

UNIT 4

INTRODUCTION TO PHYSICAL CHEMISTRY

Answers

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



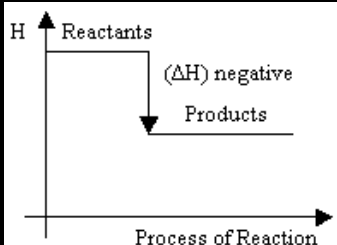
Thinkabout Activity 1.1: What is potential energy?

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

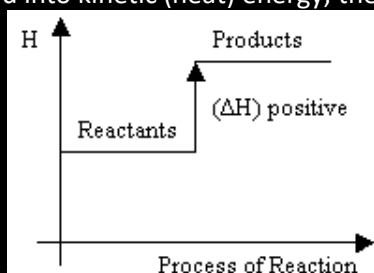


Test your knowledge 1.2: Describing Exothermic and Endothermic Reactions



(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?



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

- (a) $100/16 = 6.25$ moles; (b) $(300000 \times 0.0005)/(8.31 \times 298) = 0.0606$ moles
- $1000/180 = 5.56$ moles


Test your knowledge 2.2: Using molar enthalpy changes

- (a) **+890 kJmol⁻¹**; (b) $n = 6.25$ so $q = \Delta H \times n = 6.25 \times 890 = \mathbf{5560 \text{ kJ}}$; (c) $n = 0.0606$ so $q = \Delta H \times n = 0.0606 \times 890 = \mathbf{53.9 \text{ kJ}}$; (d) $n = q/\Delta H = 50000/890 = 56.2$ moles; $m = n \times m_r = \mathbf{899 \text{ g}}$
- (a) **-2802 kJmol⁻¹**; (b) $n = 5.56$ so $q = \Delta H \times n = 5.56 \times 2802 = \mathbf{15600 \text{ kJ}}$; (c) $n(\text{CO}_2) = 0.0606$ so $n(\text{C}_6\text{H}_{12}\text{O}_6) = 0.0101$ so $q = \Delta H \times n = 0.0101 \times 2802 = \mathbf{28.3 \text{ kJ}}$; (d) $n = q/\Delta H = 10000/2802 = 3.57$ moles; $m = n \times m_r = \mathbf{642 \text{ g}}$


Test your knowledge 2.3: Describing Special Enthalpy Changes

- $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO(g)}$
- $4\text{C(s)} + 5\text{H}_2\text{(g)} \rightarrow \text{C}_4\text{H}_{10}\text{(g)}$
- $\text{C}_4\text{H}_{10}\text{(g)} + 5\text{O}_2\text{(g)} \rightarrow 4\text{CO}_2\text{(g)} + 5\text{H}_2\text{O(l)}$
- $\text{Mg(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{MgO(s)}$
- $\text{HNO}_3\text{(aq)} + \text{KOH(aq)} \rightarrow \text{KNO}_3\text{(aq)} + \text{H}_2\text{O(l)}$
- $\text{MgCl}_2\text{(s)} \rightarrow \text{Mg}^{2+}\text{(aq)} + 2\text{Cl}^-\text{(aq)}$

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

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

Equipment needed per group: one polystyrene cup, one glass beaker (both 250 cm³), one 100 cm³ measuring cylinder, one weighing boat, one thermometer, access to distilled water, access to mass balance, access to NH₄Cl (5 g per group), stirring rod

Note: this reaction is endothermic and the temperature will decrease by 4 – 5 °C

- $q = 100 \times 4.18 \times \Delta T$
- $n = m/53.5$
- $\Delta H = q/n$ 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 $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$

Equipment needed per group: one polystyrene cup, one glass beaker (both 250 cm³), two measuring cylinders (25 or 50 cm³), one thermometer, access to 1 moldm⁻³ HCl (25 cm³ per group), one stirring rod, access to 1 moldm⁻³ NaOH (25 cm³ per group),

Note: this reaction is exothermic and the temperature will increase by 3-4 °C

- $q = 50 \times 4.18 \times \Delta T$
- $n = 0.025$
- $\Delta H = q/n$; value will be -ve as reaction is exothermic


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

- $q = 100 \times 4.18 \times 2.6 = 1087 \text{ J}$; $n = 5.73/58.5 = 0.0980$; $\Delta H = 1087/0.098 = \mathbf{+11.1 \text{ kJmol}^{-1}}$
- $q = 200 \times 4.18 \times 3.4 = 2842 \text{ J}$; $n = 2.3/95.3 = 0.0241$; $\Delta H = 2842/0.0241 = \mathbf{-118 \text{ kJmol}^{-1}}$
- $q = 100 \times 4.18 \times 0.68 = 284 \text{ J}$; $n = 0.05 \times 0.1 = 0.005$; $\Delta H = 284/0.005 = \mathbf{-56.8 \text{ kJmol}^{-1}}$
- $q = 75 \times 4.18 \times 8.3 = 2602 \text{ J}$; $n = 1 \times 0.05 = 0.05$; $\Delta H = 2602/0.05 = \mathbf{-52.0 \text{ kJmol}^{-1}}$

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Lesson 4 – How do we measure enthalpies of combustion?



Practical 4.1: Determine the molar enthalpy of combustion of ethanol

Equipment needed per group: one copper can (250 cm³), one thermometer, one spirit burner containing ethanol, one measuring cylinder (100 cm³), one stand, clamp and boss, windshield if available, access to a mass balance

- $q = 100 \times 4.18 \times 30 = 12540 \text{ J}$ (students should use whatever temperature change they actually recorded during their experiment)
- $n = m/46$
- $\Delta H = q/n$ value will be -ve as reaction is exothermic



Test your knowledge 4.2: Measuring enthalpy changes of combustion

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

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



Thinkabout Activity 5.1: Different speeds of chemical reactions

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

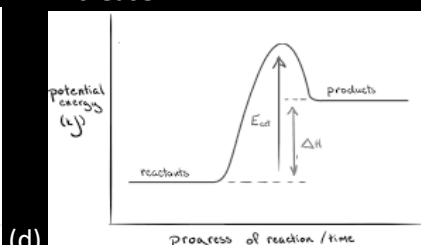
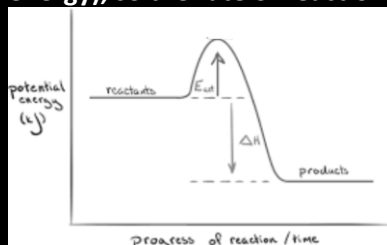
Note: students will have various suggestions, encourage any which mention collisions between particles; it is not necessary to answer this question immediately if the students do not know the answer

- Reactions can be made faster by increasing the concentration, increasing the temperature or adding a catalyst (some students may be able to explain why)



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

- (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

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



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)

Equipment needed per group: two measuring cylinders (25 cm^3) and something to label them with; one conical flask; one stopwatch, access to $0.2\text{ mol dm}^{-3}\text{ Na}_2\text{S}_2\text{O}_3$, access to $0.2\text{ mol dm}^{-3}\text{ HCl}$ (100 cm^3 of each per group)

Note: students must use separate measuring cylinders for the two reactants; they change the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ 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



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)

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 $0.2\text{ mol dm}^{-3}\text{ Na}_2\text{S}_2\text{O}_3$, access to $0.2\text{ mol dm}^{-3}\text{ HCl}$, 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

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



Practical 7.1: Investigate the effect of a catalyst on the rate of reaction between potassium peroxodisulphate ($\text{K}_2\text{S}_2\text{O}_8$) and potassium iodide (KI)

Equipment needed per group: three measuring cylinders (25 cm^3 for KI, 10 cm^3 for sodium thiosulphate and water, 10 cm^3 for $\text{K}_2\text{S}_2\text{O}_8$) and something to label them with; one conical flask; one stopwatch, access to starch solution with a dropping pipette (2 cm^3 per group), access to $0.3\text{ mol dm}^{-3}\text{ KI}$ (50 cm^3 per group), $0.02\text{ mol dm}^{-3}\text{ Na}_2\text{S}_2\text{O}_3$ (10 cm^3 per group), $0.1\text{ mol dm}^{-3}\text{ K}_2\text{S}_2\text{O}_8$ (20 cm^3 per group), $0.1\text{ mol dm}^{-3}\text{ Fe}_2(\text{SO}_4)_3$ with a dropping pipette (2 cm^3 per group), 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**



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

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

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Test your knowledge 7.3: Understanding the factors affecting 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



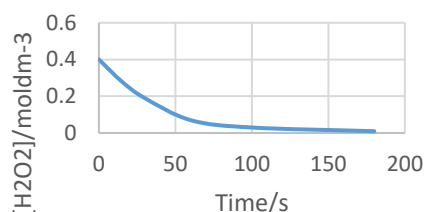
Extension 7.4: Understanding the factors affecting the rate of a reaction

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

Lesson 8 – How can we measure rates of reaction?



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



Note: students should draw a full A4 graph in order to calculate the gradients of tangents accurately

- a) $(0.40 - 0.20) / 20 = 0.010 \text{ mol dm}^{-3} \text{ s}^{-1}$
- b) $(0.288 - 0.114) / 30 = 0.0058 \text{ mol dm}^{-3} \text{ s}^{-1}$
- c) $(0.134 - 0.036) / 30 = 0.0033 \text{ mol dm}^{-3} \text{ s}^{-1}$



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

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 mol dm⁻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 cm^3s^{-1} as the experiment measures volume not concentration

Lesson 9 – What is chemical equilibrium?



Test your knowledge 9.1: Understanding Dynamic Equilibrium and Equilibrium Constants

- (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) $\frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$, (ii) $\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$, (iii) $\frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$, (iv) $\frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]}$
- (f) 0.0420 mol dm⁻³
- (g) 0.00133 mol dm⁻³

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



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

- (a) Equilibrium position would:
 - (i) move to the right to replace water, resulting in more Cl₂ and less HCl
 - (ii) move to the right to remove oxygen, resulting in more Cl₂ and less HCl
 - (iii) move to the right to decrease pressure, resulting in more Cl₂ and less HCl
 - (iv) move to the left to decrease temperature, resulting in less Cl₂ 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

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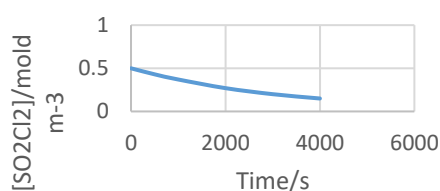
Lesson 11 – What have you understood about Physical Chemistry?

11.1 END-OF-TOPIC QUIZ
TOPIC 4 – INTRODUCTION TO PHYSICAL CHEMISTRY



1. $1000/30 = 33.3$ moles, so $q = 1556 \times 33.3 = 51,900$ kJ
2. $q = 50 \times 4.18 \times 6.9 = 1440$ J; $n = 2/111.1 = 0.0180$; $\Delta H = 1440/0.0180 = 80, 100$ Jmol⁻¹ = 80.1 kJmol⁻¹; T increases so $\Delta H = -80.1$ 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 CaCO₃ increases so collision frequency increases

4.



gradient of tangent at $t = 0 = (0.50 - 0.3475)/1000 = 1.5 \times 10^{-4}$ mol dm⁻³s⁻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 SO₃
(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