

4.2.1 Total entropy and feasibility

Name: _____ Class: _____ Date: _____

Total: 21 marks

KEY WORDS entropy

Objective

Calculate system, surroundings and total entropy with consistent units. Questions and marking guidance are original.

1 Key knowledge and worked examples

Entropy measures dispersal of energy among accessible arrangements. More gas particles often mean greater system entropy, but calculate from given standard values when available. $\Delta S_{system} = \sum \nu S(products) - \sum \nu S(reactants)$.

■ Worked method

At 298 K, a reaction has $\Delta H = -40.0 \text{ kJ mol}^{-1}$ and $\Delta S_{system} = -100 \text{ J mol}^{-1} \text{ K}^{-1}$.

$$\Delta S_{surroundings} = -\Delta H/T = 40000/298 = +134 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S_{total} = -100 + 134 = +34 \text{ J mol}^{-1} \text{ K}^{-1}$$

Positive total entropy favours the forward direction thermodynamically. It does not promise a fast reaction: a large activation barrier may still prevent an observable change. Temperature boundaries assume the supplied enthalpy/entropy values remain approximately constant over the range.

2 Practice

2.1 Predict the likely sign of system entropy for $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, with a reason. [2]

2.2 For $A(g) \rightarrow 2B(g)$, $S^\circ(A) = 200$ and $S^\circ(B) = 150 \text{ J mol}^{-1} \text{ K}^{-1}$. Calculate standard system entropy change. [2]

2.3 At 300 K a reaction has $\Delta H = +18.0 \text{ kJ mol}^{-1}$ and $\Delta S(\text{system}) = +90.0 \text{ J mol}^{-1} \text{ K}^{-1}$. Calculate total entropy. [3]

3 Exam-style questions

3.1 A reaction has $\Delta H = +36.0 \text{ kJ mol}^{-1}$ and $\Delta S(\text{system}) = +120 \text{ J mol}^{-1} \text{ K}^{-1}$. Find the temperature boundary and predict the favourable side. State an assumption. [4]

3.2 A reaction is exothermic and has negative system entropy. Explain why it may be favoured only at lower temperatures, and why thermodynamic favourability does not imply fast reaction. [3]

3.3 (a) State the entropy of a perfect crystal at 0 K, then describe how its entropy changes as it warms within a phase and passes through melting and boiling. (b) Explain why dissolving an ionic crystal does not always give a positive system entropy change. (c) Explain spontaneous spreading of a gas through a sealed room in terms of arrangements and total entropy. [7]

Solutions

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

2.1 Positive: a gas is produced from solids, increasing dispersal/accessible arrangements.

2.2 $\Delta S = 2(150) - 200 = +100 \text{ J mol}^{-1} \text{ K}^{-1}$.

2.3 $\Delta S_{\text{surroundings}} = -18000/300 = -60.0 \text{ J mol}^{-1} \text{ K}^{-1}$. Total = $90.0 - 60.0 = +30.0 \text{ J mol}^{-1} \text{ K}^{-1}$.

3.1 At the boundary $0 = 120 - 36000/T$, so $T = 300 \text{ K}$. Above 300 K total entropy is positive. ΔH and system ΔS are treated as temperature-independent over the range.

3.2 The positive surroundings term $-\Delta H/T$ decreases as T rises, so it may cease to outweigh negative system entropy. Rate depends on activation energy/pathway rather than total entropy alone.

3.3 (a) Zero at 0 K for a perfect crystal; entropy increases on warming within a phase; it increases on melting and again on boiling as particles/energy have more accessible arrangements. (b) Released ions disperse through the solvent, but hydration can order surrounding water, so the net system change need not be positive. (c) Dispersal through the larger volume permits more molecular arrangements; the spontaneous direction increases total entropy of the gas and surroundings, without requiring molecules to disappear.