Class 11 Chemistry · Chapter 5: Thermodynamics

Answer key and marking scheme · 20 marks · about 40 minutes · based on NCERT

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1. An ideal gas expands isothermally from one bulb into a second, evacuated bulb when the stopcock between them is opened. Which of the following is not zero for this change? [1]

(a) q (b) w
(c) ΔS of the gas (d) ΔU

Answer: (c) Expansion into vacuum is free expansion: $p_{ex} = 0$, so w = 0; Joule found q = 0, so ΔU = q + w = 0. The expansion is spontaneous and irreversible, so $\Delta S_{total} > 0$; the surroundings receive no heat ($\Delta S_{surr} = 0$), so the whole increase is in the gas, which has spread into a larger volume: ΔS of the gas > 0.

2. Which of the following has a standard enthalpy of formation equal to zero at 298 K? [1]

(a) C(diamond) (b) S(rhombic)
(c) $Br_2(g)$ (d) $O_3(g)$

Answer: (b) $\Delta_f H^\ominus$ is zero only for an element in its reference state, its most stable form at 25 °C and 1 bar. For sulphur that is rhombic sulphur; C(diamond) is +1.89 and $Br_2(g)$ is +30.91 kJ mol^{-1} (bromine's reference state is the liquid), and oxygen's reference state is $O_2(g)$, not O_3.

3. A sealed glass ampoule containing a reaction mixture is dipped in a water bath at 60 °C. Taking the ampoule and its contents as the system, it is [1]

(a) an open system (b) a closed system
(c) an isolated system (d) an adiabatic system

Answer: (b) Glass conducts heat, so energy passes between the bath and the mixture, but the seal stops any matter leaving or entering: a closed system.

4. The entropy of which of the following approaches zero as the temperature approaches absolute zero? [1]

(a) a pure crystalline solid (b) a supercooled liquid
(c) a solution of two solids (d) any substance cooled to 0 K

Answer: (a) The third law is confined to pure crystalline solids, which are perfectly ordered at 0 K; the entropy of solutions and supercooled liquids is not zero at absolute zero.

5. A 200 g block of a metal absorbs 3.6 kJ of heat and its temperature rises by 20 K. The specific heat of the metal is [1]

(a) 1.11 J g^{-1} K^{-1} (b) 18 J g^{-1} K^{-1}
(c) 0.90 J g^{-1} K^{-1} (d) 9.0×10^{-4} J g^{-1} K^{-1}

Answer: (c) q = c × m × ΔT, so c = 3600 J / (200 g × 20 K) = 0.90 J g^{-1} K^{-1}.

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6. A reaction has positive ΔH and positive ΔS. Explain why it is non-spontaneous at low temperature but spontaneous at high temperature, and why such reactions are often carried out at high temperature. [2]

$\Delta G = \Delta H - T\Delta S$. At low T the positive ΔH outweighs $T\Delta S$ and $\Delta G > 0$. As T rises, $T\Delta S$ grows until it exceeds ΔH and $\Delta G < 0$. When ΔS is small, T must be large for $T\Delta S$ to outweigh ΔH, which is one reason reactions are run at high temperature.

- low T: $\Delta H > T\Delta S$, $\Delta G > 0$; high T: $T\Delta S > \Delta H$, $\Delta G < 0$ (1)
- small ΔS needs large T: hence high-temperature operation (1)

7. A cylinder holds 2 mol of nitrogen at 300 K. A partition divides it into two equal halves. For one half, state whether each of these changes from its value for the whole gas: (i) volume, (ii) temperature, (iii) molar volume, (iv) enthalpy. Give the reason in one line. [2]

(i) Volume halves and (iv) enthalpy halves: both are extensive and depend on the amount of matter. (ii) Temperature stays 300 K and (iii) molar volume V/n stays the same: they are intensive and do not depend on the amount.

- volume and enthalpy halve (extensive) (1)
- temperature and molar volume unchanged (intensive) (1)

8. For a solid X at a certain temperature, $\Delta_{sub}H^{\ominus} = 62.0$ kJ mol^{-1} and $\Delta_{fus}H^{\ominus} = 8.0$ kJ mol^{-1}. Find $\Delta_{vap}H^{\ominus}$ of liquid X at the same temperature, and name the property of enthalpy that makes this possible. [2]

Solid → gas directly and solid → liquid → gas start and end at the same states. Since H is a state function, $\Delta_{sub}H^{\ominus} = \Delta_{fus}H^{\ominus} + \Delta_{vap}H^{\ominus}$, so $\Delta_{vap}H^{\ominus} = 62.0 - 8.0 = 54.0$ kJ mol^{-1}.

- $\Delta_{vap}H^{\ominus} = 54.0$ kJ mol^{-1} (1)
- enthalpy is a state function (Hess's law): the two routes share their ends (1)

9. Classify each as an open, closed or isolated system, with a reason: (i) hot tea in a tightly closed thermos flask; (ii) a sealed steel can of juice cooling in a refrigerator; (iii) water boiling in an uncovered pan. Which of them also has an adiabatic boundary? [3]

(i) Isolated: the closed insulated flask allows neither matter nor energy to pass. (ii) Closed: no matter leaves the sealed can, but heat flows out through the conducting steel. (iii) Open: steam escapes and heat enters, so both matter and energy are exchanged. Only the thermos flask (i) has an adiabatic wall, allowing no heat exchange.

- (i) isolated, no exchange of matter or energy (1)
- (ii) closed, energy but no matter; (iii) open, both (1)
- thermos flask is adiabatic (1)

10. A reaction at 300 K and constant pressure has $\Delta_r H = +30.0$ kJ mol^{-1}, and the total entropy change of system and surroundings is -20 J K^{-1} mol^{-1}. (a) Find ΔS_{surr} and ΔS_{sys}. (b) Is the reaction spontaneous? (c) Find ΔG from $\Delta H - T\Delta S_{sys}$ and show that it equals $-T\Delta S_{total}$. [3]

(a) $\Delta S_{surr} = -\Delta_r H/T = -30000/300 = -100$ J K^{-1} mol^{-1}. $\Delta S_{sys} = \Delta S_{total} - \Delta S_{surr} = -20 - (-100) = +80$ J K^{-1} mol^{-1}. (b) $\Delta S_{total} < 0$: not spontaneous. (c) $\Delta G = \Delta H - T\Delta S_{sys} = 30.0 - 300 \times 0.080 = +6.0$ kJ mol^{-1}; $-T\Delta S_{total} = -300 \times (-0.020) = +6.0$ kJ mol^{-1}, the same, since $T\Delta S_{total} = T\Delta S_{sys} - \Delta H_{sys}$.

- $\Delta S_{surr} = -100$ J K^{-1} mol^{-1} and $\Delta S_{sys} = +80$ J K^{-1} mol^{-1} (1)
- $\Delta S_{total} < 0$, not spontaneous (1)
- $\Delta G = +6.0$ kJ mol^{-1} both ways (1)

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11. In a reversible isothermal expansion at 300 K, 1.00 mol of an ideal gas absorbs 3.46 kJ of heat. Find ΔU, w, and the factor by which the volume increased. ($R = 8.314\ J\ K^{-1}\ mol^{-1}$; $\ln 4 = 1.386$) [3]

Isothermal change of an ideal gas: $\Delta U = 0$, so $w = -q = -3.46$ kJ. For the reversible path $q = nRT \ln(V_f/V_i)$: $\ln(V_f/V_i) = 3460 / (1.00 \times 8.314 \times 300) = 3460/2494.2 = 1.387$, so $V_f/V_i = 4.0$. The volume increased four times.

- $\Delta U = 0$ for isothermal change of an ideal gas (1)
- $w = -3.46$ kJ (1)
- $\ln(V_f/V_i) = 1.387$, factor 4 (1)

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