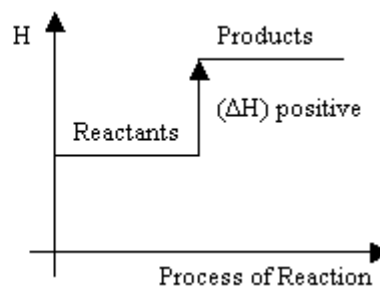
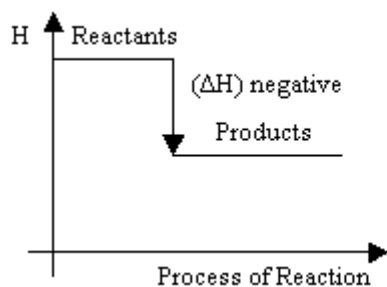


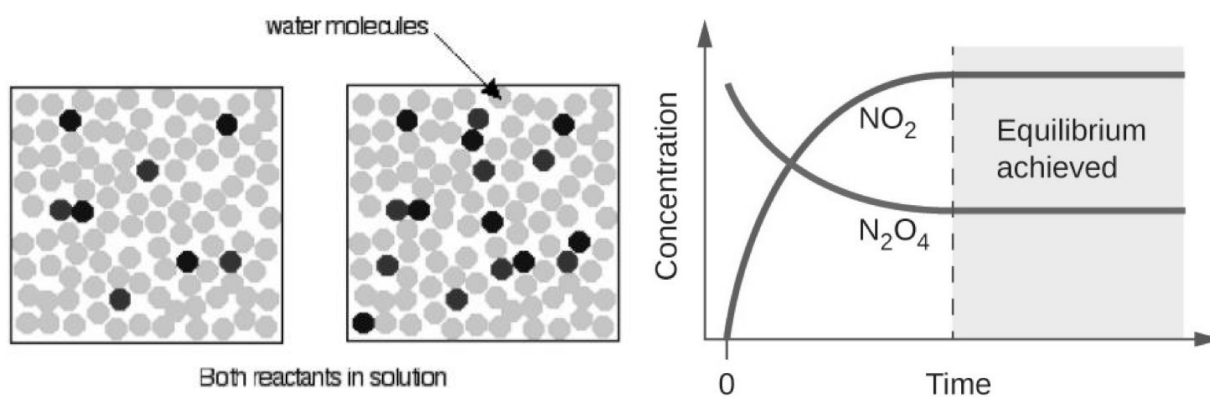
UNIT 4

INTRODUCTION TO PHYSICAL CHEMISTRY

Student Version



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Contents

- Energy Changes
- Rates of Reaction
- Equilibrium

Key words: enthalpy, enthalpy change, exothermic, endothermic, enthalpy level diagram, molar enthalpy change, enthalpy of formation, enthalpy of combustion, enthalpy of neutralisation, enthalpy of solution, energy content, collision, effective collision, collision frequency, collision energy, activation energy, catalyst, surface area, concentration-time graph, gradient, tangent, dynamic equilibrium, equilibrium constant, Le Chatelier's Principle

Units which must be completed before this unit can be attempted:

Unit 1 – Atoms and the Periodic Table

Unit 2 – Particles, Bonding and Structures

Unit 3 – Amount of Substance and Measurement

Estimated Teaching Time: 11 hours

Lesson 1 – What are the energy changes taking place during chemical reactions?



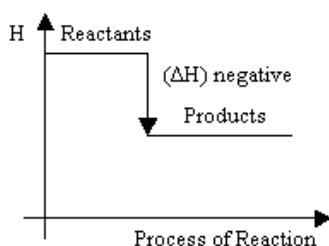
Thinkabout Activity 1.1: What is potential energy?

- What does the term “potential energy” mean? How many different types of potential energy can you name?
- What type of potential energy do all objects have on the surface of the earth? How can you increase or decrease this energy? How can you have zero potential energy in this situation?
- What type of potential energy exists between protons and electrons? How can you increase or decrease this energy? How can you have zero potential energy in this situation?
- When potential energy decreases, what usually happens to that energy?

(a) Energy Changes in Chemical Reactions

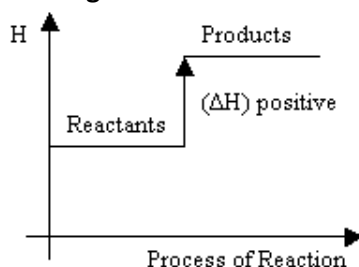
(i) Exothermic and endothermic reactions

- **Potential energy** is a type of energy resulting from the attraction or repulsion between different particles
- Particles which repel each other have a positive potential energy; as repelling particles are forced closer together, their potential energy increases; as they move further apart, their potential energy decreases until they are an infinite distance apart and they have zero potential energy (eg the north poles of two magnets)
- Particles which are attracted to each other have a negative potential energy; as attracting particles get closer together, their potential energy becomes more negative (ie it decreases); as attracting particles are pulled further apart, their potential energy becomes less negative (ie it increases) until they are pulled an infinite distance apart and they have zero potential energy (eg a spaceship and a planet)
- All chemical substances are held together by the attraction between protons and electrons; all chemical substances therefore have a negative potential energy (called **chemical potential energy**); the stronger the attractive forces holding the substance together, the more negative (ie the lower) the potential energy of the substance and the more stable it is
- Chemical potential energy is also known as **enthalpy** and is given the symbol H
- When a chemical reaction takes place, the products and reactants have different potential energies and thus there is a change in enthalpy; however since **total energy is always conserved**, any change in enthalpy must be balanced by an equal and opposite change in kinetic, or heat energy; the change in enthalpy during a chemical reaction is shown by the symbol ΔH
- In some reactions, the products are more stable than the reactants; the products therefore have a lower enthalpy than the reactants, and the enthalpy of the reacting species decreases; this can be shown in an **enthalpy level diagram**:



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- In these reactions the enthalpy decreases so there is a negative enthalpy change. ($\Delta H = -ve$); since the total energy is always conserved, the heat energy of the species must increase by an equal amount; the surrounding temperature therefore increases
- In these reactions, there is a transfer of energy from chemical potential energy to heat energy and an increase in temperature; such reactions **give out heat** and are said to be **EXOTHERMIC**
- In practice, not all of the energy will be transferred into heat (kinetic) energy; in some cases, sound energy will be produced as well; it is also possible in some cases to produce electrical energy rather than heat energy; but the loss in chemical potential energy will always be equal to the total gain in heat, kinetic, electrical or sound energy
- Almost all combustion reactions are exothermic (eg burning methane, burning charcoal, respiration)
- In other reactions, the reactants are more stable than the products; the products therefore have a higher enthalpy than the reactants, and the enthalpy of the reacting species increases
- This can be shown in an **enthalpy level diagram**:



- In these reactions the enthalpy increases so there is a positive enthalpy change ($\Delta H = +ve$); since the total energy is always conserved, the heat energy of the species must decrease by an equal amount; the surrounding temperature therefore decreases
- In these reactions, there is a transfer of energy from heat energy to chemical potential energy and a decrease in temperature; such reactions **absorb heat** and are said to be **ENDOTHERMIC**
- Photosynthesis is an example of an endothermic reaction; ice melting and water boiling are also endothermic processes



Test your knowledge 1.2: Exothermic and Endothermic Reactions

When one mole of methane burns in oxygen to make carbon dioxide and water, the potential energy of the chemicals decreases by 890 kJ

- What type of reaction is this? Draw an enthalpy profile diagram for the reaction.
- Where does the 890 kJ of potential energy go?

When one mole of water evaporates, the potential energy of the chemicals increases by 44 kJ

- What type of reaction is this? Draw an enthalpy profile diagram for the reaction.
- Where does the 44 kJ of potential energy come from?

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Lesson 2 – How do we calculate and record enthalpy changes?

(ii) Calculating and Recording Energy Changes



Summary Activity 2.1: How can we calculate the number of moles?

- How many moles of methane (CH_4) are present in (a) 100 g of methane; (b) 500 cm^3 of methane at 298 K and 300 kPa
- How many moles of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) are present in 1000 g of glucose?

- The enthalpy change during a chemical reaction (ie the amount of heat energy absorbed or released) depends on the amount of substance used; it is therefore necessary to specify the amount of reactants used when recording energy changes; enthalpy changes are generally measured per mole of reacting substance and typically have units of kJmol^{-1} ; this is the **molar enthalpy change** of a reaction
- Given a reaction: $\text{A} + 3\text{B} \rightarrow 2\text{C} + 4\text{D}$; the molar enthalpy change for this reaction, in kJmol^{-1} , is taken to be the enthalpy change when one mole of A reacts with three moles of B to give two moles of C and four moles of D
- The heat change (q) can be converted into a molar enthalpy change (ΔH) by the following conversion: $q = \Delta\text{H} \times n$ or $\Delta\text{H} = q/n$ (n = number of moles)
Eg If 0.2 moles of A react with 0.6 moles of B, 200 kJ of energy are released. What is the molar enthalpy change of the reaction?
Ans: If 0.2 moles of A releases 200 kJ, 1 mole must release $200/0.2 = 1000$ kJ so the molar enthalpy change is -1000 kJmol^{-1}



Test your knowledge 2.2: Molar enthalpy changes

1. The combustion of methane is an exothermic reaction:
 $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta\text{H} = -890 \text{ kJmol}^{-1}$
 - (a) What will be the enthalpy change for the following reaction? $\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + 2\text{O}_2$
 - (b) Calculate the heat energy released when 100 g of methane is burned
 - (c) Calculate the heat energy released when 500 cm^3 of methane is burned at 298 K and 300 kPa
 - (d) Calculate the mass of methane required to produce 50,000 kJ of heat energy
2. Photosynthesis is an endothermic reaction:
 $6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \quad \Delta\text{H} = +2802 \text{ kJmol}^{-1}$
 - (a) What will be the enthalpy change for the following reaction? $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$
 - (b) Calculate the amount of light energy required to make 1000 g of glucose
 - (c) Calculate the amount of light energy required to absorb 500 cm^3 of carbon dioxide at 298 K and 100 kPa
 - (d) Calculate the mass of glucose which can be made when a tree absorbs 10,000 kJ of light energy

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- The enthalpy changes of some reactions are frequently used in chemistry and so have been given special names:
 - The **enthalpy of formation** of a substance is the enthalpy change when one mole of that substance is formed from the most stable allotropes of its elements in their standard states
Eg $\text{C(s)} + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}), \Delta H = -74.8 \text{ kJmol}^{-1}$
So the enthalpy of formation of methane is -74.8 kJmol^{-1}
Eg $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)}, \Delta H = -285.8 \text{ kJmol}^{-1}$;
So the enthalpy of formation of water is $-285.8 \text{ kJmol}^{-1}$
 - The standard enthalpy of formation of all elements in their standard states is zero
 - It is usually not possible to measure enthalpies of formation directly

 - The **enthalpy of combustion** of a substance is the enthalpy change when one mole of that substance is burned in an excess of oxygen
Eg $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)}, \Delta H = -285.8 \text{ kJmol}^{-1}$
So the enthalpy of combustion of hydrogen is $-285.8 \text{ kJmol}^{-1}$
Eg $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O(l)}, \Delta H = -890.3 \text{ kJmol}^{-1}$
So the enthalpy of combustion of methane is $-890.3 \text{ kJmol}^{-1}$
 - Burning a substance in oxygen is almost always exothermic, so standard enthalpies of combustion almost always have negative values
 - Substances which do not support combustion, like water, carbon dioxide and most other oxides, have zero enthalpy of combustion
 - It is usually possible to measure enthalpies of combustion directly

 - The **enthalpy of neutralisation** of an acid and a base is the enthalpy change when one mole of water is formed by the reaction of that acid with that base
Eg $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}, \Delta H = -285.8 \text{ kJmol}^{-1}$
So the enthalpy of neutralisation of HCl by NaOH is -57.3 kJmol^{-1}
It is usually possible to measure enthalpies of neutralisation directly

 - The **enthalpy of solution** is the enthalpy change when one mole of a substance is dissolved in an excess of water
Eg $\text{NaCl(s)} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}), \Delta H = +11.1 \text{ kJmol}^{-1}$
So the enthalpy of solution of NaCl is $+11.1 \text{ kJmol}^{-1}$
 - It is usually possible to measure enthalpies of solution directly



Test your knowledge 2.3: Special Enthalpy Changes

Write equations for the reactions whose molar enthalpy change is described by the following terms:

- the enthalpy of formation of carbon dioxide
- the enthalpy of formation of butane (C_4H_{10})
- the enthalpy of combustion of butane (C_4H_{10})
- the enthalpy of combustion of magnesium
- the enthalpy of neutralisation of nitric acid by potassium hydroxide
- the enthalpy of solution of magnesium chloride

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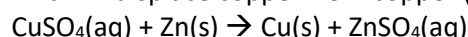
Lesson 3 – How do we measure enthalpies of neutralisation and solution?

(iii) Measuring enthalpy changes

- Energy changes are generally measured by carrying out a reaction under controlled conditions in a laboratory and measuring the temperature change
- Solution and neutralisation reactions (and many other reactions) take place in aqueous solution; when the reaction takes place, the temperature of the solution increases or decreases depending on whether the reaction is exothermic or endothermic; for accurate results, the reaction container should be well insulated so heat is not lost to the surroundings
- The amount of energy required to change the temperature of a system by 1K is known as the heat capacity of a system (H_c), measured in JK^{-1} ; the energy change (q) for a given reaction can therefore be calculated from the temperature change (ΔT) from the equation: $q = \Delta T \times H_c$
- The **specific heat capacity (c)** is the amount of heat required to heat 1 g of a substance by 1K
 - so heat capacity = specific heat capacity \times mass ($c = m \times H_c$)
 - but mass = volume \times density, so heat capacity = specific heat capacity \times volume \times density
 - so the energy change (q) = $V\rho c\Delta T$ or $q = mc\Delta T$
- If a reaction is taking place in solution (and therefore water is the main species present) it is reasonable to assume that the solution behaves as if it were pure water; the density of water is 1.0 gcm^{-3} and the specific heat capacity of water is $4.18 \text{ Jg}^{-1}\text{K}^{-1}$; so $q = \text{total volume of solution (x 1)} \times 4.18 \times \Delta T$
- The molar enthalpy change (ΔH) can then be calculated by dividing the energy change by the number of moles of reactants: $\Delta H = q/n$
- If the temperature goes up the reaction is exothermic and the enthalpy change is negative; if the temperature goes down the reaction is endothermic and the enthalpy change is positive

Example:

Zinc will displace copper from copper (II) sulphate solution according to the following equation:



If an excess of zinc powder is added to 50 cm^3 of 1.0 mol dm^{-3} copper(II) sulphate, the temperature increases by $6.3 \text{ }^\circ\text{C}$. Calculate the molar enthalpy change for the reaction.

Answer:

$m = \text{mass of solution being heated} = \text{volume} \times \text{density} = 1 \times 50 = 50 \text{ g}$

$q = \text{Heat change} = 50 \times 4.18 \times 6.3 = 1317 \text{ J} = 1.317 \text{ kJ}$

$n = \text{moles of CuSO}_4 = 50/1000 \times 1 = 0.05$

$\Delta H = \text{molar enthalpy change} = 1317/0.05 = 26.3 \text{ kJmol}^{-1}$

Temperature has increased, so reaction is exothermic, so sign should be -ve: **26.3 kJmol^{-1}**



Practical 3.1: Determine the molar enthalpy of solution of ammonium chloride (NH₄Cl)

- 1) Place a clean, dry polystyrene cup inside a glass beaker.
- 2) Pour 100 cm³ of water into the cup using a measuring cylinder. Record the initial temperature of the water.
- 3) Use a weighing boat to weigh out approximately 5 g of ammonium chloride. Record the exact mass used.
- 4) Add the ammonium chloride to the water and stir continuously, until the temperature either remains constant for over a minute or starts to change in the opposite direction. Record the final temperature reached.
- 5) Deduce the temperature change, and hence the heat energy change q ($100 \times 4.18 \times \Delta T$, then convert to kJ).
- 6) Deduce the moles (n) of ammonium chloride used ($m/53.5$).
- 7) Hence deduce the molar enthalpy change of solution of ammonium chloride (q/n); don't forget to include a sign in your answer (-ve if exothermic, +ve if endothermic)



Practical 3.2: Determine the molar enthalpy of neutralisation of hydrochloric acid by sodium hydroxide according to the equation $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$

- 1) Place a clean, dry polystyrene cup inside a glass beaker.
- 2) Pour 25 cm³ of 1 mol dm⁻³ HCl into the cup using a measuring cylinder. Record the initial temperature of the solution.
- 3) Measure out 25 cm³ of 1 mol dm⁻³ NaOH using a measuring cylinder and record the initial temperature of the solution. Hence deduce the average initial temperature of the solutions.
- 4) Add the NaOH solution to the HCl solution and stir continuously, until the temperature either remains constant for over a minute or starts to change in the opposite direction. Record the final temperature reached.
- 5) Deduce the temperature change, and hence the heat energy change q ($50 \times 4.18 \times \Delta T$, then convert to kJ).
- 6) Deduce the moles (n) of water formed $(25/1000) \times 1 = 0.025$
- 7) Hence deduce the molar enthalpy change of neutralisation of HCl by NaOH (q/n); don't forget to include a sign in your answer (-ve if exothermic, +ve if endothermic)



Test your knowledge 3.3: Measuring enthalpy changes of solution and neutralisation

- (a) When 5.73 g of sodium chloride (NaCl) dissolves in 100 cm³ of water, the temperature of the water fell from 22.4 °C to 19.8 °C. Calculate the molar enthalpy of solution of NaCl.
- (b) When 2.3 g of magnesium chloride (MgCl₂) dissolves in 200 cm³ of water, the temperature rose by 3.4 °C. Calculate the molar enthalpy of solution of MgCl₂.
- (c) If 50 cm³ of 0.1 mol dm⁻³ HCl and 50 cm³ of 0.1 mol dm⁻³ NaOH are mixed, the temperature of the solution rises by 0.68 °C. Calculate the molar enthalpy of neutralisation of HCl by NaOH.
- (d) If 50 cm³ of 1.0 mol dm⁻³ NaOH is added to 25 cm³ of 2.0 mol dm⁻³ CH₃COOH, the temperature rose by 8.3 °C. Calculate the molar enthalpy of neutralisation of CH₃COOH by NaOH.

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Lesson 4 – How do we measure enthalpies of combustion?

- Combustion reactions do not take place in aqueous solution; energy changes in combustion reactions are measured by allowing the fuel to burn inside a spirit burner; the spirit burner is placed below a copper can and the exothermic reaction is used to heat the water; the heat change can be calculated using $q = mc\Delta T$ (m = mass of water being heated); the decrease in mass of the spirit burner can be measured and used to calculate the moles of fuel used



Practical 4.1: Determine the molar enthalpy of combustion of ethanol

1. Using a measuring cylinder, pour 100 cm³ of water into a copper can.
2. Mount the can on a clamp stand and record the initial temperature of the water.
3. Take a spirit burner containing ethanol, and record its mass with the lid on.
4. Remove the lid, place the spirit burner under the calorimeter and surround it with a windshield to protect it from wind currents.
5. Light the spirit burner and allow it to heat the copper calorimeter until the temperature of the water has increased by 30 °C. Record the final temperature of the water and deduce the temperature change.
6. Put out the spirit burner by putting the lid back on.
7. Weigh the spirit burner again and record the loss in mass.
8. Calculate the heat energy change (q) in the reaction ($100 \times 4.18 \times \Delta T$, then convert to kJ)
9. Use the loss in mass to determine the number of moles of ethanol used (n) ($m/46$)
10. Hence calculate the molar enthalpy of combustion of ethanol (q/n); don't forget to include a sign in your answer (-ve if exothermic, +ve if endothermic)



Test your knowledge 4.2: Measuring enthalpy changes of combustion

- (a) A spirit burner containing ethanol (C₂H₅OH) was used to heat 100 cm³ of water in a copper can by 30 °C. As a result, the mass of the spirit burner decreased by 0.62 g. Calculate the molar enthalpy of combustion of ethanol.
- (b) A spirit burner containing butan-1-ol (C₄H₉OH) was used to heat 200 cm³ of water in a copper can by 20 °C. As a result, the mass of the spirit burner decreased by 0.81 g. Calculate the molar enthalpy of combustion of butan-1-ol.

- Measuring and understanding enthalpy changes of combustion is very useful for knowing how much energy it is possible to get from a certain quantity of fuel when it burns; this quantity is known as the **energy content** of a fuel and it is usually measured in kJg⁻¹:
 - wood has an average energy content of 17 kJg⁻¹; coal has an average energy content of 31 kJg⁻¹;
 - hydrogen has an energy content of 142 kJg⁻¹
- The measurement of the energy content of fuels by burning a fixed quantity of the fuel and measuring the temperature rise of a fixed amount of water is known as **calorimetry**
- All living organisms require energy to survive; animals get this energy by eating foods containing carbohydrates and fats, which are broken down in the body and then react with oxygen in an exothermic reaction known as respiration; plants get their energy by using photosynthesis to make glucose, which is then used in respiration

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- The energy content of foods can be measured in the same way as the energy content of other fuels; most carbohydrates have an energy content of around 17 kJg^{-1} and most fats have an energy content of around 39 kJg^{-1} ; a typical human needs to consume around 10,000 kJ per day; this is equivalent to around 250 g of pure fat or around 600 g of pure carbohydrate

Lesson 5 – Why are some chemical reactions faster than others?

(b) Rates of Reaction



Thinkabout Activity 5.1: Different speeds of chemical reactions

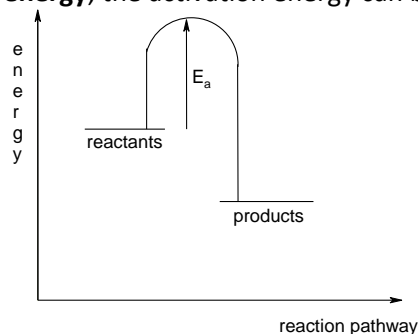
- How many chemical reactions can you think of which are fast?
- How many chemical reactions can you think of which are slow?
- Why are some chemical reactions faster than others? How can we make a reaction faster?

(i) Simple Collision Theory

- Substances in the liquid, aqueous and gaseous phase consist of particles in rapid and constant motion, which are constantly colliding with each other; according to simple collision theory, there are two requirements for a chemical reaction to take place between two particles:
 - the particles must first collide
 - the colliding particles must have enough energy to react together
- The number of collisions between particles per unit time in a system is known as the **collision frequency**; the greater the collision frequency, the faster a chemical reaction
- Not all collisions, however, result in a chemical reaction; this is because the reacting particles contain chemical bonds which must be broken before the particles can react; energy is required to break these bonds, and most of the colliding particles do not have enough energy to do this; most collisions, therefore, just result in the colliding particles bouncing off each other, with no chemical reaction taking place; collisions which do not result in a reaction are known as **unsuccessful (or ineffective) collisions**
- The combined energy of the colliding particles is called the **collision energy**; if the collision energy is sufficient to break the bonds in the reacting particles, a reaction will take place; collisions which result in a chemical reaction are known as **successful (or effective) collisions**

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- the minimum energy required to break the bonds in the reactants and allow the chemical reaction to take place is known as the **activation energy**; the activation energy can be shown in an enthalpy level diagram:



- this enthalpy diagram shows a simple exothermic reaction
 - the activation energy E_a is the energy needed to break the bonds in the colliding particles
 - the potential energy of the substance increases as the bonds are broken
 - once the bonds have been broken, new bonds can be formed and the potential energy will decrease
 - in exothermic reactions, more heat energy is released when new bonds are made than is absorbed when the original bonds are broken; so overall, heat energy is released; the opposite is true in endothermic reactions
- For a collision to be successful, the collision energy needs to be greater than the activation energy; the higher the activation energy, the smaller the fraction of collisions which will be successful



Test your knowledge 5.2: explaining why some reactions are faster than others

- If you increase the collision frequency in a reaction mixture, what will happen to the rate of reaction? Why?
- If you increase the collision energy of the reacting particles in a mixture, what will happen to the rate of reaction? Why?
- Draw an enthalpy profile diagram for an exothermic reaction, labelling the enthalpy change and the activation energy
- Draw an enthalpy profile diagram for an endothermic reaction, labelling the enthalpy change and the activation energy
- If you increase the activation energy of a reaction, what will happen to the rate of reaction? Why?

Lesson 6 – How can we make chemical reactions faster (part 1)?

(ii) Factors Affecting Rate of Reaction

- The rate of a chemical reaction can be changed in a number of ways:
 - by changing the concentration of the reacting particles
 - by changing the pressure of the system (if some of the reacting particles are in the gas phase)
 - by changing the temperature of the system
 - by adding a catalyst
 - by changing the particle size
 - by changing the solvent
- The greater the **concentration** of the species in a liquid or gaseous mixture, the greater the number of species per unit volume and the greater the frequency with which they will collide (ie the **collision frequency** increases); the **collision energy** and **activation energy** are unaffected by a change in concentration



Practical 6.1: Investigate the effect of the concentration of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) on the rate of its reaction with hydrochloric acid (HCl)

- 1) Take a piece of paper and use a thick pen to draw the letter X on it.
- 2) Measure out 20 cm^3 of 0.2 moldm^{-3} HCl into a measuring cylinder labelled "HCl" and then pour the HCl into a conical flask.
- 3) Measure out 20 cm^3 of 0.2 moldm^{-3} $\text{Na}_2\text{S}_2\text{O}_3$ into a measuring cylinder labelled " $\text{Na}_2\text{S}_2\text{O}_3$ ".
- 4) Pour the $\text{Na}_2\text{S}_2\text{O}_3$ into the same conical flask, starting the stopwatch immediately.
- 5) Record the time taken for the X to stop being visible through the conical flask.
- 6) Repeat steps 2 to 5, but using different concentrations of $\text{Na}_2\text{S}_2\text{O}_3$ in step 3, prepared as follows:

| Concentration of $\text{Na}_2\text{S}_2\text{O}_3/\text{moldm}^{-3}$ | Volume of 0.2 moldm^{-3} $\text{Na}_2\text{S}_2\text{O}_3/\text{cm}^3$ | Volume of distilled water/ cm^3 |
|--|--|--|
| 0.15 | 16 | 4 |
| 0.10 | 12 | 8 |
| 0.05 | 8 | 12 |

- 7) Compare the times taken for the X to disappear in the four reactions. How does the rate of reaction change as you change the concentration of $\text{Na}_2\text{S}_2\text{O}_3$?

Cannot do this practical? watch it here: www.youtube.com/watch?v=FSwd7X_c_Qs

- A change in **pressure** has exactly the same effect as a change in concentration; the greater the pressure in a gaseous mixture, the greater the number of species per unit volume and the greater the frequency with which they will collide (ie the collision frequency increases); the pressure of a system is generally increased by reducing its volume (compressing it); the **collision energy** and **activation energy** are unaffected by a change in pressure
- An increase in temperature increases the rate of a reaction for two reasons:
 - as the temperature is increased, the average kinetic energy of the particles increases, and so the **collision energy** increases; as the collision energy increases, there is a greater chance that the collision energy will be sufficient to overcome the activation energy, and the collision is more likely to be effective
 - in addition, at a higher temperature, the molecules have more kinetic energy and are thus moving faster; thus they collide more often, and the **collision frequency** increases
 - changing the temperature has no effect on the activation energy
 - typically, a 10°C temperature rise approximately doubles the rate of reaction.



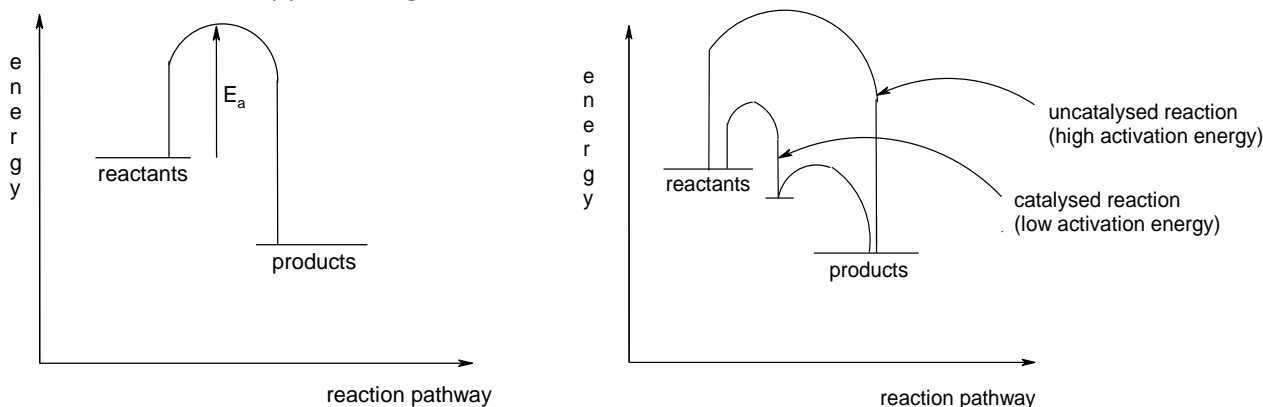
Practical 6.2: Investigate the effect of temperature on the rate of reaction between sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) and hydrochloric acid (HCl)

- 1) Set up three water baths at 30°C , 40°C and 50°C and place stock solutions of 0.2 mol dm^{-3} HCl and 0.2 mol dm^{-3} $\text{Na}_2\text{S}_2\text{O}_3$ in each water bath until they have reached the desired temperature. Keep a sample of both solutions at room temperature.
- 2) Take a piece of paper and use a thick pen to draw the letter X on it
- 3) Using the room temperature solutions, measure out 20 cm^3 of 0.2 mol dm^{-3} HCl into a measuring cylinder labelled "HCl", then measure out 20 cm^3 of 0.2 mol dm^{-3} $\text{Na}_2\text{S}_2\text{O}_3$ into a measuring cylinder labelled " $\text{Na}_2\text{S}_2\text{O}_3$ "
- 4) Pour both solutions into the same conical flask, starting the stopwatch immediately. Record the initial temperature of the mixture.
- 5) Record the time taken for the X to stop being visible through the conical flask.
- 6) Record the final temperature of the solution using a thermometer.
- 7) Repeat steps 3 to 5, but using the solutions at 30°C , then at 40°C and then at 50°C .
- 8) Compare the times taken for the X to disappear in the four reactions. How does the rate of reaction change as you change the temperature?

Cannot do this practical? watch it here: www.youtube.com/watch?v=L9nVcKYVjjA

Lesson 7 – How can we make chemical reactions faster (part 2)?

- A catalyst is a substance which changes the rate of a chemical reaction without itself being chemically altered at the end of the reaction
- Catalysts provide an alternative pathway for the reaction, usually by introducing an extra step into the reaction, which has a lower activation energy than the uncatalysed reaction; this effect can be illustrated with an enthalpy level diagram:



- the enthalpy level diagram on the left shows a reaction without a catalyst
- the diagram on the right shows the effect of adding a catalyst
- the reaction pathway changes and the activation energy is lowered

- Catalysts increase the rate of a reaction by lowering the activation energy; the collision frequency and collision energy are unchanged

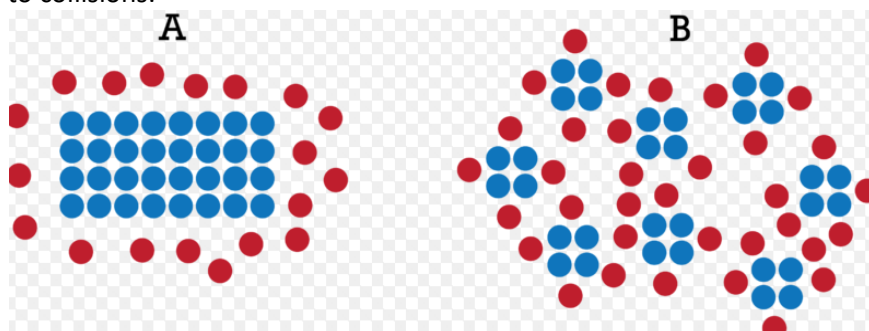


Practical 7.1: Investigate the effect of a catalyst on the rate of reaction between potassium peroxodisulphate ($K_2S_2O_8$) and potassium iodide (KI)

- 1) Mix together 25 cm^3 of 0.3 mol dm^{-3} KI, 5 cm^3 of 0.02 mol dm^{-3} sodium thiosulphate, 1 cm^3 of 1% starch solution and 10 cm^3 of distilled water into a conical flask
- 2) Add 10 cm^3 of 0.1 mol dm^{-3} $K_2S_2O_8$ and immediately start the stopwatch. Note the time taken for the mixture to turn a dark blue colour.
- 3) Repeat steps 1 and 2, but this time using 9 cm^3 of distilled water and 1 cm^3 of iron (III) sulphate solution.
- 4) Compare the reaction times in both reactions. Why is the second reaction faster?

Cannot do this practical? watch it here: www.youtube.com/watch?v=5da9e-rrjxQ

- If reactants are gaseous, or well mixed in liquid or aqueous form, then all of the particles in the sample are able to react; if one of the reactants is in the solid state, however, its particles are not free to move; only the particles at the **surface** of the solid are able to collide with other particles; this reduces the collision frequency and will reduce the rate of reaction
- Reactants in the solid state react more slowly than reactants in the liquid, gaseous or aqueous states because in a solid, the particles not at the surface are unable to take part in collisions with other reactants, reducing the collision frequency
- The rate of reaction in solids can be increased by reducing the particle size, and hence increasing the **surface area** exposed to collisions:



- A: large particle size, fewer of the blue solid particles can collide with the red particles, slower reaction.
- B: small particle size, more of the blue solid particles can collide with the red particles, faster reaction.



Demonstration 7.2: Investigate the effect of particle size on the rate of reaction between calcium carbonate and hydrochloric acid

- 1) Pour 40 cm^3 of 2 mol dm^{-3} HCl into a conical flask.
- 2) Weigh out 2.5 g of marble chips (large particle size).
- 3) Add the marble chips to the conical flask containing the HCl, start the stopwatch and weigh the conical flask with all its contents.
- 4) Weigh the conical flask again after 2 minutes and record the loss in mass.
- 5) Repeat steps 1 – 4 but using 2.5 g of marble chips (small particle size).
- 6) Why does the mass of the conical flask decrease? In which experiment is there a larger decrease in mass? Why is this?

Cannot do this demonstration? Watch it here: www.youtube.com/watch?v=p6Kq4YqztQM

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- If reactions are taking place in solution, the nature of the solvent can influence the rate of reaction; this is because different solvents can interact with the reacting particles in different ways, making them more likely, or less likely, to react with each other
 - Eg magnesium reacts rapidly with HCl dissolved in water, but very slowly with HCl dissolved in methylbenzene



Test your knowledge 7.3: Factors affecting the rate of a reaction

- Explain why increasing the concentration of one of the reactants will increase the rate of a reaction
- Explain why increasing the pressure of a gas-phase reaction will increase the rate of a reaction
- Explain why increasing the temperature will increase the rate of a reaction
- Explain why adding a catalyst will increase the rate of a reaction
- Explain why solids react more slowly than liquids and gases
- Explain why decreasing the particle size of a solid reactant will increase the rate of a reaction
- Suggest one other way to change the rate of a reaction
-



Extension 7.4: Factors affecting the rate of a reaction

Completed Test Your Knowledge 7.3? Now complete the following table to show the different ways in which the rate of a reaction can be changed (in each box, write “increases”, “decreases” or “no effect”)

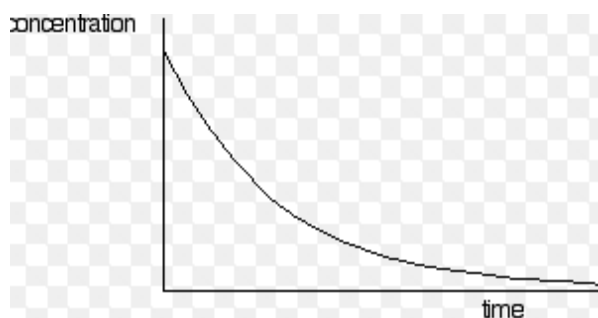
| Effect: | On collision frequency | On collision energy | On activation energy | On rate of reaction |
|-----------------------------|------------------------|---------------------|----------------------|---------------------|
| Increase concentration | | | | |
| Increase pressure | | | | |
| Increase temperature | | | | |
| Add a catalyst | | | | |
| Using solid state reactants | | | | |

Lesson 8 – How can we measure rates of reaction?

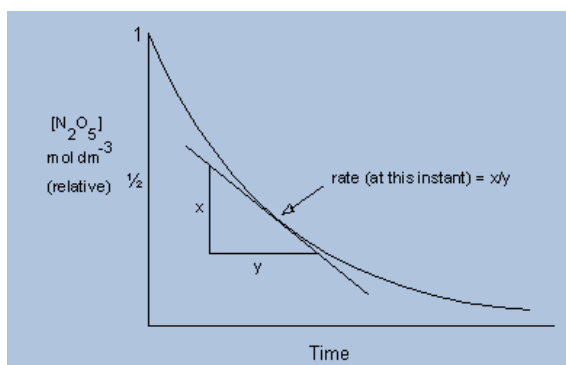
(iii) Measuring rates of reaction

- The rate of reaction can be defined as the **change in concentration of reactants or products per unit time**; it has the units $\text{mol dm}^{-3}\text{s}^{-1}$
- It is possible to determine the rate of a reaction by monitoring how the concentration of a reaction changes over time in a single reaction, and then plotting a graph of concentration against time (a **concentration-time graph**):

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- The rate of reaction is the change in concentration per unit time and can therefore be calculated from the gradient of the line at a particular time
- As the graph is a curve (its gradient is steadily decreasing with time), the gradient of the line at a particular point must be calculated by drawing a tangent to that line at a particular point and calculating the gradient of that tangent:



- The gradient of the line (and hence the rate of reaction) decreases with time; this is because as reactions proceed, the concentration of reactants decreases, making collisions between the remaining particles less frequent
- The initial rate of reaction is the gradient of the tangent to the curve at $t = 0$; the rate of reaction at a particular time is the gradient of the tangent to the curve at that time



Test your knowledge 8.1: Measuring the rate of a reaction from a concentration-time graph

Hydrogen peroxide, H_2O_2 , decomposes according to the equation: $2\text{H}_2\text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$

In an experiment, the concentration of the reactant H_2O_2 was measured over a period of time. The results are shown below:

| | | | | | | |
|---|------|------|------|------|------|------|
| Time/s | 0 | 15 | 30 | 60 | 100 | 180 |
| $[\text{H}_2\text{O}_2]/\text{mol dm}^{-3}$ | 0.40 | 0.28 | 0.19 | 0.07 | 0.03 | 0.01 |

Plot a graph to show how concentration varies with time and use your graph to calculate the rate of reaction:

- Initially
- When $[\text{H}_2\text{O}_2] = 0.20 \text{ mol dm}^{-3}$
- After 50 s


Practical 8.2: Measure the rate of the reaction between magnesium and hydrochloric acid (HCl) from a concentration-time graph

1. Clamp a gas syringe into a horizontal position so that the bung attached to it can be easily attached to a conical flask.
2. Pour 25 cm³ of 0.2 mol dm⁻³ HCl into a 100 cm³ conical flask.
3. Weigh out 1 g of magnesium on a weighing boat.
4. Add the magnesium to the conical flask, attaching the bung and starting the stopclock immediately.
5. Record the volume of gas produced every 10 seconds until the reaction stops or the volume of gas reaches 100 cm³. Record your data in the table below:

| Time/s | Volume of H ₂ produced (V _t) /cm ³ | (V _f - V _t)/cm ³ |
|--------|--|--|
| 0 | | |
| 10 | | |
| 20 | | |
| 30 | | |
| 40 | | |
| 50 | | |
| 60 | | |
| 70 | | |
| 80 | | |
| 90 | | |
| 100 | | |
| Final | | |

(V_f - V_t) gives you a value proportional to [HCl]

6. Plot a graph of (V_f - V_t) (on the y-axis) against time (on the x-axis)
7. Use your graph to determine the initial rate of reaction.

Lesson 9 – What is chemical equilibrium?

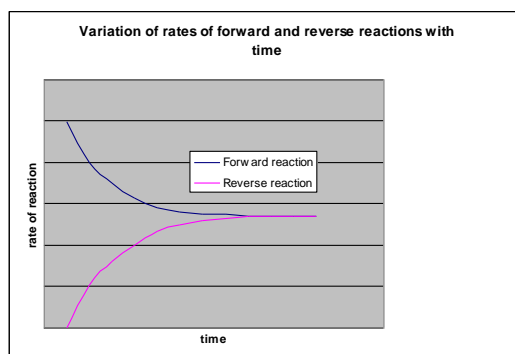
(c) Reversible Reactions and Chemical Equilibrium

(i) Dynamic Equilibrium

- A reversible reaction is a reaction which can proceed in both directions at the same time; reversible reactions are represented by the \rightleftharpoons sign instead of by a regular arrow \rightarrow
- All reactions are reversible in theory; although in practice many reactions are considered irreversible, either because the reverse reaction is insignificant or because the reverse reaction is not allowed to take place because the products escape after they are produced

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- Consider a reversible reaction $A + B \rightleftharpoons C + D$
 - as the reaction proceeds, the rate of the forward reaction decreases and the rate of the reverse reaction increases
 - eventually, the reaction will reach a stage where both forward and backward reactions are proceeding at the same rate:



- at this stage, a **dynamic equilibrium** has been reached; “dynamic” means that the reaction has not stopped; it is simply moving in both directions at the same rate; “equilibrium” means that the amount of reactants and products in the system is not changing
- A **dynamic equilibrium** is reached when the forward and reverse reactions are taking place at the same rate, which means that the concentrations of reactants and products are not changing.

(ii) open and closed systems

- A **closed system** is one from which reactants and products cannot escape; in closed systems the forward and reverse reactions continue until dynamic equilibrium is reached; all reactions in a closed system are thus reversible in theory, although they are only considered as such if both forward and reverse reactions occur to a significant extent
 - Eg $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$; in this case the reverse reaction is not significant so the reaction is represented by single arrow
 - Eg $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$; in this case the reverse reaction is significant, so the reaction is represented by an equilibrium sign
- An **open system** is one from which reactants and products can escape such as the open air or a fume cupboard; in an open system, products can be removed as soon as they are formed, so the reverse reaction is not allowed to take place; such reactions never reach equilibrium, but proceed until all the reactions have been converted into products, even if the reaction would be reversible in a closed system
 - Eg $H_2O(l) \rightarrow H_2O(g)$; this reaction would not be expected to proceed significantly under normal conditions, since water is more stable than steam at room temperature; however puddles will disappear completely if left for long enough; this is because the water vapour is removed by wind currents as soon as it is produced, and so the reverse reaction is not allowed to take place; thus the system never reaches equilibrium and the reaction is irreversible

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(iii) Equilibrium Position and Equilibrium Constants

- In a closed system, all reactions will reach equilibrium eventually; in some cases, the equilibrium mixture mostly consists of products, with only a small number of reactant particles still remaining
 - consider the following reversible reaction: $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$; the equilibrium mixture formed when this reaction reaches equilibrium contains mostly SO_3 , with not much SO_2 or O_2 ; in such cases, it is said that the **position of equilibrium** lies to the right-hand side of the reaction
 - Consider the following reversible reaction: $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$; the equilibrium mixture formed when this reaction reaches equilibrium contains mostly CH_3COOH , with not much CH_3COO^- or H^+ ; in such cases, it is said that the **position of equilibrium** lies to the left-hand side of the reaction
- The position of equilibrium can be expressed mathematically using the concentrations of reactants and products; it has been proved that product of the product concentrations raised to their stoichiometric coefficients divided by the product of the reactant concentrations raised to their stoichiometric coefficients is always a fixed value, at a given temperature; this value is known as the **equilibrium constant (K_c)** of the reaction at that temperature
 - consider the reversible reaction: $\text{A} + 3\text{B} \rightleftharpoons \text{C} + 2\text{D}$; the K_c for this reaction is $\frac{[\text{C}][\text{D}]^2}{[\text{A}][\text{B}]^3}$
 - the square brackets [] are used to represent the concentration of that reactant, so [A] means the concentration of A in mol dm^{-3}
 - the value of K_c for a reaction is always the same at a particular temperature, no matter what amounts of reactants and products are present at the start of the reaction



Test your knowledge 9.1: Dynamic Equilibrium and Equilibrium Constants

- Why does the rate of the forward reaction decrease as the reaction proceeds?
- Why does the rate of the reverse reaction increase as the reaction proceeds?
- What will eventually happen to the rate of the forward and reverse reactions?
- Why will this often not happen in an open system?
- Write expressions for the equilibrium constants for the following reactions:
 - $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$
 - $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
 - $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
 - $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
- For the equilibrium $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, the equilibrium concentrations of PCl_5 , PCl_3 and Cl_2 are 1.0, 0.205 and 0.205 mol dm^{-3} respectively. Calculate the value of K_c
- For the equilibrium $2\text{N}_2\text{O}_5(\text{g}) \rightleftharpoons 2\text{N}_2\text{O}_4(\text{g}) + \text{O}_2(\text{g})$, the equilibrium concentrations are $[\text{N}_2\text{O}_5] = 1.0 \text{ mol dm}^{-3}$, $[\text{N}_2\text{O}_4] = 0.11 \text{ mol dm}^{-3}$, $[\text{O}_2] = 0.11 \text{ mol dm}^{-3}$. Calculate the value of K_c

Lesson 10 – How can we change the position of equilibrium?

(iv) Le Chatelier's Principle

- If the conditions are changed after equilibrium has been established, the system may no longer be at equilibrium and may move in one direction or another to re-establish equilibrium; the direction in which the system will move to re-establish equilibrium can be predicted by **Le Chatelier's principle**: "**If a constraint is imposed on a system at equilibrium, then the system will respond in such a way as to oppose the effect of that constraint**"; the constraints imposed could be the addition or removal of one of the reactants or products, a change in pressure, a change in temperature or the addition or removal of a catalyst; it is possible to use Le Chatelier's principle to predict what will happen if any of these conditions are changed
- If the **concentration** of one of the reactants is increased, the equilibrium position will move to the right in order to decrease the concentration of that reactant; if the reactant's concentration is decreased, the equilibrium position will move to the left in order to replace that reactant; similarly, if a product's concentration is increased then the equilibrium position will move to the left and if a product's concentration is decreased then the equilibrium position will move to the right (the equilibrium constant will not change)
 - Eg in the reaction $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$, an increase in the concentration of SO_2 or O_2 , or a decrease in the concentration of SO_3 , will move the equilibrium position to the right; a decrease in the concentration of SO_2 or O_2 , or an increase in the concentration of SO_3 , will move the equilibrium position to the right
- The **pressure** in a system depends on the number of gas molecules in the system; if the pressure of the system is increased, the system will move towards the side which has fewer gas molecules in order to decrease the pressure
 - if the pressure of the system is decreased, the system will move towards the side which has more gas molecules in order to increase the pressure
 - if the number of gas moles on both sides is the same, then pressure has no effect on the equilibrium position (the equilibrium constant will not change)
 - Eg in the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, there is one gas molecule on the left and two on the right; if the pressure is increased, the equilibrium position will move to the left, where there are fewer gas molecules, in order to decrease the pressure; if the pressure is decreased, the equilibrium position will move to the right, where there are more gas molecules, in order to increase the pressure

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- If the **temperature** of a system is increased, the reaction will move in the endothermic direction in order to decrease the temperature; if the temperature of a system is decreased, the reaction will move in the exothermic direction to increase the temperature
 - if the forward reaction is exothermic, an increase in temperature will cause the equilibrium position to shift to the left, (ie the endothermic direction) to decrease the temperature, and a decrease in temperature will cause the equilibrium position to shift to the right (ie the exothermic direction) to increase the temperature
 - if the forward reaction is endothermic, an increase in temperature will cause the equilibrium position to shift to the right (ie the endothermic direction) to decrease the temperature and a decrease in temperature will cause the equilibrium position to shift to the left (ie the exothermic direction) to increase the temperature
 - If $\Delta H = 0$, then a change in temperature will have no effect on the position of equilibrium
 - Eg the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ is known to be exothermic (in the forward direction); an increase in temperature will cause the equilibrium position to move to the left (in the endothermic direction) to reduce the temperature; an decrease in temperature will cause the equilibrium position to move to the right (in the exothermic direction) to increase the temperature
 - A change in temperature does change the value of the equilibrium constant; if the reaction is exothermic, then an increase in temperature will cause the value of K_c to decrease; if the reaction is endothermic, then an increase in temperature will cause the value of K_c to increase
- The addition or removal of a **catalyst** will have no effect on the position of equilibrium; it will change the rate of the forward and reverse reactions, but by the same amount; the position of equilibrium and the equilibrium constant will thus be unchanged



Test your knowledge 10.1: Predict how the position of equilibrium will move

- (a) Consider the following exothermic reaction: $4\text{HCl}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
State, with a reason, what would happen to the amounts of chlorine and hydrogen chloride in the system if the following changes were made after equilibrium had been established in a sealed container:
- water is removed from the system
 - extra oxygen is added to the system
 - the volume of the container was reduced
 - the temperature of the container was increased
 - a catalyst was added
- (b) For each of the following reactions, state and explain whether a high or low temperature and a high or low pressure should be used to maximize the yield of product:
- $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}), \Delta H = -\text{ve}$
 - $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}), \Delta H = +\text{ve}$
 - $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g}), \Delta H = -\text{ve}$
 - $\text{HCOOH}(\text{l}) + \text{CH}_3\text{OH}(\text{l}) \rightleftharpoons \text{HCOOCH}_3(\text{l}) + \text{H}_2\text{O}(\text{l}), \Delta H = 0$

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Lesson 11 – What have you understood about Physical Chemistry?

11.1 END-OF-TOPIC QUIZ

TOPIC 4 – INTRODUCTION TO PHYSICAL CHEMISTRY



1. The enthalpy of combustion of ethane (C_2H_6) is -1556 kJmol^{-1} . How much heat energy is released when 1000 g of ethane is burned?
2. When 2.0 g $CaCl_2$ is dissolved in 50 cm^3 of water, the temperature increases by $6.9 \text{ }^\circ\text{C}$. Calculate the enthalpy of solution of $CaCl_2$.
3. Consider the following reaction: $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2 + H_2O(l)$
Explain why the rate of this reaction would increase if you:
 - (a) Increased the molarity of the HCl
 - (b) Increased the temperature of the HCl
 - (c) Crushed the $CaCO_3$ before the reaction

4. In an experiment to measure the initial rate of the following reaction: $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$, the concentration of the reactant SO_2Cl_2 was measured over a period of time. The results are shown below:

| | | | | | | |
|---------------------------------|------|------|------|------|------|------|
| Time/s | 0 | 500 | 1000 | 2000 | 3000 | 4000 |
| $[SO_2Cl_2]/\text{mol dm}^{-3}$ | 0.50 | 0.43 | 0.37 | 0.27 | 0.20 | 0.15 |

Plot a concentration-time graph for this reaction and use it to determine the initial rate of reaction.

5. Explain what is meant by the term “dynamic equilibrium”.
6. For the reaction: $2SO + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta H = -294 \text{ kJmol}^{-1}$
 - (a) Write an expression for the equilibrium constant K_c
 - (b) Explain how the position of equilibrium would move if some SO_3 was removed from the system after equilibrium had been reached
 - (c) Explain how the position of equilibrium would move if the temperature was increased after equilibrium had been reached
 - (d) Explain whether a high or low pressure would give you the best yield of SO_3 .