07 Chemical Energetics II

Set B **Answer key**

A Multiple choice

4 MARKS

1 **C** Rusting of an iron bar to form iron(III) oxide. [1]

In the process of rusting, $O_2(g)$ reacts with solid iron to form solid iron oxide. Hence there is a decrease in the number of gaseous particles and ΔS is negative.

A Thermal decomposition of solid $CaCO_3$ forms $CO_2(g)$ and increases the number of gaseous particles. Hence ΔS is positive, as there are more ways that particles and the energy can be distributed in gases than in solids.

B Sublimation causes solid CO_2 to become gaseous CO_2. Hence ΔS is positive.

D The reaction between NaOH and ammonium chloride produces $NH_3(g)$. Hence ΔS is positive.

2 **A** $N_2O(g) \rightarrow N_2(g) + \frac{1}{2}O_2(g)$ $\Delta H = -82\ kJ\ mol^{-1}$ [1]

$\Delta G = \Delta H - T\Delta S$. For the reaction to be always spontaneous, ΔH needs to be negative (options C and D are incorrect as they have positive ΔH values) and ΔS needs to be positive.

ΔS is positive in option A because there is an increase in the number of moles of gas.

3 **C** ΔH +, ΔS +, ΔG − [1]

"Cold packs" indicates that the dissolution of NH_4NO_3 in water is an endothermic process, thus $\Delta H > 0$.

Ions in solution are more disordered than in the regular ionic lattice, thus $\Delta S > 0$.

Since the process occurs readily (spontaneously), $\Delta G < 0$.

4 **A** $-66\ J\ K^{-1}\ mol^{-1}$ [1]

When water freezes at 0 °C, the equilibrium $H_2O(l) \rightleftharpoons H_2O(s)$ exists. Hence $\Delta G = 0$.

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{-6.0 - 0}{273} = -0.0220\ kJ\ K^{-1}\ mol^{-1}$$

Amount of water = 54 ÷ 18 = 3 mol. Required entropy change = −0.0220 × 3 = −0.066 kJ K^{-1} mol^{-1} = −66 J K^{-1} mol^{-1}

B Structured questions

22 MARKS

5 (a) $2NO_2(g) \rightarrow N_2O_4(g)$. When $NO_2(g)$ is converted to $N_2O_4(g)$, entropy decreases because there is a decrease in the number of gaseous molecules (from 2 molecules of NO_2 to 1 molecule of N_2O_4). Hence there are fewer ways of arranging the particles, resulting in a decrease in disorder of the system. [1]

(b) $\Delta H^{\ominus} = \Sigma\Delta H_f^{\ominus}(\text{products}) - \Sigma\Delta H_f^{\ominus}(\text{reactants})$

$= [2(-393.5) + 0 + 4(-241.8)] - [(+48.9) + 2(-19.6)] = -1763.9 \text{ kJ mol}^{-1}$ [1]

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} = -1763.9 - [298(+1141.2 \times 10^{-3})]$ [1]

$= \mathbf{-2.10 \times 10^3 \text{ kJ mol}^{-1}}$ [1]

6 (a) The standard enthalpy change of hydration, $\Delta H_{hyd}^{\ominus}$, of an ion is the heat energy evolved when one mole of the free gaseous calcium ions is completely surrounded (hydrated) by water molecules at 298 K and 1 bar. [1]

(b) Energy cycle: $Ca(s) \rightarrow Ca^{2+}(aq) + 2e^-$ directly (+268), or $Ca(s) \rightarrow Ca(g)$ (+178), then $Ca(g) \rightarrow Ca^{2+}(g) + 2e^-$ (1st IE + 2nd IE = +1740), then $Ca^{2+}(g) \rightarrow Ca^{2+}(aq)$ (x). [1]

By Hess' Law, $\Delta H_r = +178 + 1740 + x = +268$

$x = \mathbf{-1650 \text{ kJ mol}^{-1}}$ [1]

(c) ΔS is negative as there is a decrease in the number of moles of gaseous particles when the calcium ion is hydrated, which results in a decrease in disorderliness. [1]

7 (a) $\Delta G = \Delta H - T\Delta S$. During melting and boiling, $\Delta G = 0$, so $\Delta S = \Delta H \div T$

$\Delta S_{melting} = +2.3 \times 1000 \div 234 = \mathbf{+9.83 \text{ J mol}^{-1} \text{ K}^{-1}}$ [1]

(b) $\Delta S_{vap} = +59 \times 1000 \div 630 = \mathbf{+93.7 \text{ J mol}^{-1} \text{ K}^{-1}}$ [1]

8 (a) $\Delta S^{\ominus} > 0$. This endothermic reaction is thermodynamically feasible when $T > \Delta H \div \Delta S$. [1]

(b) $\Delta S^{\ominus} < 0$. This exothermic reaction is thermodynamically feasible when $T < \Delta H \div \Delta S$. [1]

(c) $\Delta S^{\ominus} > 0$. The reaction is feasible ($\Delta G < 0$ for all temperatures). [1]

(d) $\Delta S^{\ominus} < 0$. The reaction is not feasible ($\Delta G > 0$ for all temperatures). [1]

9 (a) Sum of $\Delta G_f^{\ominus}$ of reactants = $-1012 \text{ kJ mol}^{-1}$. Sum of $\Delta G_f^{\ominus}$ of products = $-569 + (-394) = -963 \text{ kJ mol}^{-1}$

So the free energy change, $\Delta G^{\ominus} = -963 - (-1012) = \mathbf{+49 \text{ kJ mol}^{-1}}$ [1]

The reaction will not take place spontaneously because $\Delta G^{\ominus} > 0$. [1]

(b)

For the reaction to be spontaneous, $\Delta G = \Delta H - T\Delta S = 101 - T(0.159) < 0$, so $101 < T(0.159)$

A temperature above **635 K** (362 °C) is needed for the reaction to take place. [1] [1]

NOTE Here, we assume that ΔH and ΔS do not change with temperature.

10 **(a)**

$2NI_3(s) \rightarrow N_2(g) + 3I_2(g) \quad \Delta H < 0, \Delta S > 0$ [1]

As 4 moles of gases are produced, there is a very large increase in the entropy of the system. This reaction is also exothermic (formation of the N≡N bond). Hence, highly explosive. [1]

(b)

$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq) \quad \Delta H > 0, \Delta S > 0$ [1]

Aqueous ions are formed from ions held fixed in an orderly crystalline lattice, resulting in a large increase in the entropy of the system. Even though the reaction is endothermic, the increase in entropy compensates for the endothermic ΔH, so that $\Delta G = \Delta H - T\Delta S < 0$ even under standard conditions, and NH_4NO_3 dissolves readily. [1]