Year 12 Chemistry

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Contents

Chapter 1

Module 5   Equilibrium and Acid Reactions

1.1   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:

1.1.1   Effect of Concentration

$$N_{2(g)} + 3\,H_{2(g)} \rightleftharpoons 2\,NH_{3(g)} \quad \Delta H^{\ominus} = -92.5\,\text{kJ}\,\text{mol}^{-1} \tag{1.1}$$
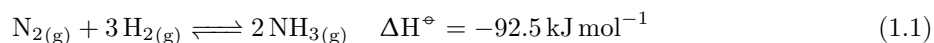
1.1.2   Effect of Pressure

1.1.3   Effect of Partial Pressure

1.1.4   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.

1.1.5   Effect of Temperature

filler text

1.1.6   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.

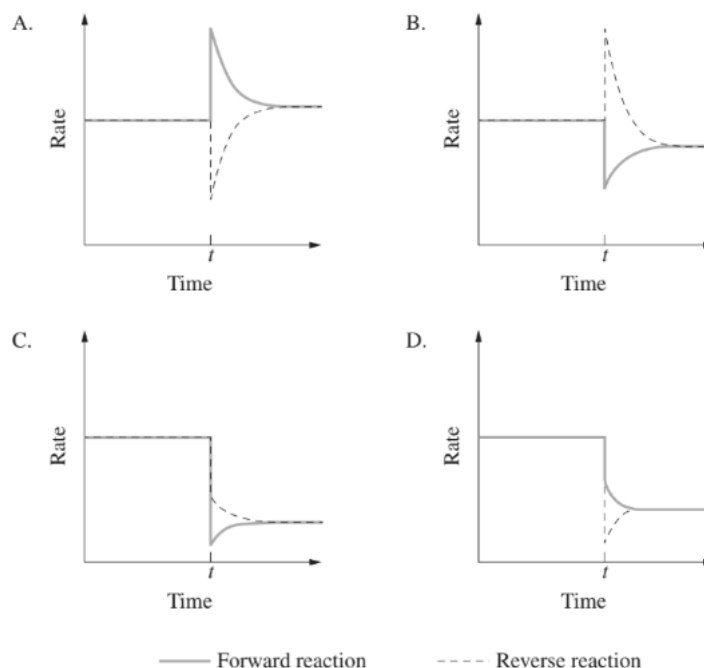$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57.2 \text{ kJ mol}^{-1}$$

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?

——— Forward reaction   - - - - Reverse reaction

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.

1.2 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

1.2.1 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

1.2.2 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

1.2.3 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

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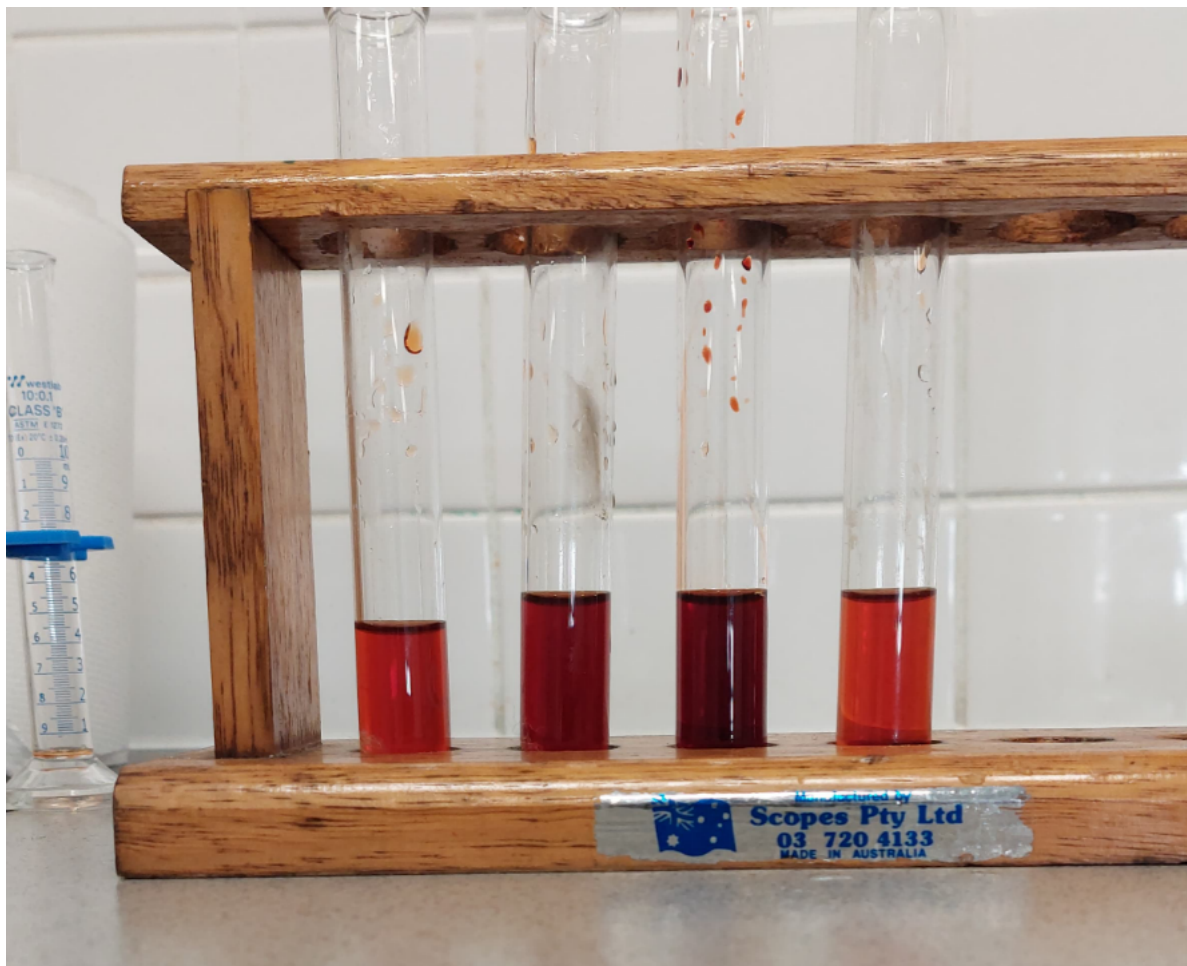
Figure 1.1: Test tubes A, B, C, D

1.2.5 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

1.2.6 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.

1.3 Calculating the Equilibrium Constant

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

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

For reaction:

$$aA + bB \rightleftharpoons cC + dD$$
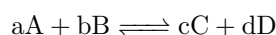
the equilibrium expression is:

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

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. H_2O isn't required when calculating

1.3.1 Reaction Quotient (Q)

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

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

1.3.2 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.

1.3.3 Calculating the equilibrium expression

Consider the reaction between hydrogen and iodine producing hydrogen iodide:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2\,HI_{(g)}$$
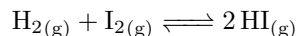
1.4 ICE Tables

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

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

Eg. $A + B \rightleftharpoons C + D$

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

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		

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

1.5 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

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

1.5.1 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)**

   $$N_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2\,NO_{(g)}$$
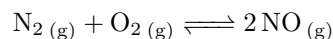
2. **Explain, using collision theory, how an increase in temperature would affect the value for K_{eq} for this system. Refer to the diagram in your answer.**

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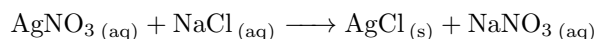
$$= \frac{[1.15][0.65]}{[0.85][0.85]}$$

$$= K_{eq}$$

1.6 Applications of the Equilibrium Constant

1.6.1 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.
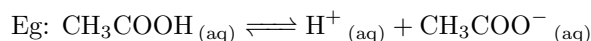
1.6.2 Use of the Equilibrium Constant for the Dissociation of Acids and Bases

Acids

Strong acids dissociate completely in solution. The reaction goes to completion and is not an equilibrium system
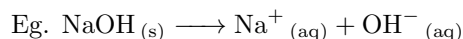
Eg: $HCl_{(l)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$
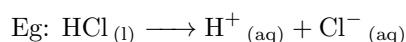
Weak acids do not dissociate completely, instead forming an equilibrium system
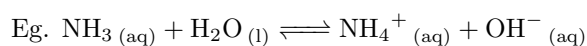
Eg: $CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$

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

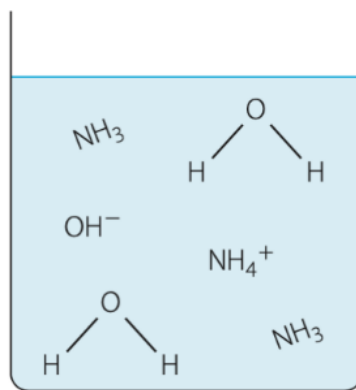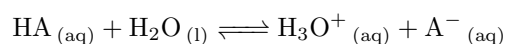The base dissociation constant is expressed as $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$

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.
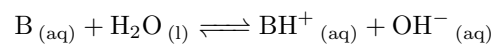
Weak Acid

General equation:

$$\text{HA}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+{}_{(aq)} + \text{A}^-{}_{(aq)}$$

General expression for equilibrium constant:

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

Weak Base

General equation:

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

General expression for equilibrium constant:

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

1.6.3 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 $\left(c = \frac{n}{V}\right)$

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:

$$\text{aA}_{(g)} + \text{bB}_{(g)} \rightleftharpoons \text{cC}_{(g)} + \text{dD}_{(g)}$$
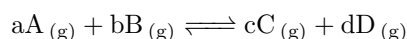
, where a, b, c and d are the number of moles

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

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

Expression of equilibrium constant in terms of pressure:

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

1.7 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 $Fe_3^+{}_{(aq)} + SCN^-{}_{(aq)} \rightleftharpoons FeSCN_2^+{}_{(aq)}$ FeSCN is red, $\therefore$ a green filter is needed
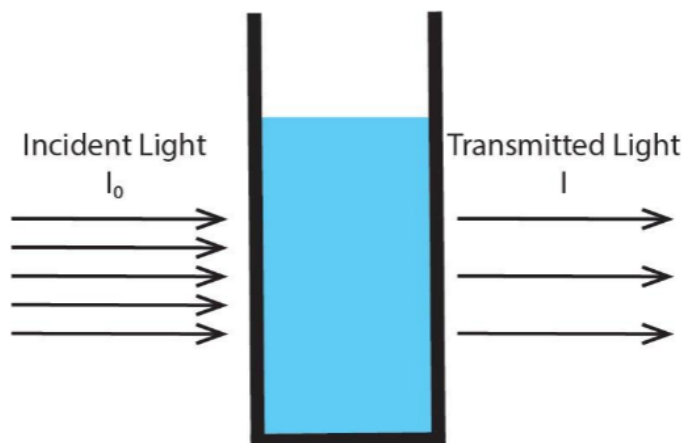
$$A = \log_{10} \frac{I_o}{I} = \varepsilon l c$$

1.7.1 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}**

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

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

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

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

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

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

1.7.2 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.
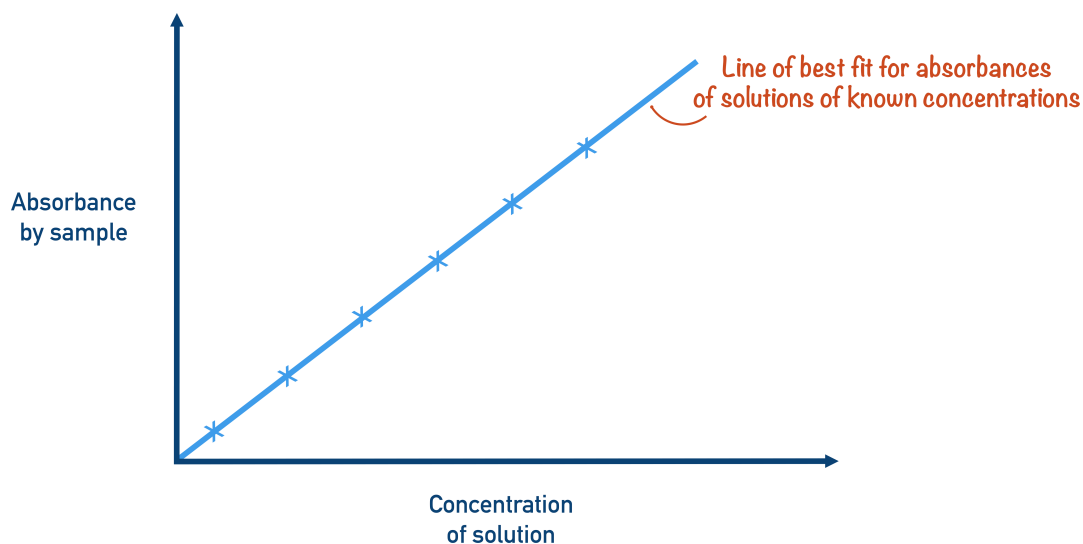
Beer Lambert's Law collapses at high and low concentrations, where $c < 20\%$, $c > 80\%$

1.8 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

1.8.1 Materials

- 200 mL 0.2 mol L^{-1} $Fe(NO_3)_3$
- 100 mL 0.002 mol L^{-1} KSCN
- 500 mL 0.5 mol L^{-1} HNO_3
- 60 mL 0.002 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

1.8.2 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

1.8.3 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 mol L^{-1} $Fe(NO_3)$

3. 3 to flask A.

4. Use a graduated 10 mL pipette to transfer 1.00 mL of the 0.002 mol L^{-1}

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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. HNO_3 can be used to reduce the concentration of 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)

1.9 Solution Equilibria - Dissolution of Ionic Compounds

1.9.1 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 $g\,L^{-1}$, g/100 g, or g/100 mL

1.9.2 Factors influencing solubility

- Activation energy required to break lattice

- Strength of ionic bonding

- Size of ions

- Charge of ions

1.9.3   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 ($g\,L^{-1}$ 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

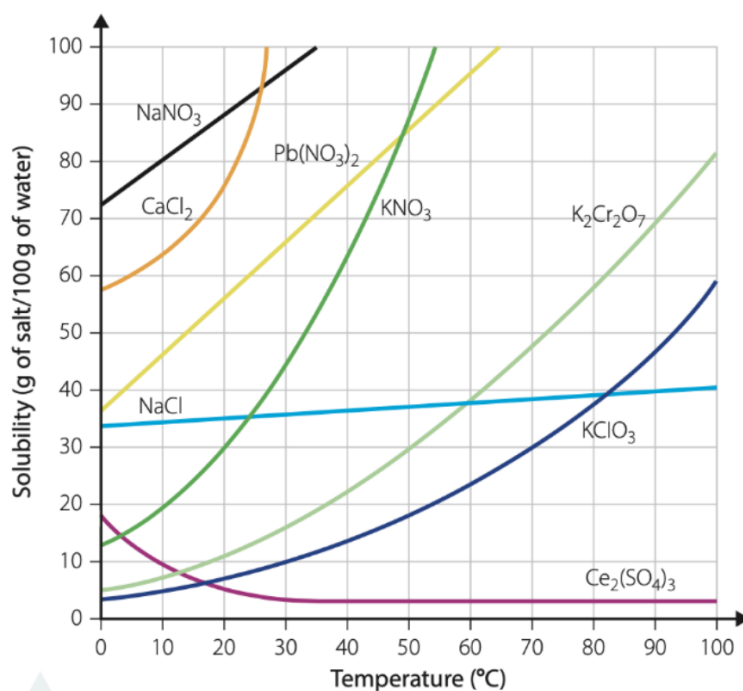- Solubility curves show how much of a solute dissolves at a given temperature

FIGURE 4.8 A selection of solubility curves for various salts

1.9.4   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

1.9.5

TODO: water of crystallisation

1.9.6   Dissolution of Ionic Compounds

1.10   Measuring Solubility

TODO: measuring solubility

1.10.1   Solubility Rules

1.11   Solubility Product