

A-Level Chemistry – Physical: Energetics and Kinetics

A-Level Chemistry (Edexcel/AQA/OCR) · Total marks: 41 · Answers on the last page

Practice questions on enthalpy and calorimetry, Born-Haber cycles and Hess's law, and entropy, Gibbs free energy and reaction kinetics, matching the A-Level Chemistry physical chemistry specification. A calculator is required; take the specific heat capacity of aqueous solutions as $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ and the gas constant $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$.

Section A – Enthalpy and Calorimetry

- In a calorimetry experiment, 0.0500 mol of a solid reacts completely in 100 g of aqueous solution. The temperature of the solution rises by 6.8°C .
 - Calculate the heat released by the reaction.
 - Calculate the molar enthalpy change of the reaction, in kJ mol^{-1} , including its sign. [4]
- State the definition of the standard enthalpy change of combustion of a substance. [2]
- Given the following enthalpy changes:
 $\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$, $\Delta H_1 = -394 \text{ kJ mol}^{-1}$
 $\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$, $\Delta H_2 = -286 \text{ kJ mol}^{-1}$
 $\text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(l)$, $\Delta H_3 = -1411 \text{ kJ mol}^{-1}$
Use Hess's law to calculate the standard enthalpy of formation of ethene, $\text{C}_2\text{H}_4(g)$. [4]
- Use the following mean bond enthalpies to calculate the enthalpy change for the complete combustion of methane, $\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$:
 $\text{C-H} = 414$, $\text{O=O} = 498$, $\text{C=O} = 804$, $\text{O-H} = 463 \text{ kJ mol}^{-1}$. [4]

Section B – Born-Haber Cycles

- Define lattice enthalpy (of formation) and state whether it is always exothermic or endothermic, giving a reason. [2]
- Use the following data to calculate the lattice enthalpy of formation of sodium chloride, $\text{NaCl}(s)$:
Enthalpy of formation of $\text{NaCl}(s)$: -411 kJ mol^{-1}
Enthalpy of atomisation (sublimation) of $\text{Na}(s)$: $+107 \text{ kJ mol}^{-1}$
First ionisation energy of $\text{Na}(g)$: $+496 \text{ kJ mol}^{-1}$
Bond dissociation enthalpy of $\text{Cl}_2(g)$: $+242 \text{ kJ mol}^{-1}$
First electron affinity of $\text{Cl}(g)$: -349 kJ mol^{-1} [5]
- For sodium chloride, the lattice enthalpy calculated from the Born-Haber cycle (an experimental value) agrees closely with the theoretical lattice enthalpy calculated from a purely ionic (point-charge) model. Explain what this agreement suggests about the type of bonding in NaCl . [2]
- For silver chloride, AgCl , the experimental (Born-Haber) lattice enthalpy is considerably more exothermic than the theoretical lattice enthalpy calculated from a purely ionic model. Explain this difference in terms of ionic polarisation. [3]

Section C – Entropy, Gibbs Energy and Kinetics (Calculator required)

- For a reaction, $\Delta H = -92.0 \text{ kJ mol}^{-1}$ and $\Delta S = -198 \text{ J K}^{-1} \text{ mol}^{-1}$.
 - Calculate ΔG at 298 K and state whether the reaction is feasible (spontaneous) at this tem-

perature.

(b) Calculate the temperature above which the reaction is no longer feasible. [5]

10. Explain, in terms of the number and arrangement of particles, why a reaction in which the number of moles of gas increases has a positive entropy change, ΔS . [3]

11. The Arrhenius equation is $k = Ae^{-E_a/RT}$. For a reaction, $E_a = 75.0 \text{ kJ mol}^{-1}$ and $A = 4.0 \times 10^{13} \text{ s}^{-1}$.

(a) Calculate the rate constant k at 300 K.

(b) Calculate the rate constant k at 310 K.

(c) Calculate the ratio $\frac{k(310 \text{ K})}{k(300 \text{ K})}$. [5]

12. Using the Arrhenius equation, explain why a relatively small increase in temperature (e.g. 10 K) can cause a large increase in the rate constant of a reaction. [2]

Answers

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

- $q = mc\Delta T = 100 \times 4.18 \times 6.8 = 2840 \text{ J}$ (3 s.f.).
 - $\Delta H = \frac{-2840}{0.0500 \times 1000} = -56.8 \text{ kJ mol}^{-1}$ (exothermic).
- The enthalpy change when one mole of a substance is completely burned in excess oxygen, under standard conditions (100 kPa, and a stated temperature, usually 298 K), with all reactants and products in their standard states.
- $\Delta H_f(\text{C}_2\text{H}_4) = 2\Delta H_1 + 2\Delta H_2 - \Delta H_3 = 2(-394) + 2(-286) - (-1411) = +51 \text{ kJ mol}^{-1}$.
- Bonds broken: $4(\text{C-H}) + 2(\text{O=O}) = 4(414) + 2(498) = 2652 \text{ kJ mol}^{-1}$. Bonds formed: $2(\text{C=O}) + 4(\text{O-H}) = 2(804) + 4(463) = 3460 \text{ kJ mol}^{-1}$. $\Delta H = 2652 - 3460 = -808 \text{ kJ mol}^{-1}$.
- Lattice enthalpy of formation is the enthalpy change when one mole of a solid ionic compound is formed from its constituent gaseous ions. It is always exothermic, because energy is released when oppositely charged gaseous ions come together and are attracted to form a stable, ordered ionic lattice.
- $\Delta H_f = \Delta H_{\text{sub}} + IE_1 + \frac{1}{2}\Delta H_{\text{diss}} + EA_1 + \Delta H_{\text{lattice}}$. $-411 = 107 + 496 + 121 + (-349) + \Delta H_{\text{lattice}} \Rightarrow \Delta H_{\text{lattice}} = -411 - 375 = -786 \text{ kJ mol}^{-1}$.
- The close agreement suggests that the bonding in sodium chloride is well described by a purely ionic model, i.e. the ions behave essentially as non-polarised point charges, with negligible covalent character.
- The small, highly-charged Ag^+ ion has a high polarising power and distorts (polarises) the electron cloud of the larger Cl^- ion, giving the bond some covalent character (electron density shared between the ions). This extra covalent bonding makes the lattice stronger than a purely ionic model predicts, so the experimental lattice enthalpy is more exothermic than the theoretical value.
- $\Delta G = \Delta H - T\Delta S = -92.0 - 298(-0.198) = -33.0 \text{ kJ mol}^{-1}$. Since $\Delta G < 0$, the reaction is feasible at 298 K.
 - $\Delta G = 0 \Rightarrow T = \frac{\Delta H}{\Delta S} = \frac{-92.0 \times 1000}{-198} = 465 \text{ K}$. Above this temperature, ΔG becomes positive and the reaction is no longer feasible.
- Gas particles are much more disordered (have many more possible arrangements/microstates) than particles in liquids or solids. Increasing the number of moles of gas increases the number of ways the particles and their energy can be arranged, so the disorder of the system increases, giving a positive ΔS .
- $k(300) = 4.0 \times 10^{13} e^{-75000/(8.31 \times 300)} = 3.4 \text{ s}^{-1}$.
 - $k(310) = 4.0 \times 10^{13} e^{-75000/(8.31 \times 310)} = 9.1 \text{ s}^{-1}$.
 - Ratio $= \frac{9.1}{3.4} = 2.6$.
- Because E_a/RT appears in the exponent of the Arrhenius equation, a small increase in T causes a proportionally larger decrease in E_a/RT , and since k depends exponentially (not linearly) on this term, even a small change in temperature causes a large increase in the fraction of molecules with energy $\geq E_a$, and hence a large increase in k .

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