentration of H_3O^+

$$
\begin{aligned}
[\mathrm{OH}^-] &= [\mathrm{H_3O^+}] \\
K_w &= [\mathrm{OH}^-][\mathrm{H_3O^+}] = 1.0 \times 10^{-14} \\
[\mathrm{H_3O^+}]^2 &= 1.0 \times 10^{-14} \\
[\mathrm{H_3O^+}] &= \sqrt{10^{-14}} \\
&= 10^{-7} M
\end{aligned}
$$

2.10.2 Calculating the pH of solutions using the self-ionisation constant

Once the hydronium concentration $[\mathrm{H_3O^+}]$ is known, the pH can be calculated.

$$
\begin{aligned}
K_w = [\mathrm{OH}^-][\mathrm{H_3O^+}] &= 1.0 \times 10^{-14} \\
pH &= -\log{[H+]}
\end{aligned}
$$

Eg. Find the pH of a 0.02 $\mathrm{mol\,L^{-1}}$ solution of sodium hydroxide

$$
\begin{aligned}
&\mathrm{NaOH(aq)} \longrightarrow \mathrm{Na^+(aq)} + \mathrm{OH^-(aq)} \\
&\text{Therefore, } [NaOH] = 0.02 mol L^{-1} \\
&\qquad K_w = [\mathrm{H_3O^+}][\mathrm{OH}^-] = 1 \times 10^{-14} \\
&\qquad\quad = [\mathrm{H^+}][0.02]
\end{aligned}
$$

$$
\begin{aligned}
[\mathrm{H^+}] &= \frac{1 \times 10^{-14}}{0.02} = 5 \times 10^{-13} \\
pH &= -\log{[\mathrm{H^+}]} = 12.3
\end{aligned}
$$

2.11 Revisiting Neutralisation

If the correct amounts of acid and base are mixed, then the resultant solution is neutral. However it is only neutral when strong acids and strong bases react.

If an acid reacts with a base other than its conjugate base or water, it will always react completely, provided the reaction quantities meet the required stoichiometric ratios

Eg. sulfuric acid is **diprotic** and undergoes ionisation in two steps, however when it is the limiting reagent, all of the protons will react and undergoes ionisation in two steps

$$\mathrm{H_2SO_4(aq)} + 2\,\mathrm{NaOH(aq)} \longrightarrow \mathrm{Na_2SO_4(aq)} + 2\,\mathrm{H_2O(l)}$$

$$c(\mathrm{NaOH}) = 0.7 mol L^{-1} \; V = 0.055 L$$
$$n(\mathrm{NaOH}) = 0.0385 \, \text{mol}$$
$$n(\mathrm{H_2SO_4}) = 0.0165 \, \text{mol}$$
$$n(\mathrm{H_3O^+}) = 2 \times 0.0165 = 0.033 \, \text{mol} \; (\mathrm{H_2SO_4} \text{ can donate 2 protons})$$

2.11.1 Salts: Not necessarily neutral

The pH of the final solution may not be neutral due to the pH of the salt produced. Earlier definitions of acids and bases couldn't explain why, but Bronsted-Lowry could.

The strength of the conjugate acid or base produced is dependent on the strength of the original acid or base

Eg. $HCl + NH_3 \longrightarrow Cl^- + NH_4^+$

Salts produced from the neutralisation of a **strong acid and strong base are neutral** because they don't hydrolyse (react with water), eg. NaCl is neutral

Eg. **Acidic salt**

When a strong acid and weak base react, the resulting solution is acidic

$$\mathrm{HCl(aq) + NH_3(aq) \longrightarrow NH_4Cl(aq)}$$
$$\mathrm{NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)}$$

The conjugate acid of the weak base will hydrolyse to produce H_3O^+ so the solution will be acidic

Eg. **Basic salt**

When a weak acid and strong base react, the resulting solution is basic

$$\mathrm{HF(aq) + NaOH(aq) \rightleftharpoons NaF(aq) + H_2O(aq)}$$
$$\mathrm{F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)}$$

Eg. **Both**

A reaction of a weak acid and a weak base will result in either an acidic or basic solution depending on which one is stronger

$$\mathrm{HCOOH(aq) + NH_3(aq) \rightleftharpoons NH_4HCOO(aq)}$$
$$\mathrm{NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)} \; , \; K_a = 5.6 \times 10^{-10}$$
$$\mathrm{HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq)} \; , \; K_b = 6.25 \times 10^{-11}$$

therefore is acidic

2.12 Practical Investigation 7.2 - Making a primary standard solution

Aim: To make a primary standard solution.

2.12.1 Materials

- 250 mL volumetric flask with lid
- Electronic balance
- Clean, dry 150 mL beaker
- Spatula
- 1.5 g anhydrous sodium carbonate
- 300 mL distilled water
- Wash bottle with distilled water
- Filter funnel
- Stirring rod
- Disposable droppers
- Safety glasses

2.12.2 Method

1. Rinse the volumetric flask with a small volume of distilled water
2. Place the beaker on the electronic balance and tare the balance
3. Measure 1.4 g of anhydrous sodium carbonate into the beaker
4. Add 80 mL of distilled water to the beaker and stir until the sodium carbonate has completely dissolved
5. Place the filter funnel into the neck of the volumetric flask
6. Pour the sodium carbonate solution into the volumetric flask
7. Pour a small volume of distilled water into the beaker, swirl and pour into the volumetric flask. Repeat three times
8. Rinse the filter funnel by pouring some distilled water from the wash bottle into the volumetric flask
9. Remove the filter funnel
10. Fill the volumetric flask with distilled water until the bottom of the meniscus is just touching the line on the volumetric flask
11. Place a lid of the volumetric flask, hold the lid in place, invert and swirl the contents of the flask so that mixing occurs

2.12.3 Notes

$$
\begin{aligned}
m_{\mathrm{Na_2CO_3}} &= 1.48g \\
n_{\mathrm{Na_2CO_3}} &= \frac{mass}{molarmass} \\
&= \frac{1.48}{2 \times 23 + 12.0 + 3 \times 16.0} \\
&= 0.01396\,\text{mol}
\end{aligned}
$$

2.13 Volumetric Analysis - Titration

Titration is a laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of a known concentration

Involves determining the concentration of a sample by measuring the volume of the sample that reacts with a known volume of another substance of known concentration

The equivalence point is the point at which the reactants are present in the same mole ratio given in the balanced equation for the reaction.

Strong acids and bases should be used because they completely dissociate.

Eg.

$$2\,NaOH(aq) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2\,H_2O(l)$$

Uses the process of **neutralisation** to determine the concentration of an unknown. The unknown solution is usually in the volumetric flask. An appropriate **indicator** is chosen so that the **equivalence point** can be determined. Alternatively, a pH metre can be used

2.13.1 Choosing an Indicator

- Identify the salt that is formed
- Determine whether either ion in the salt is a weak acid or a weak base or neither
- Decide whether the resultant solution will have a pH greater than 7, less than 7, or equal to 7

2.14 Titration

2.14.1 Terminology

- **Titre** - the volume of solution delivered from the burette that achieves the end point
- **Titrant** - the solution that is added from the burette
- **Aliquot** - a known volume of liquid

- **Primary standard** - reagent that is extremely pure, stable, has no waters of hydration and has a high molecular mass
- **Secondary standard** - solution whose concentration has been determined using a primary standard
- **End point** - the stage in titration where the indicator changes colour
- **Equivalence point** - point where moles of acid = moles of base

2.15 Practical Investigation 7.3 - Performing a titration

Aim: To determine the concentration of a hydrochloric acid solution using volumetric analysis.

2.15.1 Materials

- 250 mL of primary standard (Na_2CO_3)
- 200 mL hydrochloric acid of unknown concentration
- 50 mL burette
- Retort stand and burette clamp
- 25 mL pipette and pipette filler
- 2 × 150 mL beakers
- 3 × 250 mL conical flasks
- Dropper bottle containing methyl orange indicator
- Beaker labels
- Wash bottle with distilled water
- Filter funnel
- Safety glasses

2.15.2 Method

1. Rinse one of the 150 mL beakers with a small amount of the hydrochloric acid solution, empty it, label, and fill with about 100 mL of hydrochloric acid solution.
2. Prepare burette with hydrochloric acid solution
3. Rinse one of the 150 mL beakers with a small amount of the sodium carbonate solution, empty it, label, and fill with about 100 mL of sodium carbonate solution.
4. Rinse the conical flask with water.
5. Prepare the pipette, then use the pipette to transfer 25.00 mL of the sodium carbonate solution to the conical flask.

6. Add two drops of methyl orange indicator to the conical flask and swirl to mix.
7. Place the conical flask under the burette and begin the titration.
8. When the first permanent colour change has occurred, record all results.
9. Repeat the titration several more times until the titrant added is within 0.03 mL.

2.15.3 Results

Attempt 1: 23.8 mL of unknown concentration of HCl was required to neutralise the Na_2CO_3

Attempt 2: 23.9, 23.5, 23.5, 23.3

Attempt 2 (part 2): 24.1, 23.4

Average titre: 23.467 mL

By Jeffrey Wang's calculation: Concentration of HCl is 0.119 molL^{-1}

Concordant titres refers to the volume to the volume of two or more titres that are similar in quantity (less than $\pm$ 0.1 mL difference between each other)

2.16 Titration (cont.)

Potassium hydrogen phthalate ($KH(C_8H_4O_4)$) is a good primary standard for standardising alkali solutions

$$KH(C_8H_4O_4)(aq) + NaOH(aq) \longrightarrow Na^+(aq) + K(C_8H_4O_4)^-(aq) + H_2O(l)$$

27.4 26.7 26.8

Concordant titre average: 26.75 mL

$$0.119 \times 0.025 = 2.975 \times 10^{-3}\,\text{mol}$$
$$\frac{2.975 \times 10^{-3}}{0.02675} = 0.111\text{molL}^{-1}$$

2.17 Other Types of Titrations

Other applications of titrations include:

- using pH curves to determine the end point
- using conductivity graphs to determine the end point
- using back titrations to determine the concentration or mass of a substance that is not able to be determined directly
- performing a redox titration

2.17.1 pH Curves

If the solution being analysed is not clear (eg. malt vinegar, orange juice, and red wine), sometimes it is too dark for an indicator to be used. In this case, a pH meter can be used instead.

The data of the pH meter can be recorded with a datalogger and plotted onto a graph. The generated graph generally has an nearly vertical inflexion point, indicating the equivalence point of the substance. However, for weak acid + weak base reactions, there is no vertical inflexion point, making it more difficult to determine the equivalence point. (This situation is uncommon)

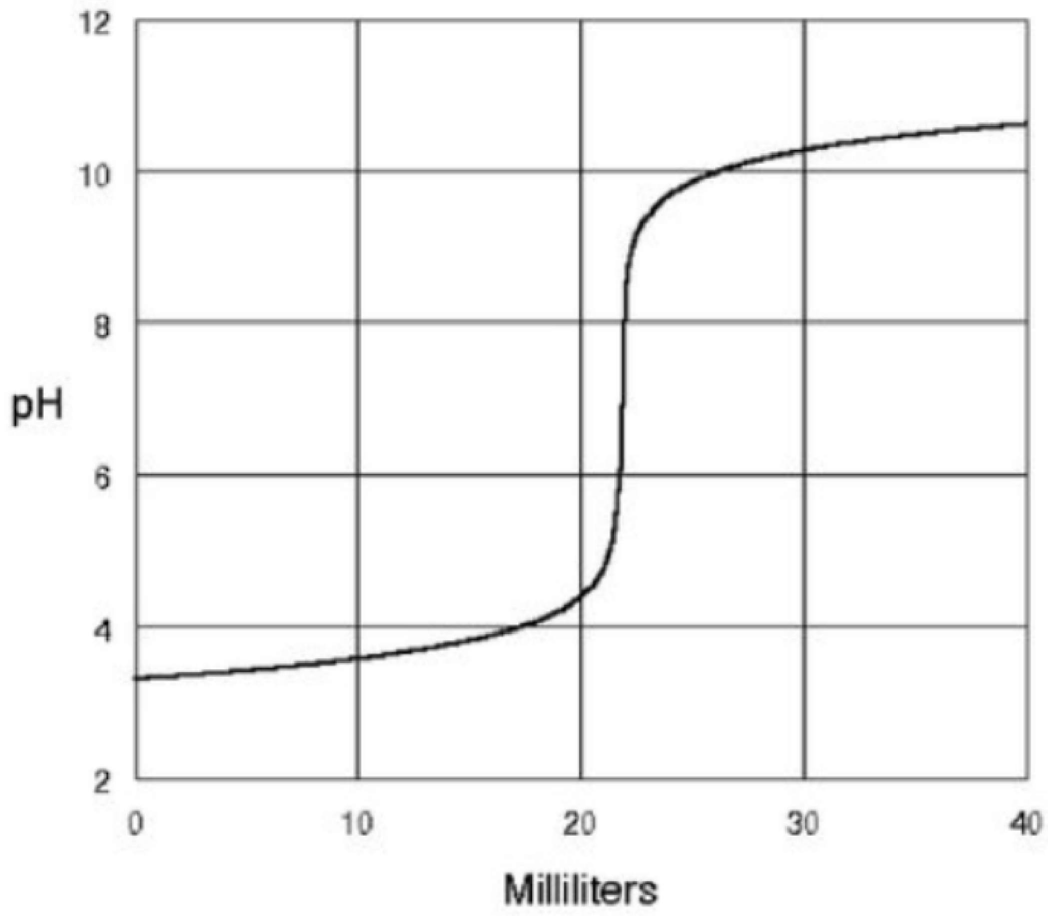
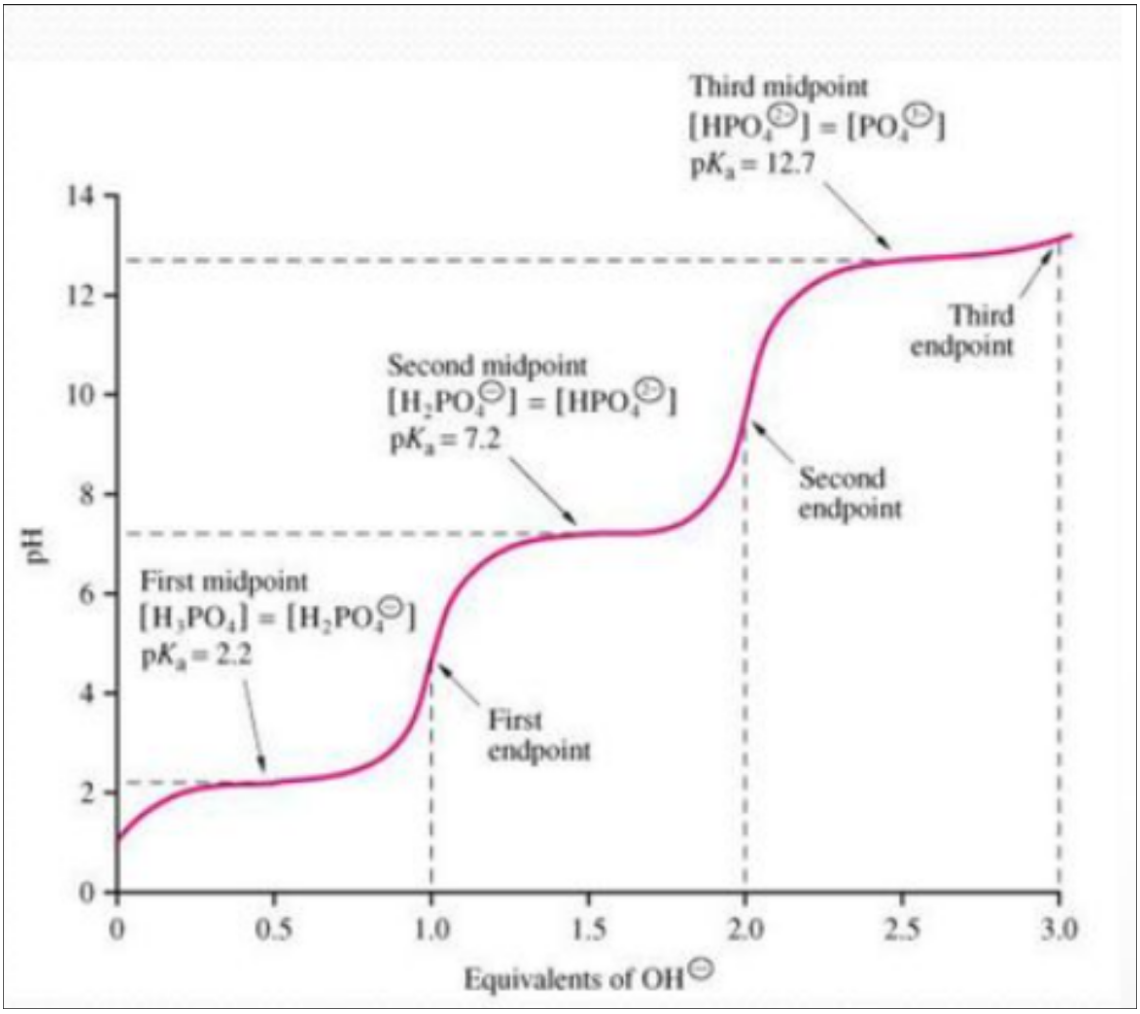


Fig.1. Titration curve for typical wastewater.

When using a pH logger, points beyond the equivalence point should be collected to make the inflexion more obvious

Polyprotic acids (eg. H_3PO_4) have multiple equivalence points, therefore will have three endpoints. Each "curve" represents the equivalence point of each of the three hydrogen ions



2.17.2 Activity Sheet 7.4 - Titration Curves

Titration of the strong acid in solution

1. What would you expect to be the pH of the titration solution after exact neutralisation of a strong acid with a strong base? If an indicator that changes colour close to this pH were used, would the colour change indicate the equivalence point accurately? The pH would be around a pH of 7. If an indicator was used, the pH could be accurately determined through a colour change.

2. Suppose that we use an indicator that changes colour near pH 5. According to the graph, does the colour change endpoint accurately indicate the equivalence point? Explain why this is the case.

   The equivalence point determined by the graph is around 10. Therefore, an indicator that demonstrates a colour change near a pH of 5 would not be appropriate.

3. If we use an indicator that changes colour near pH 9, does the colour change endpoint accurately indicate the equivalence point? Explain why.

   Yes. The equivalence point sits around pH 9, therefore an indicator around this would be appropriate.

Titration of the weak acid in solution

1. If a solution of a weak acid is titrated with a NaOH solution, would you expect the pH at exact equivalence to be at pH = 7, at pH > 7, or at pH < 7? Explain why.

   NaOH is a strong base, therefore when combined with a weak acid the resulting solution would be basic, ie. pH > 7.

2. Suppose we use an indicator that changes colour near pH 9. Reading the graph as accurately as possible, what volume of titrant (the NaOH solution) is added before the indicator changes colour? Does the indicator colour-change endpoint accurately indicate the equivalence point?

2.18 Acid/base Analysis by Aboriginal and Torres Strait Islander Peoples

2.18.1 Grey Mangroves

The grey mangroves are used to treat stingray injury by prevent infection and neutralise the mildly acidic stingray venom. This is done by smashing the grey mangroves' leaves to create a basic mixture that can be applied to the wound caused by the stingray

2.18.2 Yellow Ochre

Aboriginal and Torres Strait Islander Peoples used yell ochre (hydrated iron hydroxide) to treat stomach upsets. The yellow ochre is basic and can react and neutralise with any excess hydrochloric acid in the stomach

2.18.3 Davidson Plum

The Davidson plum is a natural Australian fruit with 100 times more of ascorbic acid (vitamin C) than contained in an orange. Therefore, it is very sour

Aboriginal and Torres Strait Islander Peoples consumed the Davidson plum as way to boost their body's nutrient level which reduced their chance of having scurvy disease.

2.18.4 Soap Tree

Soap tree's leaves contain saponin acid that has the ability to suppress bateria growth

2.18.5 Goat's Foot (Coastal Morning Glory)

The leaves (heated on rocks) can be applied as a poultice were used to relieve stings and bites from insects. It is poisonous if incorrectly applied

2.18.6 Clay Eating

Clay possesses antacid and ati-diarrhoeal functions by assisting with the absorption and assimilation of fluids into the intestine, in which it acts to prevent fluid loss through diarrhoea.

Clay has the ability to deactivate toxins within the stomach. This increases the tolerance of poisonous plants and unlock a forbidden diet

It acts as a detoxifying agent. This property is referred to as its poly cationic nature, which leads to the absorption of negative charge toxins. It works like activated charcoal which is known as a digestive aid.

Its magnetic feature draws cadium, lead, and other toxins to it. The clay moves the toxins molecules through the intestines

2.19 Conductometric Titration

Another method of determining when the equivalence point is reached is by **measuring the change in conductivity of the analyte using a conductivity probe**. Conductivity refers to a flow of ions that can be positive or negative, ie. not necessarily electricity. A titration that uses this property is called a conductometric titration.

2.19.1 Advantages

Can be applied to:

- Very diluted solutions - species at trace levels
- Coloured or turbid solutions
- Relatively incomplete reactions
- Acid-base, redox, precipitation and non-aqueous titrations

- The electrical conductivity of a solution depends on the concentration of ions in the solution
- Conductivity of strong base or strong acid is stronger than that of a weak base or weak acid
- Change in conductivity during conductometric titration is due to one of the ions being replaced by another of different conductivity

Equivalence occurs when conductance is at minimum - no free ions. It does not reach 0 because there are still some ions present to transfer charge

Example Question (HSC 2019 Q24)

The graph initially shows a negative gradient as barium hydroxide solution is introduced into the standardised HCl solution. This is due to the reaction of H^+ ions in the HCl solution with the OH^- ions from the barium hydroxide. This decreases the number of conductive ions in the solution, hence decreasing the solution's conductivity. When the equivalence point is reached (around 17mL), the number of OH^- ions present exceed that of HCl, therefore the number of OH^- ions increases and the graph depicts the solution has an increase in conductivity.

Example Question (HSC 2024 Q34)

$$H^+(aq) + NH_3(aq) \longrightarrow NH_4{}^+(aq)$$
$$NH_3(aq) + HCl(aq) \rightleftharpoons NH_4Cl$$

The graph initially decreases in conductivity as ammonia solution is introduced. This is due to hydrochloric acid being neutralised by the added ammonia.

The highly conductive H^+ ions react with the NH_3 ions, decreasing the overall conductivity of the solution.

After the equivalence point, the excess ammonia will produce some NH_4 and OH^- ions, both of which have greater conductivity than the reactant molecules.

2.20 Back Titration

Back titrations are indirect titrations that can be used when:

- the reaction is too slow so it is difficult to determine endpoints
- the sample is not soluble in water, but will react with an acid for example
- the sample is toxic
- the sample is volatile
- the sample is gaseous and in a mixture of gases
- the sample is fairly unreactive

Example

A back titration could be used to determine the percentage of calcium carbonate in a sample of limestone. It is not soluble in water, so it cannot be dissolved to form a solution. However, it will react with HCl. For example:

$$CaCO_3(s) + 2\,HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

A known excess volume of a standardised HCl solution (this can be created by titration) would be added to the limestone. It is assumed that the acid only reacts with calcium carbonate, not with any of the other impurities. If the HCl reacts with impurities, the final result will be greater than the actual amount of $CaCO_3$ present.

The least amount of measurements made reduces the amount of total errors in the experiment and providing a more accurate result.

2.21 Titration of Household Chemicals

2.21.1 Wine Industry

The use of analytical instruments in the wine industry allows scientists to learn more about the

As fermentation proceeds, the density of the mixture decreases. This is due to ethanol's lower density in comparison to water.

Titration to find SO_2 content in wine

Sulphur dioxide is used to kill or inhibit unwanted yeasts and bacteria in wine and to protect the wine from oxidation. When sulphur dioxide is added to wine, there are three forms present: molecular SO_2, ${SO_3}^{2-}$ and smth

2.21.2 Mining Industry

Ore needs to be dissolved to be tritrated. Done using particular acids.

2.22 Buffers

Keeping the balance

It is important that environments meet the needs of the organisms that live there. This means that conditions such as pH, concentration of ions, and temperature are maintained at suitable levels.

In a natural environment, the levels of these conditions in a particular environment will dictate what organisms are able to survive

2.22.1 Buffers

Buffers are utilised in the natural environment and biological systems to maintain an optimal pH.

It is a solution of a weak acid and its conjugate base (or vice versa) that is **able to resist a change in pH** when an acid or base is added

It achieves this due to the equilibrium established between the weak acid (or base) and its conjugate.

Example

A solution of carbonic acid and sodium hydrogen carbonate (H_2CO_3 / HCO_3^-)

The pH of a buffer is determined by the:

- Equilibrium constant K_a of the weak acid
- Ratio of weak base [A^-] to weak acid HA in solution

If a buffer has more acid than base, more H^+ ions are present and the pH is lower.

When the concentrations of A^- and HA are equal, [H^+] is equal to K_a and the pH is equal to pKa.

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

When a strong acid is added, LCP pushes the reaction to the left. The pH will increase near to the original value.

When a strong base is added, the concentration of H_3O decreases and the system will oppose this change. The pH is decreased to near the original value.

The pH is maintained by manipulating the proportion of weak base (A^-) and weak acid (HA) in solution. As long as $\frac{[A^-]}{[HA]}$ is between 0.1 and 10, the pH is within 1 unit and the solution is therefore buffered.

2.22.2 Buffer Capacity

The buffer capacity is the amount of the acid or base that can be added without a significant change in pH. The buffer capacity is greatest when there are equal number of moles of the weak acid and the conjugate base. In this case, it can counteract both the addition of an acid or base. The more of each weak acid and conjugate base, the greater the buffer capacity.

2.22.3 Buffering in the Environment

With increasing carbon dioxide levels in the atmosphere, there is a major concern that the oceans and soil are being acidified.

In ocean waters, carbon dioxide is found in higher concentrations than other non-polar gases as it reacts with water. The changes in pH at these levels are significant and are altering the thickness of shells of aquatic organisms and the ability of organisms to take up calcium.

2.22.4 Buffer in sea water

In sea water, the buffer is due to bicarbonate and carbonate ions.

In the following reaction:

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

The HCO_3 is the weak acid, and CO_3^{2-} is its conjugate base.

With increasing carbon dioxide levels in the atmosphere, there is a major concern that the oceans are being acidified. The breakdown of organic matter and fish waste also causes the water to become more acidic. The buffer is able to counteract this change so that the pH is not affected.

Calcium and magnesium ions cause the water to become more alkaline. This happens when items such as shells are added to the environment and when minerals in the surrounding soil are in run-off entering the water.

Natural sea water has a pH of 8.0 - 8.3. At this pH, there are appropriately equal amounts of bicarbonate and carbonate ions.