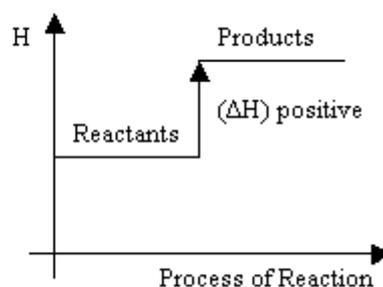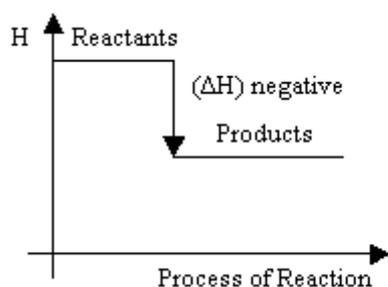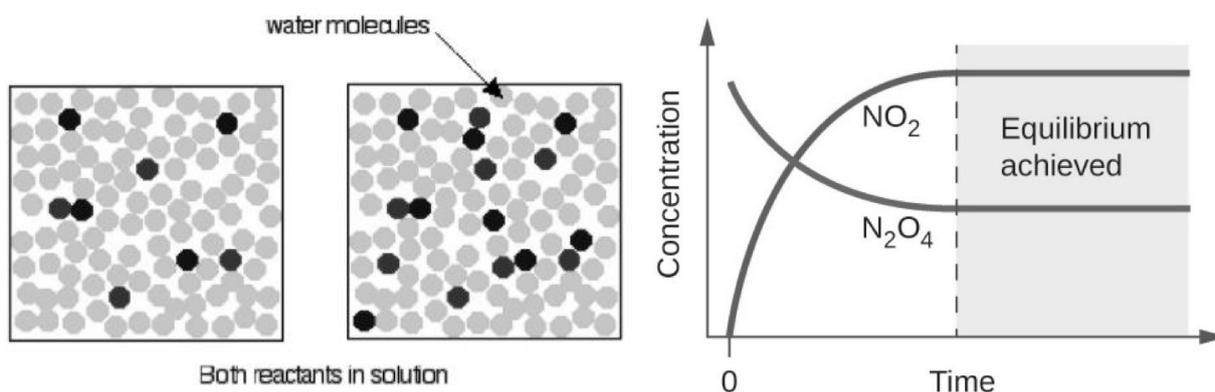# UNIT 4

INTRODUCTION TO PHYSICAL CHEMISTRY

Teacher Version

www.swotrevision.com

www.chemguide.co.uk   www.khanacademy.org

Contents

a) Energy Changes
b) Rates of Reaction
c) 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

UNIT 4 – INTRODUCTION TO PHYSICAL CHEMISTRY

UNIT 4 SUMMARY AND SYLLABUS REFERENCE

Lesson	Title and Syllabus Reference
1	**Energy Changes in Chemical Reactions** ***CA6a Energy changes in physical and chemical processes*** *(enthalpy, energy diagrams, forms of energy, energy content, transfer of energy);* ***CA6b description, definition and illustrations of energy changes and effects*** *(exothermic and endothermic processes, total energy of a system as the sum of various forms of energy e.g. kinetic, potential, electrical, heat, sound etc)*
2	**Defining and Calculating Molar Enthalpy Changes** ***CA6b description, definition and illustrations of energy changes and effects*** *(enthalpy changes of the following: formation, combustion, solution, neutralization);* ***CC3 enthalpies of reaction***
3	**Measuring Enthalpy Changes** ***CA6b description, definition and illustrations of energy changes and effects*** *(practical knowledge of the measurement of the heats of neutralisation and solution);* ***CA13iv General Skills and Principles - measurement of heats of neutralisation and solution***
4	**Enthalpies of Combustion and Fuels** ***CA6b description, definition and illustrations of energy changes and effects*** *(uses of energy changes including energy content of foods and fuels);* ***CC3 enthalpies of reaction*** *(measurement of the enthalpy of combustion (in outline) by calorimetry)*
5	**Simple Collision Theory** ***CA9aii theory of reaction rates*** *(collision theory and activation energy theory to be treated qualitatively only, effective collision, activation energy, energy profile showing activation energy and enthalpy change)*
6	**Factors Affecting Rates of Reaction I** ***CA9ai factors affecting rates: concentration of reactants, temperature*** *(for gaseous systems, pressure may be used as concentration term, appropriate experimental demonstration for each factor is required);* ***CA9aii theory of reaction rates*** *(factors influencing collisions: temperature and concentration)*
7	**Factors Affecting Rates of Reaction II** ***CA9ai factors affecting rates: physical states, catalysts and medium*** *(appropriate experimental demonstration for each factor is required)*
8	**Measuring Rates of Reaction** ***CA9a rate of reaction*** *(definition of reaction rates);* ***CA13avi determination of rates of reaction from concentration versus time curves***
9	**Reversible Reactions and Equilibrium** ***CA9bi general principles*** *(reversible reactions i.e. dynamic equilibrium, the equilibrium constant K must be treated qualitatively, it must be stressed that K for a system is constant at constant temperature)*
10	**Le Chatelier's Principle** ***CA9bii Le Chatelier's Principle*** *(prediction of the effects of external influence of concentration, temperature and pressure changes on equilibrium systems)*
11	**Unit 4 Revision and Summary**

The Periodic Table of the Elements

Key

relative atomic mass
symbol
name
atomic (proton) number

1.0 **H** hydrogen 1

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
																	4.0 **He** helium 2
6.9 **Li** lithium 3	9.0 **Be** beryllium 4											10.8 **B** boron 5	12.0 **C** carbon 6	14.0 **N** nitrogen 7	16.0 **O** oxygen 8	19.0 **F** fluorine 9	20.2 **Ne** neon 10
23.0 **Na** sodium 11	24.3 **Mg** magnesium 12											27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	96.0 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La *** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac †** actinium 89	[267] **Rf** rutherfordium 104	[268] **Db** dubnium 105	[271] **Sg** seaborgium 106	[272] **Bh** bohrium 107	[270] **Hs** hassium 108	[276] **Mt** meitnerium 109	[281] **Ds** darmstadtium 110	[280] **Rg** roentgenium 111							

Elements with atomic numbers 112–116 have been reported but not fully authenticated

* 58 – 71 Lanthanides

140.1 **Ce** cerium 58	140.9 **Pr** praseodymium 59	144.2 **Nd** neodymium 60	[145] **Pm** promethium 61	150.4 **Sm** samarium 62	152.0 **Eu** europium 63	157.3 **Gd** gadolinium 64	158.9 **Tb** terbium 65	162.5 **Dy** dysprosium 66	164.9 **Ho** holmium 67	167.3 **Er** erbium 68	168.9 **Tm** thulium 69	173.1 **Yb** ytterbium 70	175.0 **Lu** lutetium 71

† 90 – 103 Actinides

232.0 **Th** thorium 90	231.0 **Pa** protactinium 91	238.0 **U** uranium 92	[237] **Np** neptunium 93	[244] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[247] **Bk** berkelium 97	[251] **Cf** californium 98	[252] **Es** einsteinium 99	[257] **Fm** fermium 100	[258] **Md** mendelevium 101	[259] **No** nobelium 102	[262] **Lr** lawrencium 103

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?

Note: students are likely to have very different and inaccurate understandings of what potential energy is at this stage; the purpose of this opening activity and discussion is to address some of the misconceptions about energy in general and potential energy in particular
- Energy associated with attraction or repulsion
- Gravitational, chemical, nuclear, spring
- Gravitational; you increase it by moving away from the earth and decrease it by moving towards the earth; if you have zero gravitational potential energy you are completely free of the earth's gravitational pull; otherwise you have negative gravitational potential energy
- chemical; you increase it by moving electron away from the nucleus and decrease it by moving it towards the nucleus; if the electron has zero chemical potential energy it is completely free of the nuclear pull (the atom has been ionised); otherwise it has negative chemical potential 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**:
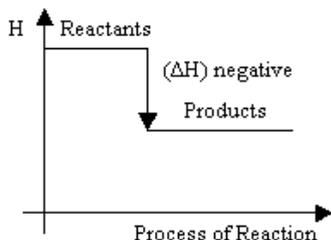
- In these reactions the enthalpy decreases so there is a negative enthalpy change. (**ΔH = -ve**); since the total energy is always conserved, the heat energy of the species must increase by an equal amount; the surrounding temperature therefore increases

- 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**:
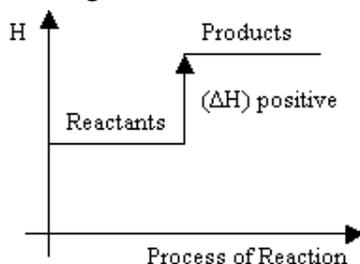
- In these reactions the enthalpy increases so there is a positive enthalpy change (**ΔH = +ve**); since the total energy is always conserved, the heat energy of the species must decrease by an equal amount; the surrounding temperature therefore decreases

- 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: Describing 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

    (a) What type of reaction is this? Draw an enthalpy profile diagram for the reaction.

    (b) 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

    (a) What type of reaction is this? Draw an enthalpy profile diagram for the reaction.

    (b) Where does the 44 kJ of potential energy come from?
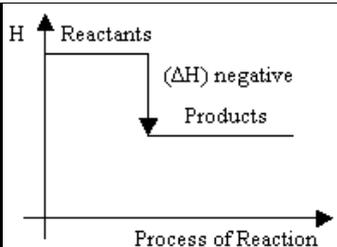
(a) Exothermic

(b) It is converted into kinetic (heat) energy; the particles get hotter /move faster
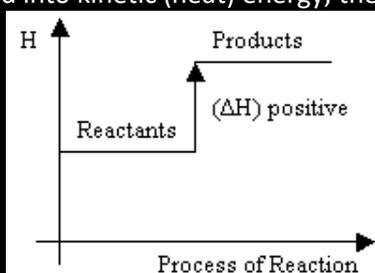
(a) Endothermic

(b) It comes from kinetic (heat) energy; the particles get colder /move more slowly

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 ($C_6H_{12}O_6$) are present in 1000 g of glucose?
- (a) 100/16 = 6.25 moles; (b) (300000 x 0.0005)/(8.31 X 298) = 0.0606 moles
- 1000/180 = 5.56 moles

- 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: A + 3B → 2C + 4D; 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: $q = \Delta H \times n$ or $\Delta H = q/n$ (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: Using molar enthalpy changes

1. The combustion of methane is an exothermic reaction:

   $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $\Delta H = -890\ kJmol^{-1}$

   (a) What will be the enthalpy change for the following reaction? $CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$

   (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:

   $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ $\Delta H = +2802\ kJmol^{-1}$

   (a) What will be the enthalpy change for the following reaction? $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

   (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

1. (a) **+890 $kJmol^{-1}$**; (b) n = 6.25 so q = $\Delta H \times n$ = 6.25 x 890 = **5560 kJ**; (c) n = 0.0606 so q = $\Delta H \times n$ = 0.0606 x 890 = **53.9 kJ**; (d) n = q/ΔH = 50000/890 = 56.2 moles; m = n x mr = **899 g**
2. (a) **-2802 $kJmol^{-1}$**; (b) n = 5.56 so q = $\Delta H \times n$ = 5.56 x 2802 = **15600 kJ**; (c) n (CO_2) = 0.0606 so n ($C_6H_{12}O_6$) = 0.0101 so q = $\Delta H \times n$ = 0.0101 x 2802 = **28.3 kJ**; (d) n = q/ΔH = 10000/2802 = 3.57 moles; m = n x mr = **642 g**

- 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 $C(s) + 2H_2(g) \rightarrow CH_4(g)$, $\Delta H = -74.8\ kJmol^{-1}$

    So the enthalpy of formation of methane is -74.8 $kJmol^{-1}$

    Eg $H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$, $\Delta H = -285.8\ kJmol^{-1}$;

    So the enthalpy of formation of water is -285.8 $kJmol^{-1}$
  - 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 $H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$, $\Delta H = -285.8\ kJmol^{-1}$

    So the enthalpy of combustion of hydrogen is -285.8 $kJmol^{-1}$

    Eg $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$, $\Delta H = -890.3\ kJmol^{-1}$

    So the enthalpy of combustion of methane is -890.3 $kJmol^{-1}$
  - 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 HCl(aq) + NaOH(aq) → NaCl(aq) + $H_2O(l)$, ΔH = -285.8 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 NaCl(s) → Na$^+$(aq) + Cl$^-$(aq), ΔH = +11.1 kJmol^{-1}
So the enthalpy of solution of NaCl is +11.1 kJmol^{-1}
- It is usually possible to measure enthalpies of solution directly

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Test your knowledge 2.3: Describing Special Enthalpy Changes

Write equations for the reactions whose molar enthalpy change is described by the following terms:
   (a) the enthalpy of formation of carbon dioxide
   (b) the enthalpy of formation of butane (C_4H_{10})
   (c) the enthalpy of combustion of butane (C_4H_{10})
   (d) the enthalpy of combustion of magnesium
   (e) the enthalpy of neutralisation of nitric acid by potassium hydroxide
   (f) the enthalpy of solution of magnesium chloride

   (a) C(s) + O_2(g) → CO(g)
   (b) 4C(s) + 5H_2(g) → C_4H_{10}(g)
   (c) C_4H_{10}(g) + 5O_2(g) → 4CO_2(g) + 5H_2O(l)
   (d) Mg(s) + ½O_2(g) → MgO(s)
   (e) HNO_3(aq) + KOH(aq) → KNO_3(aq) + H_2O(l)
   (f) $MgCl_2$(s) → Mg^{2+}(aq) + 2Cl$^-$(aq)

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 = ΔT x 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 x mass (c = m x H_c)
   - but mass = volume x density, so heat capacity = specific heat capacity x volume x density
   - so the energy change (q) = VρcΔT or **q = mcΔT**

- 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 $Jg^{-1}K^{-1}$; so q = total volume of solution (x 1) x 4.18 x ΔT

- 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

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Example:
Zinc will displace copper from copper (II) sulphate solution according to the following equation:
$CuSO_4(aq) + Zn(s) \rightarrow Cu(s) + ZnSO_4(aq)$
If an excess of zinc powder is added to 50 cm^3 of 1.0 $moldm^{-3}$ copper(II) sulphate, the temperature increases by 6.3 °C. Calculate the molar enthalpy change for the reaction.
Answer:
m = mass of solution being heated = volume x density = 1 x 50 = 50 g
q = Heat change = 50 x 4.18 x 6.3 = 1317 J = 1.317 kJ
n = moles of $CuSO_4$ = 50/1000 x 1 = 0.05
ΔH = molar enthalpy change = 1317/0.05 = 26.3 $kJmol^{-1}$
Temperature has increased, so reaction is exothermic, so sign should be -ve: **26.3 $kJmol^{-1}$**
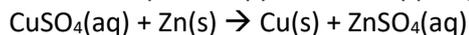
Practical 3.1: Determine the molar enthalpy of solution of ammonium chloride (NH₄Cl)
1) Place a clean, dry polystyrene cup inside a glass beaker.
2) Pour 100 cm^3 of water into the cup using a measuring cylinder. Record the initial temperature of the water.
3) Use a weighing boat to weigh out approximately 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 x 4.18 x ΔT, 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)

Equipment needed per group: one polystyrene cup, one glass beaker (both 250 cm^3), one 100 cm^3 measuring cylinder, one weighing boat, one thermometer, one stirring rod, access to distilled water, access to mass balance, access to NH₄Cl (5 g per group)
Note: this reaction is endothermic and the temperature will decrease by 4 – 5 °C
- q = 100 x 4.18 x ΔT
- n = m/53.5
- ΔH = q/n value will be +ve as reaction is endothermic

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

1) Place a clean, dry polystyrene cup inside a glass beaker.
2) Pour 25 cm^3 of 1 moldm^{-3} HCl into the cup using a measuring cylinder. Record the initial temperature of the solution.
3) Measure out 25 cm^3 of 1 moldm^{-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 x 4.18 x ΔT, then convert to kJ).
6) Deduce the moles (n) of water formed (25/1000) x 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)

Equipment needed per group: one polystyrene cup, one glass beaker (both 250 cm3), two measuring cylinders (25 or 50 cm^3), one thermometer, access to 1 moldm^{-3} HCl (25 cm^3 per group), stirring rod, access to 1 moldm^{-3} NaOH (25 cm^3 per group),
Note: this reaction is exothermic and the temperature will increase by 3-4 °C
- **q = 50 x 4.18 x ΔT**
- **n = 0.025**
- **ΔH = q/n; value will be -ve as reaction is exothermic**

Test your knowledge 3.3: Measuring enthalpy changes of solution and neutralisation
(a) When 5.73 g of sodium chloride (NaCl) dissolves in 100 cm^3 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 (MgCl$_2$) dissolves in 200 cm^3 of water, the temperature rose by 3.4 °C. Calculate the molar enthalpy of solution of MgCl$_2$.
(c) If 50 cm^3 of 0.1 moldm^{-3} HCl and 50 cm^3 of 0.1 moldm^{-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 cm^3 of 1.0 moldm^{-3} NaOH is added to 25 cm^3 of 2.0 moldm^{-3} CH$_3$COOH, the temperature rose by 8.3 °C. Calculate the molar enthalpy of neutralisation of CH$_3$COOH by NaOH.

(a) q = 100 x 4.18 x 2.6 = 1087 J; n = 5.73/58.5 = 0.0980; ΔH = 1087/0.098 = +11.1 kJmol^{-1}
(b) q = 200 x 4.18 x 3.4 = 2842 J; n = 2.3/95.3 = 0.0241; ΔH = 2842/0.0241 = -118 kJmol^{-1}
(c) q = 100 x 4.18 x 0.68 = 284 J; n = 0.05 x 0.1 = 0.005; ΔH = 284/0.005 = -56.8 kJmol^{-1}
(d) q = 75 x 4.18 x 8.3 = 2602 J; n = 1 x 0.05 = 0.05; ΔH = 2602/0.05 = -52.0 kJmol^{-1}

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 = mcΔT (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 cm^3 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 x 4.18 x ΔT, 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)

Equipment needed per group: one copper can (250 cm^3), one thermometer, one spirit burner containing ethanol, one measuring cylinder (100 cm^3), one stand, clamp and boss, windshield if available, access to a mass balance
- q = 100 x 4.18 x 30 = 12540 J (students should use whatever temperature change they actually recorded during their experiment
- n = m/46
- ΔH = q/n value will be -ve as reaction is exothermic

Test your knowledge 4.2: Measuring enthalpy changes of combustion
(a) A spirit burner containing ethanol (C_2H_5OH) was used to heat 100 cm^3 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 (C_4H_9OH) was used to heat 200 cm^3 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.

(a) q = 100 x 4.18 x 30 = 12540 J; n = 0.62/46 = 0.0135; ΔH = 12540/0.0135 = -930 kJmol^{-1}
(b) q = 200 x 4.18 x 20 = 16720 J; n = 0.81/74 = 0.0109; ΔH = 2842/0.0241 = -1530 kJmol^{-1}

- 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

- 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?

Note: this activity is designed to discover what students know about the rates of chemical reactions
- Fast reactions: explosions, neutralisation reactions etc
- Slow reactions: rusting, decompositions etc

Note: reactions are not "fast" or "slow"; students may be able to rank different reactions in terms of how long they take to complete
Note: students will have various suggestions, encourage any which mention collisions between particles; it is not necessary to answer this question immediately if the students do not know the answer
- Reactions can be made faster by increasing the concentration, increasing the temperature or adding a catalyst (some students may be able to explain why)

(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**

- 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:
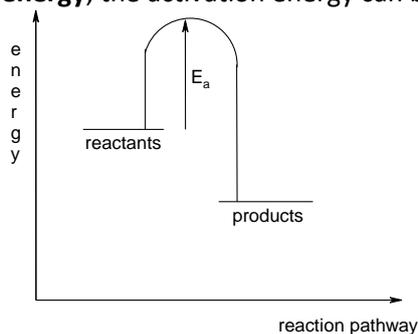
- this enthalpy diagram shows a simple exothermic reaction
- the activation energy E_a is the energy needed to break the bonds in the colliding particles
- he potential energy of the substance increases as the bonds are broken
- once the bonds have been broken, new bonds can be formed and the potential 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
  (a) If you increase the collision frequency in a reaction mixture, what will happen to the rate of reaction? Why?
  (b) If you increase the collision energy of the reacting particles in a mixture, what will happen to the rate of reaction? Why?
  (c) Draw an enthalpy profile diagram for an exothermic reaction, labelling the enthalpy change and the activation energy
  (d) Draw an enthalpy profile diagram for an endothermic reaction, labelling the enthalpy change and the activation energy
  (e) If you increase the activation energy of a reaction, what will happen to the rate of reaction? Why?

(a) Particles will collide with each other more often, so the rate of reaction will increase
(b) Collisions are more likely to be successful (the collision energy is more likely to exceed the activation energy), so the rate of reaction will increase
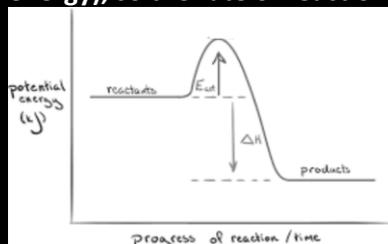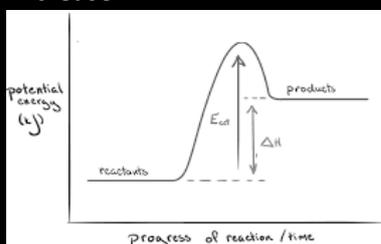
(c)   **(d)**
(e) If the activation energy is higher, it is less likely that the collision energy of the colliding particles will be greater than the activation energy, so the reaction will be slower

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

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Practical 6.1: Investigate the effect of the concentration of sodium thiosulphate ($Na_2S_2O_3$) 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} $Na_2S_2O_3$ into a measuring cylinder labelled "$Na_2S_2O_3$".
4) Pour the $Na_2S_2O_3$ 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 $Na_2S_2O_3$ in step 3, prepared as follows:

Concentration of $Na_2S_2O_3$moldm^{-3}	Volume of 0.2 moldm^{-3} $Na_2S_2O_3$/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 $Na_2S_2O_3$?

Equipment needed per group: two measuring cylinders (25 cm^3) and something to label them with; one conical flask; one stopwatch, access to 0.2 moldm^{-3} $Na_2S_2O_3$, access to 0.2 moldm^{-3} HCl (100 cm^3 of each per group)

Note: students must use separate measuring cylinders for the two reactants; they change the concentration of $Na_2S_2O_3$ by adding smaller volumes of it into the measuring cylinder and adding water to make the total volume up to 20 cm^3

- As the concentration is decreased, it will take longer for the X to disappear, showing that decreasing the concentration of one of the reactants will decrease the rate of reaction

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

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- 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 ($Na_2S_2O_3$) and hydrochloric acid (HCl)
1) Set up three water baths at $30\,^{\circ}$C, $40\,^{\circ}$C and $50\,^{\circ}$C and place stock solutions of 0.2 moldm^{-3} HCl and 0.2 moldm^{-3} $Na_2S_2O_3$ 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 moldm^{-3} HCl into a measuring cylinder labelled "HCl", then measure out 20 cm^3 of 0.2 moldm^{-3} $Na_2S_2O_3$ into a measuring cylinder labelled "$Na_2S_2O_3$"
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 $30\,^{\circ}$C, then at $40\,^{\circ}$C and then at $50\,^{\circ}$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?

Equipment needed per group: two measuring cylinders (25 cm^3) and something to label them with; one conical flask; one stopwatch, access four different bottles of 0.2 moldm^{-3} $Na_2S_2O_3$, access to 0.2 moldm^{-3} HCl, each at different temperatures (100 cm^3 of each per group)
  - **as** the temperature is increased, it will take less time for the X to disappear, showing that increasing the temperature will increase the rate of reaction

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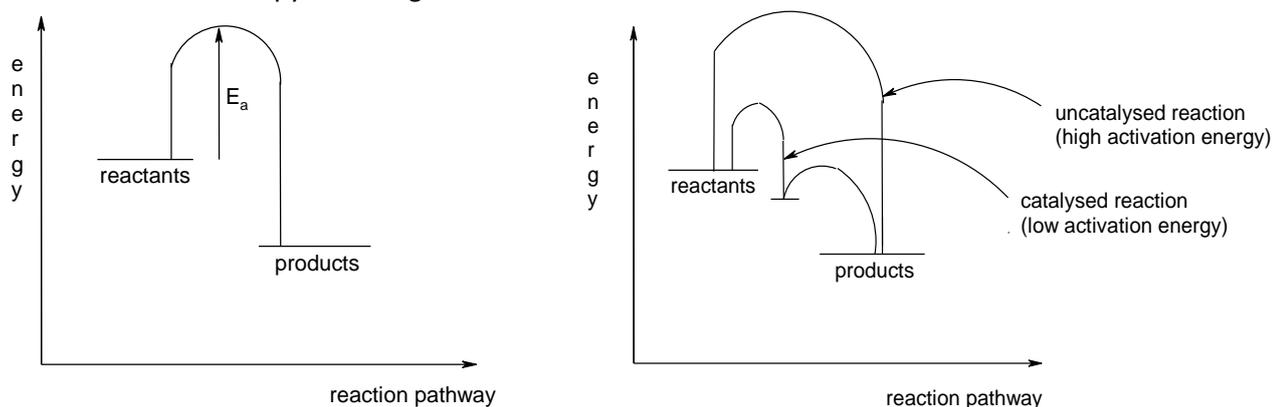
- - the enthalpy level diagram on the left shows a reaction without a catalyst
  - the diagram on the right shows the effect of adding a catalyst
  - the reaction pathway changes and the activation energy is lowered

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

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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 moldm^{-3} KI, 5 cm^3 of 0.02 moldm^{-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 moldm^{-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?

Equipment needed per group: three measuring cylinders (25 cm^3 for KI, 10 cm^3 for sodium thiosulphate and water, 10 cm^3 for $K_2S_2O_8$) and something to label them with; one conical flask; one stopwatch, access to starch solution with a dropping pipette, access to 0.3 moldm^{-3} KI (50 cm^3 per group), 0.02 moldm^{-3} $Na_2S_2O_3$ (10 cm^3 per group), 0.1 moldm^{-3} $K_2S_2O_8$ (20 cm^3 per group), 0.1 moldm^{-3} $Fe_2(SO_4)_3$ with a dropping pipette, and distilled water
- **When the** iron (III) sulphate is added in the second experiment, it takes much less time for the mixture to turn dark blue, showing that a catalyst increases the rate of reaction

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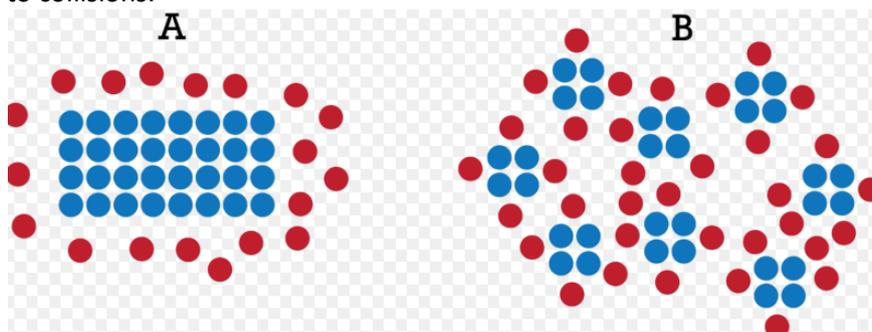
- A: large particle size, fewer of the blue solid particles can collide with the red particles, slower reaction.
- B: small particle size, more of the blue solid particles can collide with the red particles, faster reaction.

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 moldm^{-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?

Equipment needed: one measuring cylinder (50 cm^3), one conical flask, stopwatch, two different sizes of marble chips (2.5 g of each), mass balance
- The mass of the conical flask and contents decreases because a gas (CO_2) is escaping
- When the smaller chips are used, there is a greater decrease in mass; this means that more gas is escaping which means that the reaction is faster; the smaller chips have a larger overall surface area, which means that the collision frequency between the marble chips and the HCl increases

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

- 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: Understanding the factors affecting the rate of a reaction
(a) Explain why increasing the concentration of one of the reactants will increase the rate of a reaction
(b) Explain why increasing the pressure of a gas-phase reaction will increase the rate of a reaction
(c) Explain why increasing the temperature will increase the rate of a reaction
(d) Explain why adding a catalyst will increase the rate of a reaction
(e) Explain why solids react more slowly than liquids and gases
(f) Explain why decreasing the particle size of a solid reactant will increase the rate of a reaction
(g) Suggest one other way to change the rate of a reaction

(a) **More particles per unit volume so greater collision frequency**
(b) **More particles per unit volume so greater collision frequency**
(c) **Particles have more energy so collision energy is higher, a greater fraction of the collisions are successful**
(d) **Catalyst lowers activation energy so a greater fraction of the collisions are successful**
(e) **In solids, only the particles at the surface can collide with other reactants; in liquids and gases, all particles can collide so the collision frequency is higher**
(f) **The surface area increases so collision frequency increases**

Extension 7.4: Understanding the 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				

Effect:	On collision frequency	On collision energy	On activation energy	On rate of reaction
Increase concentration	increases	No effect	No effect	Increases
Increase pressure	Increases	No effect	No effect	Increases
Increase temperature	Increases	Increases	No effect	Increases
Add a catalyst	No effect	No effect	Decreases	Increases
Using solid state reactants	Increases	No effect	No effect	Increases

UNIT 4 – INTRODUCTION TO PHYSICAL CHEMISTRY

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 $moldm^{-3}s^{-1}$

- 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**):
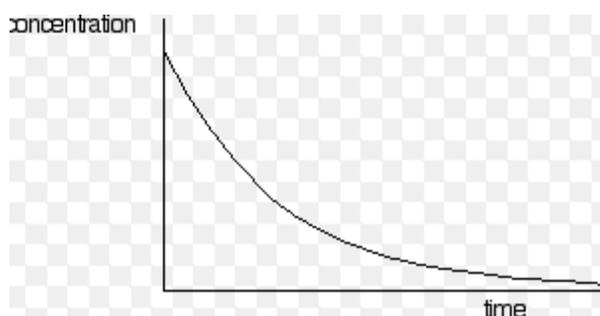
- The rate of reaction is the change in concentration per unit time and can therefore be calculated from the gradient of the line at a particular time

- 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:
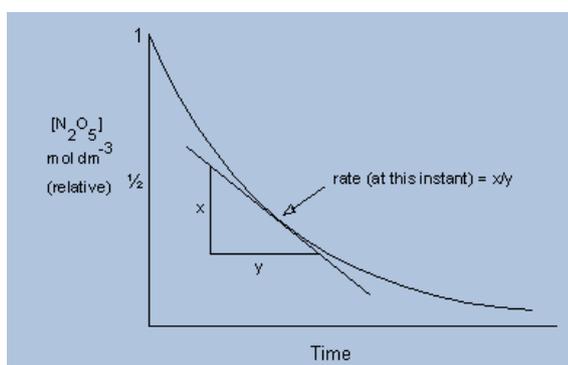
- The gradient of the line (and hence the rate of reaction) decreases with time; this is because as reactions proceed, the concentration of reactants decreases, making collisions between the remaining particles less frequent

- 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: $2H_2O_2(g) \rightarrow 2H_2O(g) + O_2(g)$

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
$[H_2O_2]$/moldm^{-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:
   a) Initially
   b) When $[H_2O_2]$= 0.20 moldm^{-3}
   c) After 50 s
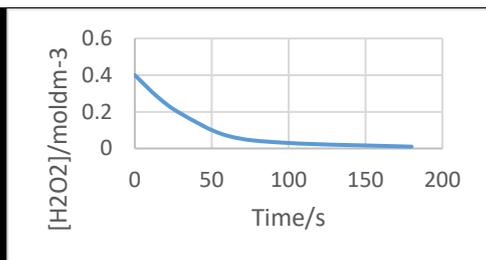
Note: students should draw a full A4 graph in order to calculate the gradients of tangents accurately
   a) (0.40-0.20)/20 = 0.010 moldm^{-3}s^{-1}
   b) (0.288-0.114)/30 = 0.0058 moldm^{-3}s^{-1}
   c) (0.134-0.036)/30 = 0.0033 moldm^{-3}s^{-1}

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 moldm⁻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) /cm³	($V_f - V_t$)/cm³
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.

Equipment needed per group: gas syringe (100 cm³) attached to delivery tube through a bung; stand, clamp and boss; conical flask which fits the bung attached to the gas syringe; measuring cylinder (25 cm³); weighing boat; access to a mass balance; access to 0.2 moldm⁻³ HCl (25 cm³ per group); access to Mg (1 g per group)
- **The final value of ($V_f - V_t$) will be equal to 0**
- **The first value of ($V_f - V_t$) will be the largest; the values will then decrease steadily**
- **The initial rate of reaction is determined by drawing a tangent to the line at t = 0 and calculating its gradient; the units of rate will be in cm³s⁻¹ as the experiment measures volume not concentration**

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 ⇌ sign instead of by a regular arrow →

- 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

- Consider a reversible reaction A + B ⇌ C + D

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- 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:
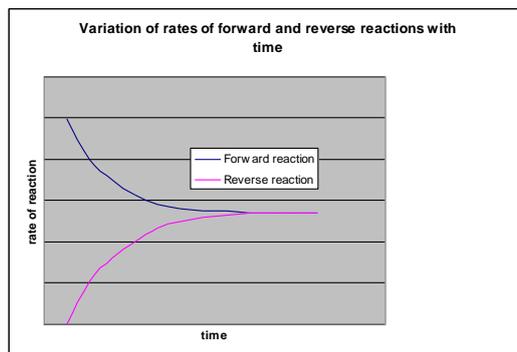
- at this stage, a **dynamic equilibrium** has been reached; "dynamic" means that the reaction has not stopped; it is simply moving in both directions at the same rate; "equilibrium" means that the amount of reactants and products in the system is not changing

- **A dynamic equilibrium is reached when the forward and reverse reactions are taking place at the same rate, which means that the concentrations or 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

(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: $2SO_2 + O_2 \rightleftharpoons 2SO_3$; 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: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$; 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: $A + 3B \rightleftharpoons C + 2D$; the K_c for this reaction is $\frac{[C][D]^2}{[A][B]^3}$
    - the square brackets [] are used to represent the concentration of that reactant, so [A] means the concentration of A in $moldm^{-3}$
    - 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

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Test your knowledge 9.1: Understanding Dynamic Equilibrium and Equilibrium Constants
(a) Why does the rate of the forward reaction decrease as the reaction proceeds?
(b) Why does the rate of the reverse reaction increase as the reaction proceeds?
(c) What will eventually happen to the rate of the forward and reverse reactions?
(d) Why will this often not happen in an open system?
(e) Write expressions for the equilibrium constants for the following reactions:

      (i) $2NO_2(g) \rightleftharpoons N_2O_4(g)$

      (ii) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

      (iii) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

      (iv) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(f) For the equilibrium $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the equilibrium concentrations of PCl_5, PCl_3 and Cl_2 are 1.0, 0.205 and 0.205 $moldm^{-3}$ respectively. Calculate the value of K_c

(g) For the equilibrium $2N_2O_5(g) \rightleftharpoons 2N_2O_4(g) + O_2(g)$, the equilibrium concentrations are $[N_2O_5]$ = 1.0 $moldm^{-3}$, $[N_2O_4]$ = 0.11 $moldm^{-3}$, $[O_2]$ = 0.11 $moldm^{-3}$. Calculate the value of K_c

(a) Reactant concentration decreases so collision frequency decreases
(b) Product concentration increases so collision frequency increases
(c) Eventually the rates of the forward and reverse reactions will equalise – dynamic equilibrium will be reached
(d) One or more of the products might escape
(e) (i) $\frac{[N_2O_4]}{[NO_2]^2}$; (ii) $\frac{[HI]^2}{[H_2][I_2]}$; (iii) $\frac{[SO_3]^2}{[SO_2]^2[O_2]}$; (iv) $\frac{[NH_3]^2}{[H_2]^3[N_2]}$
(f) 0.0420 $moldm^{-3}$
(g) 0.00133 $moldm^{-3}$

UNIT 4 – INTRODUCTION TO PHYSICAL CHEMISTRY

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 equilbrium 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"; t**he 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 $2SO_2 + O_2 == 2SO_3$, 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 in the same, then pressure has no effect on the equilibrium position (the equilibrium constant will not change)
  - Eg in the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, 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

- 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 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ 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

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

(a) Consider the following exothermic reaction: $4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)$
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:
(i)   water is removed from the system
(ii)   extra oxygen is added to the system
(iii)   the volume of the container was reduced
(iv)   the temperature of the container was increased
(v)   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:

(i) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, ΔH = -ve

(ii) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, ΔH = +ve

(iii) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, ΔH = -ve

(iv) $HCOOH(l) + CH_3OH(l) \rightleftharpoons HCOOCH_3(l) + H_2O(l)$, ΔH = 0

(a) Equilibrium position would:
(i) move to the right to replace water, resulting in more Cl_2 and less HCl
(ii) move to the right to remove oxygen, resulting in more Cl_2 and less HCl
(iii) move to the right to decrease pressure, resulting in more Cl_2 and less HCl
(iv) move to the left to decrease temperature, resulting in less Cl_2 and more HCl
(v) not change as the rates of both forward and reverse reactions would be increased equally
(b) (i) high pressure as fewer gas molecules on RHS, low temperature as forward reaction exothermic; (ii) low pressure as more molecules on RHS, high temperature as forward reaction endothermic; (iii) pressure will make no difference as equal number of gas molecules on both sides; low temperature as forward reaction exothermic

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 °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]/moldm^{-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: $2SO + O_2(g) \rightleftharpoons 2SO_3(g)$, ΔH = -294 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.

1. 1000/30 = 33.3 moles, so q = 1556 x 33.3 = 51,900 kJ
2. q = 50 x 4.18 x 6.9 = 1440 J; n = 2/111.1 = 0.0180; ΔH = 1440/0.0180 = 80, 100 Jmol^{-1} = 80.1 kJmol^{-1}; T increases so ΔH = -80.1 kJmol^{-1}
3. (a) More HCl particles per unit volume so frequency of collisions increases
   (b) HCl particles have more energy so collision energy increases and collisions are more likely to be successful
   (c) Surface area of $CaCO_3$ increases so collision frequency increases
4.
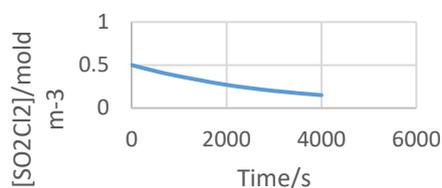
gradient of tangent at t = 0 = (0.50-0.3475)/1000 = 1.5 x 10^{-4} moldm^{-3}s^{-1}
5. Rate of forward reaction = rate of reverse reaction so amounts of reactants and products are not changing
6. (a) $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$
   (b) To the right, to replace the lost SO_3
   (c) To the left, in the endothermic direction, to reduce the temperature
   (d) A high pressure, as there are fewer gas moles on the right, so high pressure will cause the position of equilibrium will move to the right to reduce the pressure