

# IB DP CHEMISTRY

**Reactivity 1 · What Drives Chemical Reactions?**

## MARK SCHEME

R1.1 Measuring Enthalpy Changes · R1.2 Energy Cycles in Reactions

R1.3 Energy From Fuels · R1.4 Entropy and Spontaneity

Standard and Higher Level · Syllabus 2025

**Fahad H. Ahmad**

+92 323 509 4443 | [Megalecture.com](https://Megalecture.com)

## Section A — Multiple Choice: Answer Key (15 marks)

1. Answer: **B** — Enthalpy change,  $\Delta H$ , is defined as the heat energy exchanged with the surroundings during a reaction carried out at constant pressure.
2. Answer: **B** — An exothermic reaction releases heat energy to the surroundings, so  $\Delta H$  is negative and the temperature of the surroundings increases.
3. Answer: **B** — In  $q = mc\Delta T$ ,  $m$  is the mass of solution,  $c$  is its specific heat capacity, and  $\Delta T$  is the temperature change;  $q$  is the heat energy transferred.
4. Answer: **B** — Extrapolating the cooling (or warming) line back to the moment of mixing corrects for the gradual heat loss to (or gain from) the surroundings that occurs throughout the experiment, giving a more accurate estimate of the true temperature change.
5. Answer: **A** — Hess's Law states that the total enthalpy change for a chemical reaction is independent of the pathway taken, as long as the initial and final conditions are the same, because enthalpy is a state function.
6. Answer: **B** — Enthalpy is a state function: its value depends only on the current state of the system (initial and final conditions), not on the path taken to reach that state, which is why Hess's Law holds.
7. Answer: **C** — By Hess's Law, the overall enthalpy change equals the sum of the enthalpy changes for the individual steps:  $-110.5 + (-283.0) = -393.5 \text{ kJ mol}^{-1}$ .
8. Answer: **B** — The standard enthalpy change of formation is the enthalpy change when one mole of a compound is formed from its constituent elements, each in their standard states, under standard conditions.
9. Answer: **B** — Bond enthalpy (bond dissociation energy) is the energy required to break one mole of a specific covalent bond in gaseous molecules.
10. Answer: **B** — In an exothermic reaction, less energy is needed to break the bonds in the reactants than is released when the new, generally stronger, bonds form in the products, giving an overall net release of energy.
11. Answer: **B** —  $\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds formed}) = (436+242) - (2 \cdot 431) = 678 - 862 = -184 \text{ kJ mol}^{-1}$ .
12. Answer: **A** — Enthalpy of combustion is the enthalpy change when one mole of a substance undergoes complete combustion in excess oxygen under standard conditions.
13. Answer: **B** — Entropy is a measure of the number of possible arrangements of particles and energy in a system — essentially the degree of disorder or randomness.
14. Answer: **A** —  $\Delta S$  is **positive**: one mole of solid reactant produces one mole of solid and one mole of gaseous product, and gases have much greater entropy (disorder) than solids, so the overall disorder of the system increases.
15. Answer: **A** — A reaction is thermodynamically spontaneous (feasible) at a given temperature when  $\Delta G$  is negative ( $\Delta G < 0$ ); both  $\Delta H$  and  $\Delta S$  contribute to the value of  $\Delta G$  via  $\Delta G = \Delta H - T\Delta S$ .

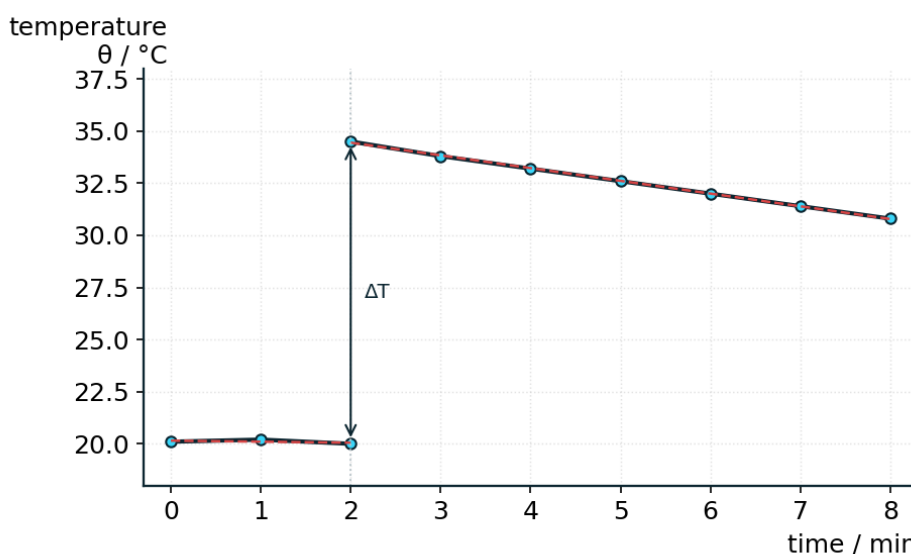
## Section B — Structured Questions: Worked Solutions (66 marks)

Mark-scheme notation: M = method mark, A = accuracy mark (dependent on the preceding M mark), R = reasoning mark.

### R1.1 Measuring Enthalpy Changes

#### Question 1 [7 marks]

A student adds a solid reactant to 100 cm<sup>3</sup> of dilute acid (density 1.00 g cm<sup>-3</sup>) in an insulated cup and records the temperature every minute, obtaining the temperature-time graph shown. The reaction released heat and 0.0500 mol of the solid reactant was used (specific heat capacity of the solution,  $c = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$ ).



Temperature-time graph for the calorimetry experiment (given data).

(a) Using the graph, determine the temperature change,  $\Delta T$ , by extrapolating both lines back to the time of mixing. [2]

$\Delta T = \text{extrapolated temperature} - \text{initial temperature} = 34.4 - 20.1 = 14.3^\circ\text{C}$  (= 14.3 K). A1 A1

(b) Calculate the heat energy,  $q$ , released by the reaction, using  $q = mc\Delta T$ . [3]

$q = mc\Delta T = 100.0 \cdot 4.18 \cdot 14.3 = 5977 \text{ J}$  (= 5.98 kJ). M1 M1 A1

(c) Calculate the enthalpy change of the reaction, in  $\text{kJ mol}^{-1}$ , using the given amount of reactant. [2]

$\Delta H = -q \div n = -(5.977 \div 0.05) = -119.5 \text{ kJ mol}^{-1}$  (negative, since the reaction is exothermic). M1 A1

#### Question 2 [6 marks]

Enthalpy changes are usually determined experimentally using calorimetry.

(a) Define the term 'enthalpy change of reaction'. [2]

The enthalpy change of reaction is the **heat energy exchanged with the surroundings** when a reaction occurs at **constant pressure**. A1 A1

**(b)** Explain why the temperature-time graph is extrapolated back to the time of mixing, rather than simply using the maximum (or minimum) temperature recorded. [2]

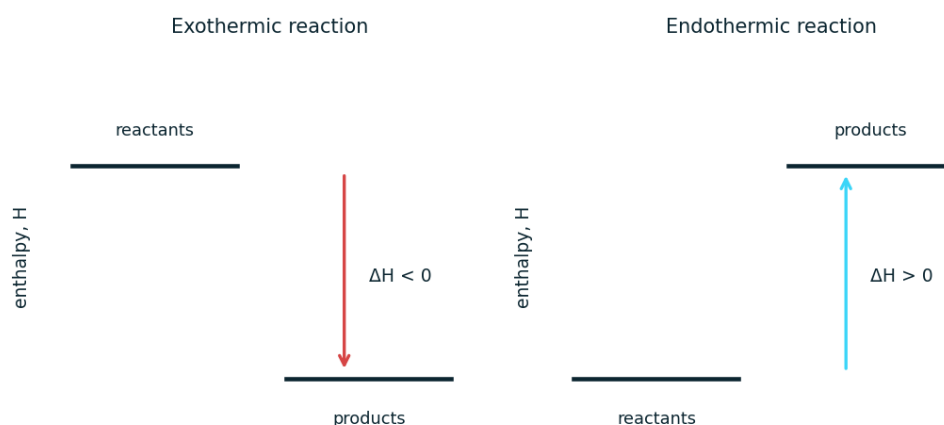
Heat is continuously lost to (or gained from) the surroundings throughout the experiment, even before and after mixing. Extrapolating both the 'before' and 'after' lines back to the time of mixing **corrects for this continuous heat loss/gain**, giving a more accurate estimate of the true temperature change that would have occurred if the reaction were instantaneous and the system perfectly insulated. R1 R1

**(c)** Suggest one modification to the experimental procedure that would improve the accuracy of the enthalpy change determined. [2]

Use a **better-insulated container** (e.g. a polystyrene cup with a lid) to reduce heat loss to the surroundings. (Other valid answers: use a more precise thermometer/data logger; stir the mixture continuously and evenly; use a lid with a hole only for the thermometer.) A1 R1

### Question 3 [7 marks]

The diagrams show enthalpy level diagrams for two types of reaction.



*Enthalpy level diagrams: exothermic and endothermic reactions (schematic).*

**(a)** Identify which diagram represents an exothermic reaction and which represents an endothermic reaction, and state the sign of  $\Delta H$  in each case. [2]

Left diagram: **exothermic**,  $\Delta H < 0$  (products lower in enthalpy than reactants). Right diagram: **endothermic**,  $\Delta H > 0$  (products higher in enthalpy than reactants). A1 A1

**(b)** Explain, in terms of the energy needed to break and form bonds, why the exothermic reaction releases energy overall. [3]

Breaking the bonds in the reactants requires an input of energy, while forming the new bonds in the products releases energy. In an exothermic reaction, the **energy released forming the new (generally stronger) bonds in the products is greater** than the energy required to break the bonds in the reactants, so there is a net release of energy to the surroundings. R1 R1 A1

**(c)** Give one example of a chemical or physical process that is endothermic. [2]

Any valid example, e.g. the **thermal decomposition of calcium carbonate** ( $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ ), or the dissolving of ammonium nitrate in water, or the melting of ice. A1 R1

## R1.2 Energy Cycles in Reactions

### Question 4 [6 marks]

Hess's Law allows enthalpy changes that are difficult (or impossible) to measure directly to be calculated using an energy cycle.

(a) State Hess's Law.

[2]

Hess's Law states that the **total enthalpy change for a reaction is independent of the pathway (route) taken**, provided the initial and final conditions are the same.

A1 A1

(b) Explain why Hess's Law is valid, in terms of the nature of enthalpy.

[2]

Enthalpy is a **state function**: its value depends only on the current state of the system (defined by the initial and final conditions), not on the particular path taken to reach that state. This means the total enthalpy change between two states must be the same regardless of the route taken.

R1 R1

(c) Using standard enthalpies of formation,  $\Delta H_f^\circ(\text{CO}_2) = -393.5 \text{ kJ mol}^{-1}$  and  $\Delta H_f^\circ(\text{H}_2\text{O}) = -285.8 \text{ kJ mol}^{-1}$  (elements in their standard states have  $\Delta H_f^\circ = 0$ ), calculate  $\Delta H^\circ$  for the combustion of one mole of carbon:  $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ .

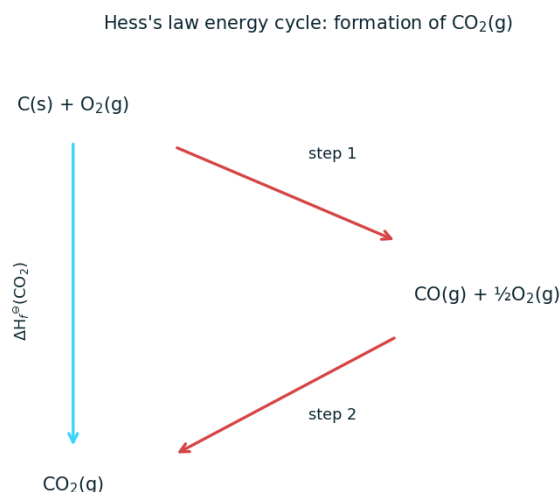
[2]

Since  $\text{C(s)}$  and  $\text{O}_2(\text{g})$  are elements in their standard states ( $\Delta H_f^\circ = 0$ ),  $\Delta H^\circ$  for this reaction is simply the enthalpy of formation of  $\text{CO}_2$ :  **$-393.5 \text{ kJ mol}^{-1}$** .

M1 A1

### Question 5 [7 marks]

The diagram shows a Hess's law energy cycle for the formation of carbon dioxide, comparing the direct route with a two-step indirect route via carbon monoxide.



*Hess's law energy cycle for the formation of  $\text{CO}_2(\text{g})$  (schematic).*

(a) Identify the direct route and the indirect route shown in the diagram.

[2]

Direct route:  **$\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$**  (single step,  $\Delta H_f^\circ$ ). Indirect route:  **$\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO(g)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$**  (via step 1 then step 2).

A1 A1

(b) Write an expression, using Hess's Law, relating  $\Delta H_f^\circ(\text{CO}_2)$  to the enthalpy changes of steps 1 and 2. [2]

$\Delta H_f^\circ(\text{CO}_2) = \Delta H(\text{step 1}) + \Delta H(\text{step 2})$  (the direct route equals the sum of the indirect route's steps). A1 A1

(c) Given  $\Delta H(\text{step 1}) = -110.5 \text{ kJ mol}^{-1}$  and  $\Delta H(\text{step 2}) = -283.0 \text{ kJ mol}^{-1}$ , calculate  $\Delta H_f^\circ(\text{CO}_2)$ . [3]

$\Delta H_f^\circ(\text{CO}_2) = (-110.5) + (-283.0) = -393.5 \text{ kJ mol}^{-1}$  (this matches the accepted literature value). M1 M1 A1

### R1.3 Energy From Fuels

#### Question 6 [6 marks]

Bond enthalpies can be used to estimate the enthalpy change of a gas-phase reaction. (Bond enthalpies:  $\text{H}-\text{H} = 436 \text{ kJ mol}^{-1}$ ;  $\text{Cl}-\text{Cl} = 242 \text{ kJ mol}^{-1}$ ;  $\text{H}-\text{Cl} = 431 \text{ kJ mol}^{-1}$ .)

(a) Define the term 'bond enthalpy'. [2]

Bond enthalpy is the **energy required to break one mole of a given covalent bond**, with all species in the gaseous state. A1 A1

(b) State whether breaking bonds is an exothermic or endothermic process, and whether forming bonds is exothermic or endothermic. [2]

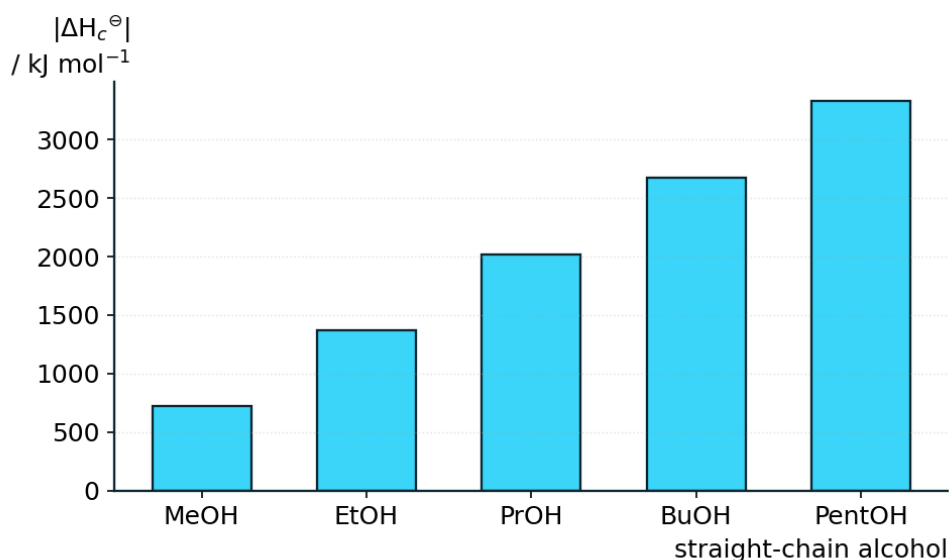
Breaking bonds is **endothermic** (requires an input of energy). Forming bonds is **exothermic** (releases energy). A1 A1

(c) Calculate the enthalpy change for the reaction  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$ , using the given bond enthalpies. [2]

$\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds formed}) = (436 + 242) - (2 \cdot 431) = 678 - 862 = -184 \text{ kJ mol}^{-1}$ . M1 A1

#### Question 7 [7 marks]

The graph shows the magnitude of the standard enthalpy of combustion for the first five members of the straight-chain, saturated alcohol homologous series.



Enthalpy of combustion of straight-chain alcohols (given data).

**(a)** Describe the trend shown in the graph as the length of the carbon chain increases. [2]

The magnitude of the enthalpy of combustion **increases** (becomes more negative/more exothermic) as the length of the carbon chain increases, from 726 kJ mol<sup>-1</sup> for methanol to 3329 kJ mol<sup>-1</sup> for pentan-1-ol. A1 A1

**(b)** Explain this trend in terms of chemical bonding. [3]

As chain length increases, each additional CH<sub>2</sub> unit adds more C—C and C—H bonds that must be broken, and more new bonds (to CO<sub>2</sub> and H<sub>2</sub>O) form on complete combustion. Since there are **more bonds broken and formed per mole** of alcohol as chain length increases, more energy is released overall, giving a greater (more negative) enthalpy of combustion. R1 R1 A1

**(c)** The enthalpy of combustion of octane (a major component of petrol/gasoline, M = 114.23 g mol<sup>-1</sup>) is -5470 kJ mol<sup>-1</sup>. Using the value for methanol (M = 32.05 g mol<sup>-1</sup>) from the graph, compare the energy released per gram of each fuel. [2]

Methanol:  $726.0 \div 32.05 = 22.7 \text{ kJ g}^{-1}$ . Octane:  $5470.0 \div 114.23 = 47.9 \text{ kJ g}^{-1}$ . Octane releases roughly twice as much energy per gram as methanol, showing that hydrocarbon fuels generally have a higher energy density than alcohols of similar chain length. M1 A1

## R1.4 Entropy and Spontaneity

### Question 8 [6 marks]

Entropy is a measure of the disorder of a system.

**(a)** Define the term 'entropy'. [2]

Entropy, S, is a measure of the **number of ways particles and energy can be arranged** in a system — a measure of the degree of disorder or randomness of the system. A1 A1

**(b)** Predict the sign of the entropy change,  $\Delta S$ , for the reaction  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ , explaining your reasoning. [2]

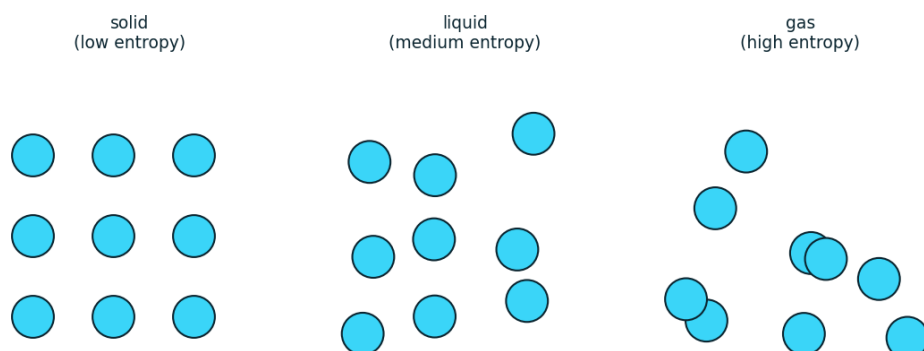
$\Delta S$  is **negative**. The reaction converts 4 moles of gaseous reactant molecules into 2 moles of gaseous product molecules, decreasing the total number of gas particles (and possible arrangements), so the disorder of the system decreases. A1 R1

**(c)** Explain why the thermal decomposition of a solid to give a gaseous product is associated with a large positive entropy change. [2]

Gas particles are much more disordered (have far more possible positions/arrangements) than particles in a solid lattice. Converting a solid into a gaseous product therefore causes a **large increase** in the number of possible arrangements of particles, giving a large positive  $\Delta S$ . R1 R1

### Question 9 [7 marks]

The diagrams show a simplified representation of particle arrangement in the solid, liquid, and gas states.



*Particle disorder in solid, liquid, and gas states (schematic).*

**(a)** Using the diagrams, rank the three states in order of increasing entropy. [2]

Increasing entropy: **solid < liquid < gas**. A1 A1

**(b)** Explain, using the diagrams, why the gas state has the highest entropy. [3]

In the solid, particles are held in **fixed, ordered positions** with very few possible arrangements. In the liquid, particles are close together but can move past one another, giving more possible arrangements. In the gas, particles are **free to move randomly throughout the whole available volume**, giving by far the greatest number of possible positions and arrangements (microstates), and therefore the highest entropy. R1 R1 A1

**(c)** Predict the sign of  $\Delta S$  for the sublimation of solid carbon dioxide (dry ice) directly to  $\text{CO}_2$  gas. [2]

$\Delta S$  is **positive**: sublimation converts a highly ordered solid directly into a highly disordered gas, greatly increasing the number of possible particle arrangements. A1 R1

### Question 10 [7 marks]

The spontaneity (thermodynamic feasibility) of a reaction is determined by the sign of the Gibbs free energy change,  $\Delta G = \Delta H - T\Delta S$ . Consider a reaction with  $\Delta H = -92.0 \text{ kJ mol}^{-1}$  and  $\Delta S = -198 \text{ J K}^{-1} \text{ mol}^{-1}$  at  $T = 298 \text{ K}$ .

**(a)** Write the Gibbs free energy equation and state the criterion for a reaction to be thermodynamically spontaneous at a given temperature. [2]

$\Delta G = \Delta H - T\Delta S$ . A reaction is spontaneous (thermodynamically feasible) at a given temperature when  **$\Delta G < 0$** . A1 A1

**(b)** Explain why a reaction with a negative  $\Delta H$  and a negative  $\Delta S$  can become non-spontaneous at high temperature. [2]

Since  $\Delta G = \Delta H - T\Delta S$ , and  $\Delta S$  is negative, the term  $-T\Delta S$  becomes an increasingly large **positive** contribution to  $\Delta G$  as temperature  $T$  increases. At sufficiently high  $T$ , this positive term can outweigh the negative  $\Delta H$ , making  $\Delta G$  positive and the reaction non-spontaneous. R1 R1

**(c)** Calculate  $\Delta G$  for this reaction at  $T = 298 \text{ K}$  (convert  $\Delta S$  to  $\text{kJ K}^{-1} \text{ mol}^{-1}$  first), and state whether the reaction is spontaneous at this temperature. [3]

$\Delta S = -198 \text{ J K}^{-1} \text{ mol}^{-1} = -0.198 \text{ kJ K}^{-1} \text{ mol}^{-1}$ . M1 M1 A1

$\Delta G = \Delta H - T\Delta S = -92.0 - [298 \cdot (-0.198)] = -92.0 - (-59.0) = \mathbf{-33.0 \text{ kJ mol}^{-1}}$ .

Since  $\Delta G < 0$ , the reaction is **spontaneous** at  $298 \text{ K}$ .

