

## 2.1.2 Hess cycles and bond-enthalpy methods

Name: \_\_\_\_\_ Class: \_\_\_\_\_ Date: \_\_\_\_\_

Total: 20 marks

**KEY WORDS** Hess's law

### Objective

Choose and check a thermochemical route, including reversal, coefficients and gaseous-bond assumptions. All questions and marking guidance are original.

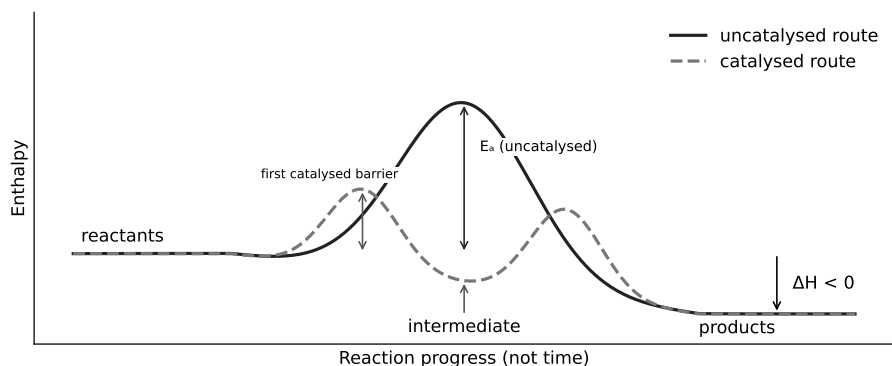
### 1 Key knowledge and worked examples

Hess's law compares routes with identical initial and final states. Reverse a chemical equation and its enthalpy sign; multiply both together. Cancel species before summing energy changes.

#### ■ Worked method

For  $\text{C(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO(g)}$ , use  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ ,  $-394 \text{ kJ mol}^{-1}$ , and reverse  $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ ,  $-283 \text{ kJ mol}^{-1}$ . Cancel  $\text{CO}_2$  and  $\frac{1}{2}\text{O}_2$  to get the target.  $\Delta H = -394 - (-283) = -111 \text{ kJ mol}^{-1}$ .

For a gas-phase bond estimate, count every bond on each side, including coefficients:  $\Delta H \approx \sum E(\text{broken}) - \sum E(\text{formed})$ . A mean bond enthalpy averages different molecules, so it is not an exact value for every environment.



## 2 Practice

**2.1** State what happens to  $\Delta H$  when a reaction equation is reversed and when all coefficients are doubled. [2]

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**2.2**  $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$  has  $\Delta H = -184 \text{ kJ mol}^{-1}$ . Calculate  $\Delta H$  for  $\text{HCl} \rightarrow \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2$ . [2]

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**2.3** Use  $\text{H-H} = 436$ ,  $\text{Cl-Cl} = 243$  and  $\text{H-Cl} = 431 \text{ kJ mol}^{-1}$  to estimate  $\Delta H$  for  $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ . [3]

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## 3 Exam-style questions

**3.1** Formation enthalpies are  $\text{CH}_4(\text{g}) -75$ ,  $\text{CO}_2(\text{g}) -394$  and  $\text{H}_2\text{O(l)} -286 \text{ kJ mol}^{-1}$ . Calculate  $\Delta H$  for  $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O(l)}$ . Explain the value used for oxygen. [4]

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**3.2** For  $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$ ,  $\Delta\text{H} = -72 \text{ kJ mol}^{-1}$ .  $\text{H-H} = 436$  and  $\text{Br-Br} = 193 \text{ kJ mol}^{-1}$ . Find the mean  $\text{H-Br}$  bond enthalpy and explain why these data cannot directly predict the rate. [4]

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**3.3** Use the following measured enthalpies to find  $\Delta\text{H}$  for  $\text{Mg}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{MgO}(\text{s})$ :  $\text{Mg}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2(\text{g})$ ,  $-466 \text{ kJ mol}^{-1}$ ;  $\text{MgO}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$ ,  $-146 \text{ kJ mol}^{-1}$ ;  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ ,  $-286 \text{ kJ mol}^{-1}$ . Show which equation is reversed and one experimental limitation. [5]

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## Solutions

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

**2.1** Reversing changes the sign; doubling coefficients doubles  $\Delta H$ .

**2.2** Reverse and halve:  $+92 \text{ kJ mol}^{-1}$ .

**2.3** Break one H–H and one Cl–Cl; form two H–Cl.  $\Delta H \approx 436 + 243 - 2(431) = -183 \text{ kJ mol}^{-1}$ .

**3.1**  $\Delta H = \sum \nu \Delta H_f(\text{products}) - \sum \nu \Delta H_f(\text{reactants})$ .  $[-394 + 2(-286)] - [-75] = -891 \text{ kJ mol}^{-1}$ . Oxygen has zero formation enthalpy in its standard state by convention.

**3.2**  $-72 = 436 + 193 - 2E(\text{H} - \text{Br})$ ;  $E = (436 + 193 + 72)/2 = 350.5 \text{ kJ mol}^{-1}$ . Rate depends on the activation pathway, not just net enthalpy or a bond sum.

**3.3** Reverse the MgO reaction, giving  $+146 \text{ kJ mol}^{-1}$ . Add the Mg reaction and hydrogen combustion, cancel HCl,  $\text{MgCl}_2$ ,  $\text{H}_2$  and  $\text{H}_2\text{O}$  to obtain the target.  $\Delta H = -466 - 286 + 146 = -606 \text{ kJ mol}^{-1}$ . Heat loss in the measured reactions or unmatched solution states/concentrations can limit the experimental cycle.