

2.1.3 Energy diagrams, Hess cycles and cooling correction

Name: _____ Class: _____ Date: _____

Total: 26 marks

KEY WORDS enthalpy change

Objective

Construct energy diagrams and a cooling correction, then check states, signs and the mole basis. All tasks and marking guidance are original.

1 Key knowledge and worked examples

An enthalpy change _____ belongs to the equation as written at constant pressure. Reversing the equation reverses its sign; multiplying all coefficients multiplies its value. A level diagram shows the initial and final enthalpy; it is not a graph of temperature against time.

■ Worked graphical method

A reaction is mixed at 120 s. Before mixing the temperature is 19.0 °C. The post-reaction line falls from 24.0 °C at 150 s to 23.4 °C at 210 s. Its gradient is $(23.4 - 24.0)/(210 - 150) = -0.010 \text{ °C s}^{-1}$. Extrapolating back 30 s gives 24.3 °C at mixing, so corrected $\Delta T = 24.3 - 19.0 = 5.3 \text{ °C}$. Use the before-mixing line at the same time, not an unrelated room-temperature reading.

For a Hess cycle, both routes must reach the same final substances, amounts and states. Mean bond enthalpies refer to gaseous bonds and average environments; a liquid-water product needs additional phase information.

2 Practice

2.1 At standard conditions, $2\text{C}_2\text{H}_4(\text{g}) + 6\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$ has $\Delta H = -2822 \text{ kJ mol}^{-1}$ for the equation as written. Define the standard enthalpy change of this reaction and calculate the value for $\text{C}_2\text{H}_4(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$. [3]

2.2 Distinguish the bond enthalpy of H–H in gaseous H_2 from a tabulated mean C–H bond enthalpy. Explain why a gas-phase bond calculation cannot directly give the exact combustion enthalpy when liquid water is a product. [3]

2.3 Comparable C–Br and C–Cl bond enthalpies are 276 and 338 kJ mol^{-1} . Which is easier to break, and what tentative indication does this give about the first cleavage? Explain why these values alone do not give a numerical reaction rate. [3]

3 Exam-style questions

3.1 Draw separate labelled enthalpy-level diagrams for an exothermic and an endothermic reaction. Show reactant/product levels, the direction of the ΔH arrow and the sign. Do not add a time axis. [4]

3.2 Construct a complete combustion Hess cycle for $\text{C}(\text{s, graphite}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$, using standard combustion enthalpies: $\text{C} -394$, $\text{H}_2 -286$ and $\text{CH}_4 -891 \text{ kJ mol}^{-1}$. Include all species, amounts, states and arrow directions, then calculate the formation enthalpy of methane. [5]

3.3 40.0 cm^3 each of 1.00 mol dm^{-3} HCl and NaOH are mixed at 120 s. Before mixing, both are at 20.0°C at 0, 60 and 120 s. After reaction, temperatures at 150, 180, 210 and 240 s are 25.2 , 24.9 , 24.6 and 24.3°C . Plot temperature against time, extrapolate the cooling line to mixing and find the corrected rise. Use solution density 1.00 g cm^{-3} , $c = 4.18 \text{ J g}^{-1}^\circ\text{C}^{-1}$ and negligible cup heat capacity to calculate neutralisation enthalpy. Explain why the uncorrected maximum gives a different result and state one limit of the extrapolation. [8]

Solutions

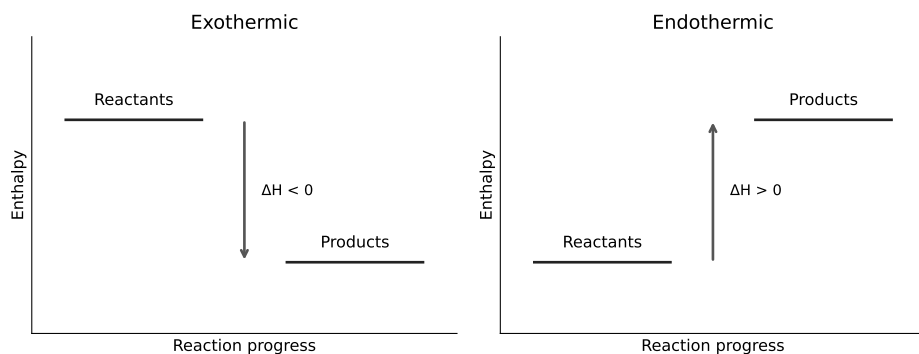
Original marking guidance: M1 method, A1 accuracy, B1 explanation.

2.1 The heat change at constant pressure for the equation as written under specified standard conditions, with reactants/products in their standard states. Halving every coefficient halves ΔH : $-1411 \text{ kJ mol}^{-1}$. The word reaction does not force a coefficient of one for every species.

2.2 Bond enthalpy is the energy needed to break one mole of the specified gaseous bonds. A mean C–H value averages different molecular environments. Liquid water has intermolecular/phase-energy differences not included in simply forming gaseous O–H bonds, so phase information is needed as well as the averaging limitation.

2.3 C–Br needs less energy to break, so it may cleave more readily/first in otherwise comparable pathways. Actual rate depends on the whole activation mechanism and conditions, so bond enthalpy alone does not fix a rate.

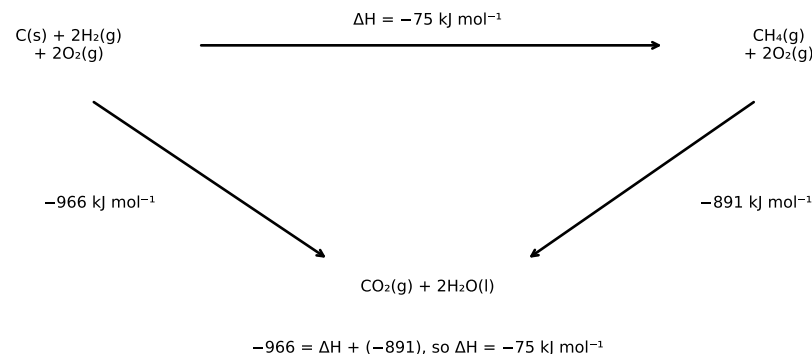
3.1



For each diagram, B1 for correct relative labelled levels and B1 for correctly directed/signed ΔH (four marks total).

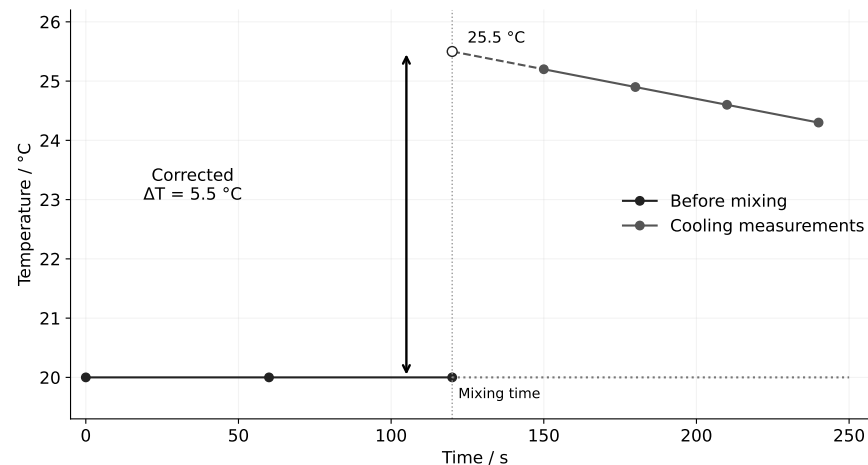
3.2

Same initial and final states: include oxygen on both top routes



Common products $\text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)}$; correctly scaled left route $-394 + 2(-286) = -966 \text{ kJ mol}^{-1}$; consistent downward arrow directions and spectator O_2 on both top routes. $-966 = \Delta H - 891$, giving $\Delta H = -75 \text{ kJ mol}^{-1}$.

3.3



Correct axes/scales and plotted measurements; cooling line extrapolated to $25.5 \text{ }^\circ\text{C}$ at 120 s; corrected rise = $5.5 \text{ }^\circ\text{C}$. $q = mc\Delta T = 80.0 \times 4.18 \times 5.5 = 1839.2 \text{ J} = 1.8392 \text{ kJ}$. $n(\text{H}_2\text{O}) = cV = 1.00 \times 0.0400 = 0.0400 \text{ mol}$. $\Delta H = -q/n = -1.8392/0.0400 = -46.0 \text{ kJ mol}^{-1}$. The first measured maximum has already lost heat, so using $5.2 \text{ }^\circ\text{C}$ gives a less negative value. The correction assumes the observed cooling trend reasonably represents heat loss near mixing; changing heat-loss rate, slow mixing or reaction continuing during cooling limits it.