

CH6 – THERMODYNAMICS

Question 1. Choose the correct answer:

A thermodynamic state function is a quantity

- (i) used to determine heat changes
- (ii) whose value is independent of path
- (iii) used to determine pressure volume work
- (iv) whose value depends on temperature only.

Answer: (ii) whose value is independent of path

Question 2. For the process to occur under adiabatic conditions, the correct condition is:

- (i)  $\Delta T = 0$  (ii)  $\Delta p = 0$
- (iii)  $q = 0$  (iv)  $w = 0$

Ans. (iii)  $q = 0$

Question 3. The enthalpies of all elements in their standard states are : ‘

- (i) unity (ii) zero
- (iii)  $< 0$  (iv) different for each element

Answer: (ii) zero

Question 4.

$\Delta U^\ominus$  of combustion of methane is  $-X \text{ kJ mol}^{-1}$ . The value of  $\Delta H^\ominus$  is

- (i)  $= \Delta U^\ominus$  (ii)  $> \Delta U^\ominus$
- (iii)  $< \Delta U^\ominus$  (iv) 0

Answer:

The balanced chemical equation for the combustion reaction is :



$$\Delta_{ng} = 1 - 3 = -2$$

$$\Delta H^\ominus = \Delta U^\ominus + \Delta_{ng} RT = \Delta U^\ominus - 2RT$$

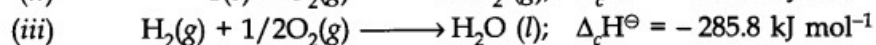
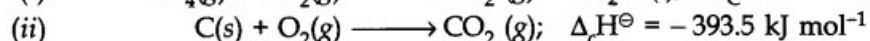
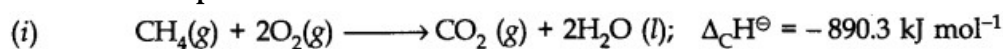
$\therefore \Delta H^\ominus < \Delta U^\ominus$  or (iii) is the correct answer.

Question 5. The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are  $-890.3 \text{ kJ mol}^{-1}$ ,  $-393.5 \text{ kJ mol}^{-1}$  and  $-285.8 \text{ kJ mol}^{-1}$  respectively. Enthalpy of formation of  $\text{CH}_4(\text{g})$  will be

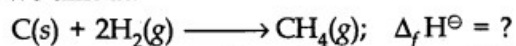
- (i)  $-74.8 \text{ kJ mol}^{-1}$  (ii)  $-52.27 \text{ kJ mol}^{-1}$

(iii) + 74.8 KJ mol<sup>-1</sup> (iv) + 52.26 KJ mol<sup>-1</sup>

Answer: As per the available data :



The equation we aim at:



Eqn. (ii) + 2 × Eqn. (iii) – Eqn. (i) and the correct  $\Delta_f H^\ominus$  value is:

$$= (-393.5) + 2 \times (-285.8) - (-890.3) = -74.8 \text{ kJ mol}^{-1}$$

∴ (i) is the correct answer.

Question 6. A reaction,  $\text{A} + \text{B} \longrightarrow \text{C} + \text{D} + q$  is found to have a positive entropy change. The reaction will be

(i) possible at high temperature (ii) possible only at low temperature

(iii) not possible at any temperature (iv) possible at any temperature

Answer: (iv) possible at any temperature

Question 7. In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

Answer: Heat absorbed by the system,  $q = 701 \text{ J}$  Work done by the system = - 394 J Change in internal energy ( $\Delta U$ ) =  $q + w = 701 - 394 = 307 \text{ J}$ .

Question 8. The reaction of cyanamide,  $\text{NH}_2\text{CN}(\text{s})$  with dioxygen was carried out in a bomb calorimeter and  $\Delta U$  was found to be  $-742.7 \text{ kJ mol}^{-1}$  at 298 K. Calculate the enthalpy change for the reaction at 298 K.  $\text{NH}_2\text{CN}(\text{s}) + 3/2\text{O}_2(\text{g}) \longrightarrow \text{N}_2(\text{g}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

Answer:  $\Delta U = -742.7 \text{ kJ mol}^{-1}$ ;  $\Delta n_g = 2 - 3/2 = +1/2 \text{ mol}$ .

$R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$ ;  $T = 298 \text{ K}$

According to the relation,  $\Delta H = \Delta U + \Delta n_g RT$

$\Delta H = (-742.7 \text{ kJ}) + (1/2 \text{ mol}) \times (8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})$

$= -742.7 \text{ kJ} + 1.239 \text{ kJ} = -741.5 \text{ kJ}$ .

Question 9. Calculate the number of kJ of heat necessary to raise the temperature of 60 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is  $24 \text{ J mol}^{-1} \text{ K}^{-1}$ .

Answer: No. of moles of Al ( $m$ ) =  $(60\text{g}) / (27 \text{ g mol}^{-1}) = 2.22 \text{ mol}$

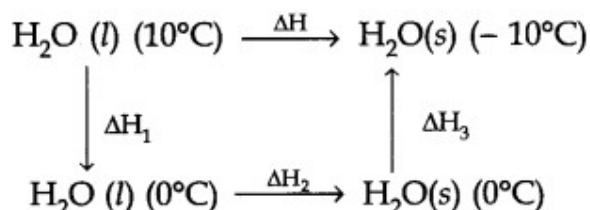
Molar heat capacity ( $C$ ) =  $24 \text{ J mol}^{-1} \text{ K}^{-1}$ .

Rise in temperature ( $\Delta T$ ) =  $55 - 35 = 20^\circ\text{C} = 20\text{ K}$

Heat evolved ( $q$ ) =  $C \times m \times T = (24\text{ J mol}^{-1}\text{ K}^{-1}) \times (2.22\text{ mol}) \times (20\text{ K})$   
 $= 1065.6\text{ J} = 1.067\text{ kJ}$

**Question 10.** Calculate the enthalpy change on freezing of 1.0 mol of water at  $10.0^\circ\text{C}$  to ice at  $-10.0^\circ\text{C}$ .  $\Delta H = 6.03\text{ kJ mol}^{-1}$  at  $0^\circ\text{C}$ .  $C_p [\text{H}_2\text{O}(l)] = 75.3\text{ J mol}^{-1}\text{ K}^{-1}$ ;  $C_p [\text{H}_2\text{O}(s)] = 36.8\text{ J mol}^{-1}\text{ K}^{-1}$ .

**Answer:** The change may be represented as:



According to Hess's Law;

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\Delta H_1 = 75.3\text{ J mol}^{-1}\text{ K}^{-1} (10\text{ K}) = 753\text{ J mol}^{-1}$$

$$\Delta H_2 (\text{solidification}) = -6.03\text{ kJ mol}^{-1} = -6030\text{ J mol}^{-1}$$

(sign changed)

$$\Delta H_3 = 36.8\text{ J mol}^{-1}\text{ K}^{-1} (-10\text{ K}) = -368\text{ J mol}^{-1}$$

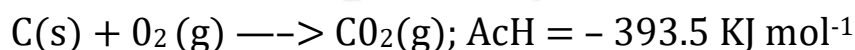
$$\Delta H = (753 - 6030 - 368)\text{ J mol}^{-1} = -5645\text{ J mol}^{-1}$$

$\therefore$

$$= -5.645\text{ kJ mol}^{-1}$$

**Question 11.** Enthalpy of combustion of carbon to carbon dioxide is  $-393.5\text{ J mol}^{-1}$ . Calculate the heat released upon formation of 35.2 g of  $\text{CO}_2$  from carbon and oxygen gas.

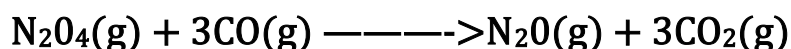
**Answer:** The combustion equation is:



Heat released in the formation of 44g of  $\text{CO}_2 = 393.5\text{ kJ}$

Heat released in the formation of 35.2 g of  $\text{CO}_2 = (393.5\text{ kJ}) \times (35.2\text{ g}) / (44\text{ g})$   
 $= 314.8\text{ kJ}$

**Question 12.** Calculate the enthalpy of the reaction:



Given that;  $\Delta_f H^\circ \text{CO}(g) = -110\text{ kJ mol}^{-1}$ ;  $\Delta_f H^\circ \text{CO}_2(g) = -393\text{ kJ mol}^{-1}$

$\Delta_f H^\circ \text{N}_2\text{O}(g) = 81\text{ kJ mol}^{-1}$ ;  $\Delta_f H^\circ \text{N}_2\text{O}_4(g) = 9.7\text{ kJ mol}^{-1}$

**Answer:** Enthalpy of reaction ( $\Delta_r H$ ) =  $[81 + 3(-393)] - [9.7 + 3(-110)]$   
 $= [81 - 1179] - [9.7 - 330] = -778\text{ kJ mol}^{-1}$

Question 13. Given :  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g}); \Delta_r H^\circ = -92.4 \text{ kJ mol}^{-1}$  What is the standard enthalpy of formation of  $\text{NH}_3$  gas?

Answer:  $\Delta_f H^\circ \text{NH}_3(\text{g}) = -(92.4)/2 = -46.2 \text{ kJ mol}^{-1}$

Question 14. Calculate the standard enthalpy of formation of  $\text{CH}_3\text{OH}$ . from the following data:

(i)  $\text{CH}_3\text{OH}(\text{l}) + 3/2 \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}); \Delta_r H^\circ = -726 \text{ kJ mol}^{-1}$

(ii)  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}); \Delta_c H^\circ = -393 \text{ kJ mol}^{-1}$

(iii)  $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l}); \Delta_f H^\circ = -286 \text{ kJ mol}^{-1}$

Answer: The equation we aim at;

$\text{C}(\text{s}) + 2\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{CH}_3\text{OH}(\text{l}); \Delta_f H^\circ = \pm? \dots \text{(iv)}$

Multiply eqn. (iii) by 2 and add to eqn. (ii)

$\text{C}(\text{s}) + 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

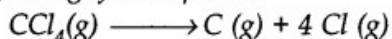
$\Delta H = -(393 + 522) = -915 \text{ kJ mol}^{-1}$  Subtract eqn. (iv) from eqn. (i)

$\text{CH}_3\text{OH}(\text{l}) + 3/2 \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}); \Delta H = -726 \text{ kJ mol}^{-1}$

Subtract:  $\text{C}(\text{s}) + 2\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{CH}_3\text{OH}(\text{l}); \Delta_f H^\circ = -239 \text{ kJ mol}^{-1}$

Question 15.

Calculate the enthalpy change for the process



and calculate bond enthalpy of C-Cl in  $\text{CCl}_4(\text{g})$

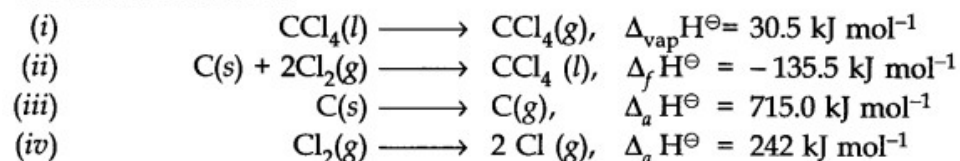
Given:  $\Delta_{\text{vap}} H^\circ(\text{CCl}_4) = 30.5 \text{ kJ mol}^{-1}; \Delta_f H^\circ(\text{CCl}_4) = -135.5 \text{ kJ mol}^{-1}$

$\Delta_a H^\circ(\text{C}) = 715.0 \text{ kJ mol}^{-1}$  where  $\Delta_a H^\circ$  is enthalpy of atomisation

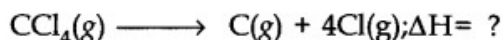
$\Delta_a H^\circ(\text{Cl}_2) = 242 \text{ kJ mol}^{-1}$ .

**Answer:**

The available data is:



The equation we aim at is:



Eqn. (iii) + 2 × Eqn. (iv) – Eqn. (i) – Eqn. (ii) gives the required equation with

$$\begin{aligned}
 \Delta H &= 715.0 + 2(242) - 30.5 - (-135.5) \text{ kJ mol}^{-1} \\
 &= 1304 \text{ kJ mol}^{-1}
 \end{aligned}$$

Bond enthalpy of C–Cl in  $\text{CCl}_4$  (average value) =  $\frac{1304}{4} = 326 \text{ kJ mol}^{-1}$ .

**Question 16.** For an isolated system  $\Delta U = 0$ ; what will be  $\Delta S$ ?

**Answer:** Change in internal energy ( $\Delta U$ ) for an isolated system is zero for it does not exchange any energy with the surroundings. But entropy tends to increase in case of spontaneous reaction. Therefore,  $\Delta S > 0$  or positive.

**Question 17.** For a reaction at 298 K



$\Delta H = 400 \text{ kJ mol}^{-1}$  and  $\Delta S = 0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}$ .

At what temperature will the reaction become spontaneous considering  $\Delta H$  and  $\Delta S$  to be constant over the temperature range?

**Answer:** As per the Gibbs Helmholtz equation:

$$\Delta G = \Delta H - T\Delta S \text{ For } \Delta G = 0; \Delta H = T\Delta S \text{ or } T = \Delta H / \Delta S$$

$$T = (400 \text{ kJ mol}^{-1}) / (0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}) = 2000 \text{ K}$$

Thus, reaction will be in a state of equilibrium at 2000 K and will be spontaneous above this temperature.

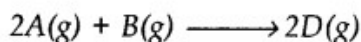
**Question 18.** For the reaction;  $2\text{Cl}(g) \longrightarrow \text{Cl}_2(g)$ ; what will be the signs of  $\Delta H$  and  $\Delta S$ ?

**Answer:**  $\Delta H$  : negative (-ve) because energy is released in bond formation

$\Delta S$  : negative (-ve) because entropy decreases when atoms combine to form molecules.

## Question 19.

For the reaction



$$\Delta U^\ominus = -10.5 \text{ kJ and } \Delta S^\ominus = -44.1 \text{ J K}^{-1}$$

Calculate  $\Delta G^\ominus$  for the reaction, and predict whether the reaction may occur spontaneously.

Answer:

$$\Delta H^\ominus = \Delta U^\ominus + \Delta n_g RT$$

$$\Delta U^\ominus = -10.5 \text{ kJ}; \quad \Delta n_g = 2 - 3 = -1 \text{ mol}$$

$$R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}; \quad T = 298 \text{ K}$$

$$\begin{aligned} \therefore \Delta H^\ominus &= (-10.5 \text{ kJ}) + [(-1 \text{ mol}) \times (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})] \\ &= -10.5 \text{ kJ} - 2.478 \text{ kJ} = -12.978 \text{ kJ} \end{aligned}$$

According to Gibbs Helmholtz equation:

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

$$\Delta G^\ominus = (-12.978 \text{ kJ}) - (298 \text{ K}) \times (-0.0441 \text{ kJ K}^{-1})$$

$$= -12.978 + 13.112 = -12.978 + 13.142 = 0.164 \text{ kJ}$$

Since  $\Delta G^\ominus$  is positive, the reaction is non-spontaneous in nature.

## Question 20.

The equilibrium constant for the reaction is 10. Calculate the value of  $\Delta G^\ominus$ ; Given

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}; \quad T = 300 \text{ K}.$$

Answer:

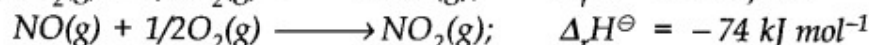
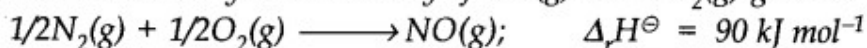
$$\Delta G^\ominus = -RT \ln K = -2.303 RT \log K.$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}; \quad T = 300 \text{ K}; \quad K = 10$$

$$\begin{aligned} \Delta G^\ominus &= -2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (300 \text{ K}) \times \log 10 \\ &= -5527 \text{ J mol}^{-1} = -5.527 \text{ kJ mol}^{-1}. \end{aligned}$$

## Question 21.

Comment on the thermodynamic stability of  $\text{NO}(g)$  and  $\text{NO}_2(g)$  given: :



Answer:

For  $\text{NO}(g)$ ;  $\Delta_f H^\ominus = +ve$  : Unstable in nature

For  $\text{NO}_2(g)$ ;  $\Delta_f H^\ominus = -ve$  : Stable in nature

## Question 22.

Calculate the entropy change in surroundings when 1.0 mol of  $\text{H}_2\text{O}(l)$  is formed under standard conditions. Given  $\Delta H^\ominus = -286 \text{ kJ mol}^{-1}$ .

Answer:

$$q_{\text{rev}} = (-\Delta_f H^\ominus) = -286 \text{ kJ mol}^{-1} = 286000 \text{ J mol}^{-1}$$

$$\Delta S_{(\text{Surroundings})} = \frac{q_{\text{rev}}}{T} = \frac{(286000 \text{ J mol}^{-1})}{298 \text{ K}} = 959 \text{ J K}^{-1} \text{ mol}^{-1}.$$

### MORE QUESTIONS SOLVED

NCERT Solutions for Class 11 Chemistry Chapter 6 Very Short Answer Type Questions

Question 1. If  $\Delta U = 0$  how are  $q$  and  $w$  related to each other?

Answer:  $\Delta U = q + w$

Question 2. When is bond energy equal to bond dissociation energy ?

Answer: For diatomic molecules e.g.  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{Cl}_2$  etc. both energies are equal.

Question 3. What is the enthalpy of formation of the most stable form of an element in its standard state?

Answer: It is zero.

Question 4. Out of diamond and graphite, which has greater entropy?

Answer: Graphite has greater entropy since it is loosely packed.

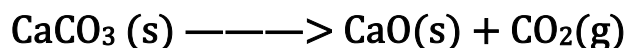
Question 5. At what temperature entropy of a substance is zero?

Answer: At absolute zero.

Question 6. From thermodynamic point of view, to which system the animals and plants belong?

Answer: Open system.

Question 7. Predict the sign of  $\Delta S$  for the following reaction heat



Answer:  $\Delta S$  is positive.

Question 8. State Hess's law.

Answer: The change of enthalpy of a reaction remains same whether the reaction is carried out in one step or several steps.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 \dots \dots \dots$$

Question 9. What is the enthalpy change for an adiabatic process?

Answer: For an adiabatic process,  $\Delta H = 0$

Question 10. What do you mean by entropy?

Answer: Entropy is a measure of randomness of a system.

**Question 11.** Give a relation between entropy change and heat absorbed or evolved for a reversible reaction occurring at temperature T.

**Answer:**  $\Delta S = q_{\text{rev}}/T$

**Question 12.** What is the condition for spontaneity in terms of free energy change?

**Answer:** If  $\Delta G$  is negative, process is spontaneous.

If  $\Delta G$  is positive, the process is non-spontaneous.

If  $\Delta G = 0$ , the process is in equilibrium.

**Question 13.** What is an adiabatic process?

**Answer:** The process in which no exchange of heat takes place between the system and the surroundings.

**Question 14.** What is free energy in terms of thermodynamics?

**Answer:** Free energy of a system is the capacity to do work.

$$G = H - T\Delta S$$

**Question 15.** Define extensive properties.

**Answer:** Properties which depend upon the amount of the substance are called as extensive properties.

**Question 16.** How are internal energy change, free energy change and entropy change are related to one another?

**Answer:**  $\Delta G = \Delta H - T\Delta S$  (At constant pressure)

**Question 17.** How is entropy of a substance related to temperature?

**Answer:** On increasing temperature, entropy of a substance increases.

**Question 18.** Define intensive properties.

**Answer:** Properties which depend on the nature of the substance and not on the amount of the substance are called intensive properties.

**Question 19.** What is Gibbs Helmholtz equation?

**Answer:**  $\Delta G = \Delta H - T\Delta S$

Where  $\Delta G$  = free energy change.

$\Delta H$  = enthalpy change.

$\Delta S$  = entropy change.

**Question 20.** What are the units of entropy?

**Answer:** SI unit of  $\Delta S = \text{JK}^{-1}\text{mol}^{-1}$ .

**Question 21.** What is a spontaneous change? Give one example.

**Answer:** A process which can take place of its own or initiate under some condition.

For example: Common salt dissolves in water of its own.

NCERT Solutions for Class 11 Chemistry Chapter 6 Short Answer Type Questions

**Question 1.** When liquid benzene is oxidised at constant pressure at 300 K, the change in enthalpy is -3728 kJ. What is the change in internal energy at the same temperature?

**Answer:** The chemical equation representing the oxidation of liquid benzene is :



$$\Delta H = -3728 \text{ kJ}; \quad \Delta n_g = 6 - \frac{15}{2} = -\frac{3}{2} \text{ mol}$$

$$R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}, \quad T = 300 \text{ K}$$

According to the relation,  $\Delta H = \Delta U + \Delta n_g RT$

$$(-3728 \text{ kJ}) = \Delta U + \left(-\frac{3}{2} \text{ mol}\right)$$

$$\times (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})$$

$$(-3728 \text{ kJ}) = \Delta U - 3.7413 \text{ kJ}$$

$$\Delta U = -3728 + 3.7413 = -3724.2587 \text{ kJ}$$

**Question 2.** The enthalpy of formation of methane at constant pressure and 300 K is -78.84 kJ. What will be the enthalpy of formation at constant volume?

**Answer:** The equation representing the enthalpy of formation of methane is:



$$\Delta H = -78.84 \text{ kJ}; \quad \Delta n_g = 1 - 2 = -1 \text{ mol}$$

$$R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}; \quad T = 300 \text{ K}$$

According to the relation,  $\Delta H = \Delta U + \Delta n_g RT$

$$\Delta U = \Delta H - \Delta n_g RT$$

$$= (-78.84 \text{ kJ}) - (1 \text{ mol})$$

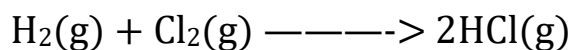
$$\times (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times 300 \text{ K}$$

$$= -78.84 - 2.49 = -81.35 \text{ kJ}$$

**Question 3.** Calculate the enthalpy change for the reaction:  $\text{H}_2(g) + \text{Cl}_2(g) \longrightarrow 2\text{HCl}(g)$ . Given that bond energies of H-H, Cl-Cl and H-Cl bonds

are 433, 244 and 431 kJ mol<sup>-1</sup> respectively.

**Answer:** The chemical equation for the reaction is:



The enthalpy of reaction is:

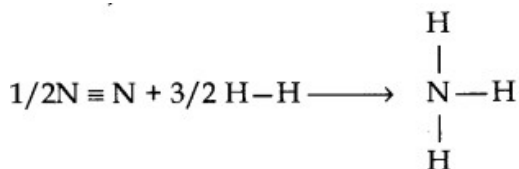
$$\Delta_r H = \sum \text{B.E. of reactants} - \sum \text{B.E. of products} = [\text{B.E. of H-H bond} + \text{B.E. of Cl-Cl bond}]$$

$$- [2 \times \text{B.E. of H-Cl bond}]$$

$$= (433 + 244) - (2 \times 431) = 433 + 244 - 862 = -185 \text{ kJ}$$

**Question 4.** The bond enthalpy of H<sub>2</sub>(g) is 436 kJ mol<sup>-1</sup> and that of N<sub>2</sub> (g) is 941.3 kJ mol<sup>-1</sup>. Calculate the average bond enthalpy of an N-H bond in ammonia. Given:  $\Delta_f H^\ominus (\text{NH}_3) = -46 \text{ kJ mol}^{-1}$

**Answer:**



$$\begin{aligned} \Delta_f H^\ominus (\text{NH}_3) &= \text{BE of reactants} - \text{BE of products} \\ &= [1/2 \text{BE of the N} \equiv \text{N bond} + 3/2 \text{BE of H-H bond}] \\ &\quad - [3 \text{BE of N-H bond}] \end{aligned}$$

$$[-46 \text{ kJ mol}^{-1}] = (1/2 \times 941.3 \text{ kJ mol}^{-1} + 3/2 \times 436 \text{ kJ mol}^{-1}) - (3 \text{BE of N-H bond})$$

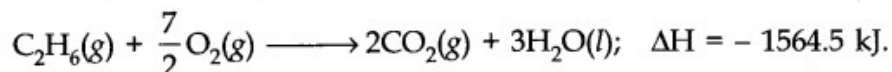
$$\text{BE of N-H bond} = 1/3 (470.65 + 654.0 + 46) = 390.2 \text{ kJ mol}^{-1}.$$

**Question 5.** When two moles of C<sub>2</sub>H<sub>6</sub>(g) are burnt, 3129 kJ of heat is liberated. Calculate the heat of formation of C<sub>2</sub>H<sub>6</sub>(g).  $\Delta_f H$  for CO<sub>2</sub>(g) and H<sub>2</sub>O(l) are -393.5 and -286 kJ mol<sup>-1</sup> respectively.

**Answer:**

The heat of combustion of  $C_2H_6(g)$  per mole ( $\Delta H$ ) =  $\frac{-3129}{2} = -1564.5 \text{ kJ}$ .

The combustion equation may be written as :



Now,

$$\begin{aligned} \Delta H &= \sum \Delta_f H^\ominus (\text{products}) - \sum \Delta_f H^\ominus (\text{reactants}) \\ &= [2\Delta_f H^\ominus CO_2(g) + 3\Delta_f H^\ominus H_2O(l)] \\ &\quad - \left[ \Delta_f H^\ominus C_2H_6(g) + \frac{7}{2}\Delta_f H^\ominus O_2(g) \right] \end{aligned}$$

On substituting the values in the above equation

$$-1564.5 = [2 \times (-393.5) + 3(-286)] - [\Delta_f H^\ominus C_2H_6(g) + \text{zero}]$$

$$-1564.5 = -787 - 858 - \Delta_f H^\ominus C_2H_6(g)$$

$$\text{or } \Delta_f H^\ominus C_2H_6(g) = -787 - 858 + 1564.5 = -80.5 \text{ kJ}$$

**Question 6.**

Calculate  $\Delta G^\ominus$  for the reaction :



Given that  $\Delta_f G^\ominus$  for the formation of  $NH_3(g)$ ,  $NO(g)$  and  $H_2O(l)$  are  $-16.8 \text{ kJ mol}^{-1}$ ,  $+86.7 \text{ kJ mol}^{-1}$  and  $-237.2 \text{ kJ mol}^{-1}$  respectively. Predict feasibility of reaction under the conditions.

**Answer:**

$$\begin{aligned} \Delta G^\ominus &= \sum \Delta_f G^\ominus (\text{products}) - \sum \Delta_f G^\ominus (\text{reactants}) \\ &= \{4 \text{ mol} \times \Delta_f G^\ominus NO(g) + 6 \text{ mol} \times \Delta_f G^\ominus H_2O(l)\} \\ &\quad - \{4 \text{ mol} \times \Delta_f G^\ominus NH_3(g) + 5 \text{ mol} \times \Delta_f G^\ominus O_2(g)\} \\ &= [4 \text{ mol} \times (86.7 \text{ kJ mol}^{-1}) + 6 \times (-237.2 \text{ kJ mol}^{-1})] \\ &\quad - [4 \text{ mol} \times (-16.8 \text{ kJ mol}^{-1}) + 5 \times \text{zero}] \\ &= (346.8 \text{ kJ} - 1423.2 \text{ kJ}) + 67.2 \text{ kJ} = -1009.2 \text{ kJ} \end{aligned}$$

Since  $\Delta G^\ominus$  is negative, the reaction is feasible in the forward direction.

**Question 7.**

Determine whether or not it is possible for sodium to reduce aluminium oxide to aluminium at 298 K.

Given:  $\Delta_f G^\ominus Al_2O_3(s) = -1582 \text{ kJ mol}^{-1}$ ;  $\Delta_f G^\ominus Na_2O(s) = -377 \text{ kJ mol}^{-1}$ .

**Answer:**

The reaction involved is

$$\begin{aligned}\text{Al}_2\text{O}_3(s) + 6\text{Na}(s) &\longrightarrow 2\text{Al}(s) + 3\text{Na}_2\text{O}(s) \\ \Delta G^\ominus &= \sum \Delta_f G^\ominus (p) - \sum \Delta_f G^\ominus (r) \\ &= [2\Delta_f G^\ominus \text{Al}(s) + 3\Delta_f G^\ominus \text{Na}_2\text{O}(s)] - [\Delta_f G^\ominus \text{Al}_2\text{O}_3(s) + 6\Delta_f G^\ominus \text{Na}(s)] \\ &= [2 \times 0 + 3 \times (-377)] - [-1582 + 6 \times 0] \\ &= 451 \text{ kJ mol}^{-1}.\end{aligned}$$

This means that sodium can not reduce aluminium oxide ( $\text{Al}_2\text{O}_3$ ) to aluminium metal because  $\Delta G^\ominus$  comes out to be positive.

**Question 8.** 1 g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation  $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$  During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7 kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm?

**Answer:** Suppose  $q$  is the quantity of heat from the reaction mixture and  $C_v$  is the heat capacity of the calorimeter, then the quantity of heat absorbed by the calorimeter.

$$q = C_v / \Delta T$$

Quantity of heat from the reaction will have the same magnitude but opposite sign because the heat lost by the system (reaction mixture) is equal to the heat gained by the calorimeter.

$$q = -C_v \times \Delta T = -20.7 \text{ kJ/K} \times (299 - 298) \text{ K} = -20.7 \text{ kJ}$$

(Here, negative sign indicates the exothermic nature of the reaction). Thus, AU for the combustion of the 1g of graphite =  $-20.7 \text{ kJ K}^{-1}$  For combustion of 1 mol of graphite,

$$\begin{aligned}&= \frac{12.0 \text{ g mol}^{-1} \times (-20.7 \text{ kJ})}{1 \text{ g}} \\ &= -2.48 \times 10^2 \text{ kJ mol}^{-1}.\end{aligned}$$

Since  $\Delta n_g = 0$ ,  
 $\Delta H = \Delta U = -2.48 \times 10^2 \text{ kJ mol}^{-1}$

**Question 9.**

Calculate  $\Delta_r G^\ominus$  for conversion of oxygen to ozone,  $3/2 \text{ O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})$  at 298 K. If  $K_p$  for this conversion is  $2.47 \times 10^{-29}$ .

**Answer:**

We know  $\Delta_r G^\ominus = -2.303 RT \log K_p$   
 and  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$   
 Therefore,  $\Delta_r G^\ominus = -2.303 (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) (\log 2.47 \times 10^{-29})$   
 $= 163000 \text{ J mol}^{-1} = 163 \text{ J mol}^{-1}$ .

**Question 10. Define the following:**

(i) First law of thermodynamics.

(ii) Standard enthalpy of formation.

**Answer:** (i) **First law of thermodynamics:** It states that energy can neither be created nor be destroyed. The energy of an isolated system is constant.

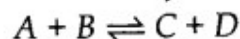
$$\Delta u = q + w$$

(ii) It is defined as the amount of heat evolved or absorbed when one mole of the compound is formed from its constituent elements in their standard states.

**Question 11.**

(a) Why is the entropy of a substance taken as zero at 0K?

(b) Calculate  $\Delta G$  and  $\Delta G^\ominus$  for the reaction.



at 27°C. Equilibrium constant (K) for this reaction =  $10^2$

**Answer:**

(a) From third law of thermodynamics, it can be explained that entropy of a perfectly crystalline substance is zero at zero kelvin.

(b)  $\Delta G = 0$  (because the reaction is in equilibrium)  
 $\Delta G^\ominus = -2.303 RT \log K$   
 $= -2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \log 10^2$   
 $= -11.488 \text{ kJ mol}^{-1}$

**Question 12. Give reason for the following:**

(a) Neither q nor w is a state function but q + w is a state function.

(b) A real crystal has more entropy than an ideal crystal.

**Answer:** (a)  $q + w = \Delta u$

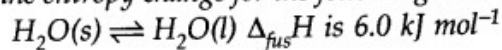
As  $\Delta u$  is a state function hence, q + w is a state function.

(b) A real crystal has some disorder due to the presence of defects in its structural arrangement whereas ideal crystal does not have any disorder. Hence, a real crystal has more entropy than an ideal crystal.

## Question 13.

(a) Under what condition, the heat evolved or absorbed in a reaction is equal to its free energy change?

(b) Calculate the entropy change for the following reversible process



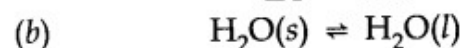
Answer:

(a)  $\Delta G = \Delta H - T\Delta S$

When the reaction is carried out at 0°K

or  $\Delta S = 0$

$$\Delta G = \Delta H$$



$$\Delta_{\text{fus}}H = 6.0 \text{ kJ mol}^{-1}$$

$$= 6000 \text{ J mol}^{-1}$$

$$T_f = 0^\circ\text{C} = (0 + 273) = 273 \text{ K}$$

$$\Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T_f} = \frac{6000 \text{ J mol}^{-1}}{273 \text{ K}} = 21.98 \text{ J K}^{-1} \text{ mol}^{-1}$$

NCERT Solutions for Class 11 Chemistry Chapter 6 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.

$\Delta G$  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,  $\Delta G$  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,  $\Delta G$  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)  $2\text{NaHCO}_3(s) \longrightarrow \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g)$

(iv)  $\text{H}_2(g) \longrightarrow 2\text{H}(g)$

**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,  $\text{NaHCO}_3$  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  $\Delta H$  and  $\Delta S$  are positive

(ii) both  $\Delta H$  and  $\Delta S$  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  $\Delta H$  and  $\Delta S$  are positive  $\Delta G$  can be - ve only if  $T\Delta S > \Delta H$  in magnitude. Thus, the temperature should be high.

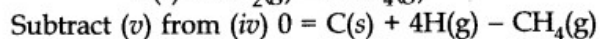
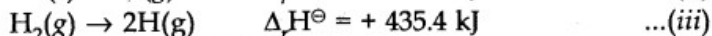
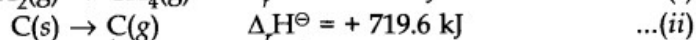
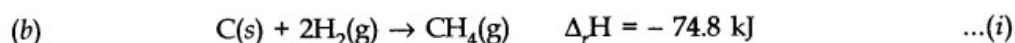
(ii) If both  $\Delta H$  and  $\Delta S$  are negative  $\Delta G$  can be negative only if  $T\Delta S < \Delta H$  in magnitude. Thus, the value of T should be low.

**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  $\text{CH}_4$ , heat of sublimation of carbon and heat of dissociation of  $\text{H}_2$  are - 74.8, + 719.6, 435.4 kJ mol<sup>-1</sup> 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.



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



$$\Delta H = +1665.2 \text{ kJ}$$

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

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

NCERT Solutions for Class 11 Chemistry Chapter 6 Multiple Choice Questions

Question 1. Thermodynamics is applicable to

- (a) macroscopic system only (b) microscopic system only  
(c) homogeneous system only (d) heterogeneous system only

Question 2. An isochoric process takes place at constant

- (a) temperature (b) pressure  
(c) volume (d) concentration

Question 3. For a cyclic process, the change in internal energy of the system is

- (A) always +ve (b) equal to zero  
(c) always -ve (d) none of the above

Question 4. Which of the following properties is not a function of state?

- (a) concentration (b) internal energy  
(c) enthalpy (d) entropy

Question 5. Which of the following relation is true?

Question 6. Which of the following always has a negative value?

- (a) heat of reaction (b) heat of solution  
(c) heat of combustion (d) heat of formation

Question 7. The bond energy depends upon

- (a) size of the atom (b) electronegativity  
(c) bond length (d) all of the above

Question 8. For an endothermic reaction.

- (a)  $\Delta H$  is -ve (b)  $\Delta H$  is +ve  
(c)  $\Delta H$  is zero (d) none of these

Question 9. The process depicted by the equation.

$\text{H}_2\text{O (S)} \longrightarrow \text{H}_2\text{O (l)}$   $\Delta H = +1.43 \text{ kcal}$  represents

- (a) fusion (b) melting  
(c) evaporation (d) boiling

Question 10. Which one is the correct unit for entropy?

- (a) KJ mol (b) JK mol  
(c) JK mol<sup>-1</sup> (d) KJ mol<sup>-1</sup>

Answer: 1. (a) 2. (c) 3. (b) 4. (a) 5. (a)

6. (c) 7. (d) 8. (b) 9. (a) 10. (c)

NCERT Solutions for Class 11 Chemistry Chapter 6 HOTS Questions

Question 1. Why standard entropy of an elementary substance is not zero whereas the standard enthalpy of formation is taken as zero?

Answer: A substance has a perfectly ordered arrangement only at absolute zero. Hence, entropy is zero only at absolute zero. Enthalpy of formation is the heat change involved in the formation of one mole of the substance from its elements. An element formed from its constituents means no heat change.

Question 2.

*The equilibrium constant for a reaction is one or more if  $\Delta G^\ominus$  for it is less than zero. Explain.*

Answer:

$\Delta_r G^\ominus = -RT \ln K$ , thus if  $\Delta_r G^\ominus$  is less than zero i.e., it is negative, then  $\ln K$  will be positive and hence  $K$  will be greater than one.

Question 3. Many thermodynamically feasible reactions do not occur under ordinary conditions. Why?

Answer: Under ordinary conditions, the average energy of the reactants may be less than the threshold energy. They require some activation energy to initiate the reaction.

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