III. Long Answer Type Questions

Question 1. (a) What is a spontaneous process? Mention the conditions for a reaction to be spontaneous at constant temperature and pressure.
(b) Discuss the effect of temperature on the spontaneity of an exothermic reaction.
Answer:
(a) A process is said to be spontaneous if it takes place by itself by own or under some condition.
ΔG gives a criteria for spontaneity at constant temperature and pressure.
(b) If the temperature is so high that $T\Delta S > \Delta H$ in magnitude, ΔG will be positive and the process will be non-spontaneous.
If the temperature is made low so that $T\Delta S < \Delta H$ in magnitude, ΔG will be negative and the process will be spontaneous.

Question 2. Predict in which of the following, entropy increases/decreases.
(i) A liquid crystallizes into a solid
(ii) Temperature of a crystallize solid is raised from 0K to 115 K
(iii) $2NaHCO_3 (s) \rightarrow Na_2 CO_3 (s) + CO_2 (g) + H_2O (g)$
(iv) $H_2(g) \rightarrow 2H(g)$
Answer:
(i) After freezing, the molecules attain an ordered state and therefore, entropy decreases.
(ii) At 0 K the constituent particles are in static form therefore, entropy is minimum. If the temperature is raised to 115 K particles begin to move and entropy increases.
(iii) Reactant, $NaHCO_3$ is solid. Thus, its entropy is less in comparison to product which has high entropy.
(iv) Here, one molecule gives two atoms. Thus, number of particles increases and this leads to more disordered form.

Question 3. Why standard entropy of an elementary substance is not zero whereas standard enthalpy of formation is taken as zero? Under what conditions will the reaction occur, if
(i) both ΔH and ΔS are positive
(ii) both ΔH and ΔS are negative
Answer:
(a) A substance has perfectly ordered arrangement of its constituent particles only at absolute zero. When the element formed from itself, this means no heat change.
Thus, $\Delta_f H = 0$
(i) If both ΔH and ΔS are positive ΔG can be - ve only if $T\Delta S > \Delta H$ in magnitude. Thus, the temperature should be high.
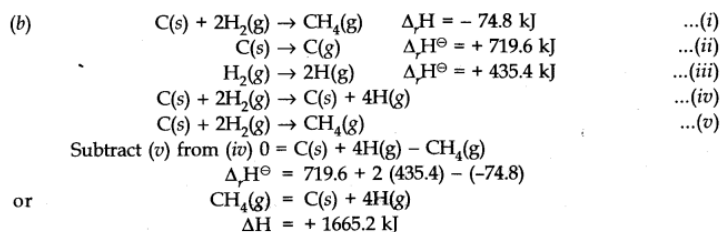(ii) If both ΔH and ΔS are negative ΔG can be negative only if $T\Delta S < \Delta H$ in magnitude. Thus, the value of T should be low.

Question 4. (a) What is bond energy? Why is it called enthalpy of atomisation?
(b) Calculate the bond energy of C-H bond, given that the heat of formation of CH_4, heat of sublimation of carbon and heat of dissociation of H_2 are - 74.8, + 719.6, 435.4 kj mol[1] respectively.
Answer:

(a) Bond energy is the amount of energy required to dissociate one mole of bonds present between the atoms in the gaseous phase. As the molecules dissociate completely into atoms in the gaseous phase therefore bond energy of a diatomic molecule is called enthalpy of atomisation.

(b)

$$C(s) + 2H_2(g) \rightarrow CH_4(g) \qquad \Delta_r H = -74.8 \text{ kJ} \qquad ...(i)$$
$$C(s) \rightarrow C(g) \qquad \Delta_r H^\ominus = +719.6 \text{ kJ} \qquad ...(ii)$$
$$H_2(g) \rightarrow 2H(g) \qquad \Delta_r H^\ominus = +435.4 \text{ kJ} \qquad ...(iii)$$
$$C(s) + 2H_2(g) \rightarrow C(s) + 4H(g) \qquad ...(iv)$$
$$C(s) + 2H_2(g) \rightarrow CH_4(g) \qquad ...(v)$$

Subtract (v) from (iv) $0 = C(s) + 4H(g) - CH_4(g)$

$$\Delta_r H^\ominus = 719.6 + 2(435.4) - (-74.8)$$

or

$$CH_4(g) = C(s) + 4H(g)$$
$$\Delta H = +1665.2 \text{ kJ}$$

This gives the enthalpy of dissociation of four moles of C—H bonds (called enthalpy of atomisation)

Hence bond energy for C—H bond $= \dfrac{1665.2}{4} = 416.3 \text{ kJ mol}^{-1}$

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