07 Chemical Energetics II

Set A **Answer key**

A From the lesson

7 MARKS

1

$\Delta H_{sol} = +711 + (-322) + (-381) =$ **$+8$ kJ mol^{-1}** [1]

2

Mg^{2+}. Mg^{2+} has a higher charge and a smaller ionic radius than Na^+, so it has a higher charge density. [1]

Hence, Mg^{2+} forms stronger ion–dipole interactions with water molecules. [1]

3

$\Delta G = -92 - 298(-0.199) = -92 + 59.3 = -32.7$ kJ mol^{-1} [1]

Since ΔG is negative, the reaction is **spontaneous** at 298 K. [1]

4

At 298 K, $\Delta G = 130 - 298(0.335) = +30.2$ kJ mol^{-1}, not spontaneous [1]

$T > \dfrac{130}{0.335} =$ **388 K** [1]

NOTE Likewise $MgCO_3$ decomposes above 576 K but $BaCO_3$ only above 1566 K: $\Delta H(MgCO_3)$ is less positive, ΔS similar.

B Practice

27 MARKS

5

A It is spontaneous only at low temperature. [1]

$\Delta S < 0$ due to a decrease in the number of moles of gas (4 mol to 2 mol). Hence $-T\Delta S > 0$.

Since $\Delta H < 0$ and $\Delta G = \Delta H - T\Delta S$, $\Delta G < 0$ when $|-T\Delta S| < |\Delta H|$. Hence the reaction is spontaneous only at low temperature.

6

D $+436$ J K^{-1} [1]

Amount of $H_2O = \dfrac{72}{18.0} = 4$ mol

At the boiling point, $\Delta G = 0$, and $\Delta G = \Delta H - T\Delta S$

$0 = (40.7 \times 10^3 \times 4) - (100 + 273)\Delta S$

$\Delta S = +436$ J K^{-1}

7 **(a)**

Energy cycle: $MgCl_2(s) + aq \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$ (ΔH_{sol}), with both sides formed from $Mg(s) + Cl_2(g)$: -641 for $MgCl_2(s)$, and $\Delta H_f = -467 + 2(-167)$ for the ions. [1]

By Hess' Law, $\Delta H_{sol} = 641 + (-467) + 2(-167) =$ **-160 kJ mol^{-1}** [1]

(b) Since ΔH_{sol} is highly exothermic, $MgCl_2$ is very soluble in water. [1]

NOTE The magnitude of ΔS is often much smaller than that of ΔH. For most reactions, ΔS is less than 100 J K^{-1} mol^{-1}. Hence when ΔH is very negative, ΔG is likely to be negative and the reaction is spontaneous.

8 **(a)** Entropy is a measure of the randomness or disorder in a system, reflected in the number of ways that the energy of a system can be distributed through the motion of its particles. [1]

(b)(i) Entropy of the system increases due to mixing of gases. The volume available for each gas increases (to keep total pressure constant), hence there are more ways in which the gas particles and their energies can be distributed. [1]

(ii) Entropy of the system increases, as an increase in temperature causes the average kinetic energy of the gas particles to increase and the range of energies to increase. This leads to the broadening of the Maxwell–Boltzmann energy distribution, and hence there are more ways in which the energy can be distributed among the gas particles. [1]

(iii) Entropy of the system decreases. The number of gas particles decreases, since there is one gaseous reactant and no gaseous product. Hence the number of ways that the particles and the energy can be distributed decreases. [1]

(iv) Entropy of the system increases, as there is an increase in the number of gas particles, and thus the system becomes more disordered and there are more ways in which the particles and energy can be distributed. [1]

9 **(a)** $\Delta H_{soln}[LiCl(s)] = -\text{lattice energy} + \Delta H_{hyd}[Li^+(g)] + \Delta H_{hyd}[Cl^-(g)]$

$= +843 + (-883) =$ **-40 kJ mol^{-1}** [1]

(b) Heat absorbed $= mc\Delta T = 50.0 \times 4.20 \times 3.3 = 693$ J [1]

$\Delta H_{soln}[KCl(s)] = +693 \div \frac{3.00}{74.6} =$ **$+17.2$ kJ mol^{-1}** (3 s.f.) [1]

(c) Since |LE| is inversely proportional to the interionic distance, the lattice energy of LiCl is slightly more exothermic than that of KCl. [1]

However, since hydration energy is proportional to charge density, Li^+ will have a much more exothermic hydration enthalpy than K^+. Therefore, the enthalpy change of solution of LiCl is more exothermic than that of potassium chloride. [1]

10 **(a)** $\Delta G_{decomposition} = \Delta H_{decomposition} - T\Delta S$

$= -1423 - [298 \times (+208 \div 1000)] = -1485$ kJ mol^{-1} [1]

Since ΔG is negative, the reaction is spontaneous at 298 K. [1]

(b)

The spontaneity is not affected by changes in temperature because $\Delta H_{decomposition}$ is negative, T is always positive and ΔS is positive (*or* $-T\Delta S$ is always negative), i.e. $\Delta G = \Delta H - T\Delta S$ = negative − [(positive) × (positive)] = negative.

Yes, the decomposition of nitroglycerin is spontaneous at all temperatures. **[1]**

11 **(a)**

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$. $\Delta G^{\ominus}$ (+172.6 kJ mol^{-1}) is positive at 298 K, hence reaction I is not spontaneous at room temperature. **[1]**

The high temperature in the car engine causes $T\Delta S^{\ominus}$ to become more positive (*or* $-T\Delta S^{\ominus}$ to become more negative). This leads to a more negative $\Delta G^{\ominus}$, and hence reaction I becomes spontaneous. **[1]**

(b)

The amount of gases decreases from 3 mol to 2 mol, hence there are fewer ways to arrange the gaseous particles and their energy in the system. **[1]**

$\Delta S^{\ominus}$ is **negative**. **[1]**

12 **(a)**

Since $\Delta H_{hyd} \propto \frac{q}{r}$, and Mg^{2+} has a higher charge and smaller ionic size than Na^{+}, the hydration energy of Mg^{2+} is more exothermic than that of Na^{+}. **[1]**

(b)

ΔH_{soln} = −(lattice energy) + ΔH_{hyd}

For NaOH: −44 = 896 + (−390) + $\Delta H_{hyd}(OH^{-})$, so $\Delta H_{hyd}(OH^{-})$ = −550 kJ mol^{-1} **[1]**

For $Mg(OH)_2$: x = 2995 − 1890 + 2(−550) = **+5.00 kJ mol^{-1}** **[1]**

(c)

There is a decrease in disorderliness as H_2O molecules are attached to the metal ion and lose their degree of freedom. As more water molecules are attached to the Mg^{2+} ion on average, the entropy of the system decreases more (ΔS is more negative) than for NaOH. **[1]**

(d)

$Mg(OH)_2$ dissolves with the formation of more mobile particles (aqueous ions), so there are more ways in which the particles and energy can be distributed, which may cause entropy to increase (ΔS is positive). **[1]**