IB Chemistry – Reactivity 1: What Drives Reactions

IB Chemistry SL & HL (2023 syllabus) · Total marks: 37 · Answers on the last page

Questions on enthalpy changes, Hess's law, Born-Haber cycles, entropy and Gibbs energy, and electrochemistry. Use $R = 8.31\,\text{J K}^{-1}\text{mol}^{-1}$, $F = 96500\,\text{C mol}^{-1}$ and the specific heat capacity of water $c = 4.18\,\text{J g}^{-1}\text{K}^{-1}$. A calculator is required throughout; Born-Haber and Gibbs energy calculations are HL extension content, marked accordingly.

Section A – Enthalpy and Hess's Law (SL and HL)

1. In a calorimetry experiment, burning a small sample of fuel raises the temperature of 100 g of water by 6.5°C. The mass of fuel burned corresponds to 0.0050 mol.
   (a) Calculate the heat energy transferred to the water, in kJ.
   (b) Calculate the molar enthalpy of combustion of the fuel, including its sign. [4]

2. State Hess's law, and explain why it is a consequence of the first law of thermodynamics (conservation of energy). [2]

3. Given the standard enthalpies of combustion $\Delta H_c^\ominus[\text{C(s)}] = -393.5\,\text{kJ mol}^{-1}$, $\Delta H_c^\ominus[\text{H}_2\text{(g)}] = -285.8\,\text{kJ mol}^{-1}$ and $\Delta H_c^\ominus[\text{CH}_4\text{(g)}] = -890.3\,\text{kJ mol}^{-1}$, use Hess's law to calculate the standard enthalpy of formation of methane, $\Delta H_f^\ominus[\text{CH}_4\text{(g)}]$, for the reaction $\text{C(s)} + 2\text{H}_2\text{(g)} \rightarrow \text{CH}_4\text{(g)}$. [3]

4. Explain, in terms of bond breaking and bond making, why some reactions are exothermic and others are endothermic. [3]

Section B – Born-Haber Cycles, Entropy and Gibbs Energy (HL)

5. Use the following data to construct a Born-Haber cycle for sodium chloride and calculate the lattice enthalpy of NaCl:
   Enthalpy of atomisation of Na(s): $+107\,\text{kJ mol}^{-1}$
   Enthalpy of atomisation of $\frac{1}{2}\text{Cl}_2\text{(g)}$: $+122\,\text{kJ mol}^{-1}$
   First ionisation energy of Na(g): $+496\,\text{kJ mol}^{-1}$
   First electron affinity of Cl(g): $-349\,\text{kJ mol}^{-1}$
   Enthalpy of formation of NaCl(s): $-411\,\text{kJ mol}^{-1}$ [4]

6. Define lattice enthalpy, and explain why lattice enthalpy values are always exothermic (negative). [2]

7. For the reaction $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$, $\Delta H^\ominus = -92\,\text{kJ mol}^{-1}$ and $\Delta S^\ominus = -198\,\text{J K}^{-1}\text{mol}^{-1}$.
   (a) Calculate $\Delta G^\ominus$ at 298 K, and state whether the reaction is spontaneous at this temperature.
   (b) Calculate the temperature above which the reaction becomes non-spontaneous under standard conditions. [5]

8. Explain why $\Delta S^\ominus$ is negative for the reaction $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$. [2]

Section C – Electrochemistry (SL and HL)

9. A voltaic cell is set up using the half-cells $\text{Zn}^{2+}\text{(aq)} + 2e^- \rightleftharpoons \text{Zn(s)}$, $E^\ominus = -0.76\,\text{V}$, and $\text{Cu}^{2+}\text{(aq)} + 2e^- \rightleftharpoons \text{Cu(s)}$, $E^\ominus = +0.34\,\text{V}$.

(a) Calculate the standard cell potential, $E^{\ominus}_{\text{cell}}$.
(b) State which electrode is the anode (oxidation) and which is the cathode (reduction). [4]

10. Using $\Delta G^{\ominus} = -nFE^{\ominus}_{\text{cell}}$, calculate the standard Gibbs energy change, in kJ mol^{-1}, for the cell reaction in the previous question ($n = 2$). [3]

11. Explain the relationship between the sign of $E^{\ominus}_{\text{cell}}$ and the sign of $\Delta G^{\ominus}$, and state what this tells you about whether a redox reaction is spontaneous. [2]

12. The enthalpy of solution of an ionic compound can be found from a Hess's law cycle linking lattice enthalpy and enthalpy of hydration. Describe this cycle, and explain, in terms of these two enthalpy changes, why some ionic compounds dissolve exothermically while others dissolve endothermically. [3]

Answers

Check your working against these. If an answer does not match, try the question again before looking for the method.

1. (a) $q = mc\Delta T = 100 \times 4.18 \times 6.5 = 2717\,\text{J} = 2.72\,\text{kJ}$.
   (b) $\Delta H_c = -\dfrac{2.72}{0.0050} = -543\,\text{kJ mol}^{-1}$ (negative because combustion is exothermic).

2. Hess's law states that the total enthalpy change for a reaction is independent of the route taken, provided the initial and final conditions are the same. This follows from conservation of energy: since enthalpy is a state function, the total energy change between two states cannot depend on the path, otherwise energy could be created or destroyed by choosing a different route.

3. $\Delta H_f^\ominus = \Delta H_c^\ominus[\text{C}] + 2\Delta H_c^\ominus[\text{H}_2] - \Delta H_c^\ominus[\text{CH}_4] = (-393.5) + 2(-285.8) - (-890.3) = -74.8\,\text{kJ mol}^{-1}$.

4. Breaking bonds in the reactants requires an input of energy (endothermic), while forming bonds in the products releases energy (exothermic). If the energy released on forming the new bonds is greater than the energy required to break the old bonds, the overall reaction is exothermic ($\Delta H < 0$); if less energy is released than absorbed, the reaction is endothermic ($\Delta H > 0$).

5. $\Delta H_f^\ominus = \Delta H_{\text{atomisation}}(\text{Na}) + \Delta H_{\text{atomisation}}(\text{Cl}) + IE_1(\text{Na}) + EA_1(\text{Cl}) + \Delta H_{\text{lattice}}$. Rearranging: $\Delta H_{\text{lattice}} = -411 - (107 + 122 + 496 - 349) = -787\,\text{kJ mol}^{-1}$.

6. Lattice enthalpy is the enthalpy change when one mole of a solid ionic compound is formed from its gaseous ions under standard conditions. It is always exothermic because oppositely charged gaseous ions are attracted to each other by electrostatic forces, so bringing them together to form a stable ionic lattice releases energy.

7. (a) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus = -92 - (298)(-0.198) = -92 + 59.0 = -33.0\,\text{kJ mol}^{-1}$. Since $\Delta G^\ominus < 0$, the reaction is spontaneous at 298 K.
   (b) The reaction becomes non-spontaneous when $\Delta G^\ominus = 0$: $T = \dfrac{\Delta H^\ominus}{\Delta S^\ominus} = \dfrac{-92}{-0.198} = 465\,\text{K}$.

8. There are 4 moles of gas on the reactant side but only 2 moles of gas on the product side. Since gases have much greater entropy (disorder) than the same substances would in a more ordered state, and fewer gas particles means fewer possible microstates (less disorder), the entropy of the system decreases, giving a negative $\Delta S^\ominus$.

9. (a) $E_{\text{cell}}^\ominus = E_{\text{cathode}}^\ominus - E_{\text{anode}}^\ominus = 0.34 - (-0.76) = +1.10\,\text{V}$.
   (b) Zinc has the more negative electrode potential, so it is oxidised at the anode ($\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$); copper is reduced at the cathode ($\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$).

10. $\Delta G^\ominus = -nFE_{\text{cell}}^\ominus = -2(96500)(1.10) = -212300\,\text{J mol}^{-1} = -212\,\text{kJ mol}^{-1}$.

11. Since $\Delta G^\ominus = -nFE_{\text{cell}}^\ominus$ and n and F are always positive, a positive $E_{\text{cell}}^\ominus$ always corresponds to a negative $\Delta G^\ominus$, and vice versa. A negative $\Delta G^\ominus$ (positive $E_{\text{cell}}^\ominus$) means the reaction is thermodynamically spontaneous (feasible) under standard conditions.

12. In the cycle, the ionic solid is first (hypothetically) converted into its gaseous ions by supplying the lattice enthalpy (the reverse of lattice formation, which is endothermic), and these gaseous ions are then hydrated by surrounding water molecules, releasing the (exothermic) enthalpies of hydration; by Hess's law, $\Delta H_{\text{solution}} = -\Delta H_{\text{lattice}} + \Delta H_{\text{hydration(cation)}} + \Delta H_{\text{hydration(anion)}}$. If the total (negative) hydration enthalpy is larger in magnitude than the lattice enthalpy, dissolution is exothermic overall; if the lattice enthalpy is larger in magnitude than the total hydration enthalpy, dissolution is endothermic overall.

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