

## Thermodynamics



## ANSWERS

## Topic 1

1. (b) : State function is a property of the system whose value depends only upon the state of the system and is independent of the path or the manner by which the state is reached.

2. (c) : Adiabatic system does not exchange heat with the surroundings.

3. Heat absorbed by the system ( $q$ ) = 701 J

Work done by the system ( $w$ ) = -394 J

According to first law of thermodynamics,

$$\Delta U = q + w = 701 + (-394) = 701 - 394 = 307 \text{ J}$$

4. Mass of Al = 60 g

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

Molar heat capacity of Al =  $24 \text{ J mol}^{-1} \text{ K}^{-1}$

Specific heat capacity of Al =  $\frac{24}{27} \text{ J g}^{-1} \text{ K}^{-1}$

$$\therefore \text{Energy required} = m \times c \times \Delta T$$

$$= 60 \times \frac{24}{27} \times 20 = 1066.67 \text{ J} \approx 1.07 \text{ kJ}$$

## Topic 2

1. (b) : By convention, the standard enthalpy of formation of every element in its standard state is zero.

2. (c) :  $\text{CH}_{4(g)} + 2\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$

$$\Delta n_g = 1 - 3 = -2$$

$$\Delta H^\circ = \Delta U^\circ + \Delta n_g RT = -X - 2RT$$

$$\therefore \Delta H^\circ < \Delta U^\circ$$

3. (a) : (1)  $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$  ;

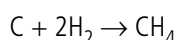
$$\Delta H = -890.3 \text{ kJ mol}^{-1}$$

(2)  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$  ;  $\Delta H = -393.5 \text{ kJ mol}^{-1}$

(3)  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$  ;  $\Delta H = -285.8 \text{ kJ mol}^{-1}$

or  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$  ;  $\Delta H = -571.6 \text{ kJ mol}^{-1}$

Add equations (2) and (3) and subtract equation (1) we get,



$$\Delta H = -393.5 - 571.6 + 890.3 = -74.8 \text{ kJ mol}^{-1}$$

$\therefore$  Enthalpy of formation of  $\text{CH}_4$  is  $-74.8 \text{ kJ mol}^{-1}$ .

4.  $\text{NH}_2\text{CN}_{(s)} + \frac{3}{2}\text{O}_{2(g)} \rightarrow \text{N}_{2(g)} + \text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)}$

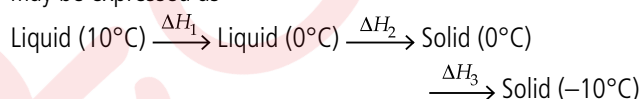
$$\Delta U = -742.7 \text{ kJ/mol}$$

$$\Delta n_g = n_p - n_R = 2 - \frac{3}{2} = +\frac{1}{2}, \quad R = \frac{8.314}{1000} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$T = 298 \text{ K}$$

$$\begin{aligned} \Delta H &= \Delta U + \Delta n_g RT = -742.7 + \frac{1}{2} \times \frac{8.314}{1000} \times 298 \\ &= -742.7 + 1.2 = -741.5 \text{ kJ/mol} \end{aligned}$$

5. The enthalpy change on freezing from  $10^\circ\text{C}$  to  $-10^\circ\text{C}$  may be expressed as



$$\begin{aligned} \Delta H_1 &= nC_p[\text{H}_2\text{O}_{(l)}] \times \Delta T = 1 \times 75.3 \text{ J mol}^{-1} \text{ K}^{-1} \times (-10) \\ &= -753 \text{ J mol}^{-1} = -0.753 \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta H_2 = n(-\Delta_{fus} H) = -1 \times 6.03 = -6.03 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta H_3 &= nC_p[\text{H}_2\text{O}_{(s)}] \times \Delta T = -1 \times 36.8 \times 10 = -368 \text{ J mol}^{-1} \\ &= -0.368 \text{ kJ mol}^{-1} \end{aligned}$$

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

$$= -0.753 - 6.03 - 0.368 \text{ kJ mol}^{-1} = -7.151 \text{ kJ mol}^{-1}$$

6.  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$  ;  $\Delta H = -393.5 \text{ kJ}$

$\therefore$  When 44 g of  $\text{CO}_2$  is formed from carbon and dioxygen gas, heat released = 393.5 kJ

$\therefore$  When 35.2 g of  $\text{CO}_2$  is formed from carbon and dioxygen gas, heat released

$$= \frac{393.5 \times 35.2}{44} = \frac{13851.2}{44} = 314.8 \text{ kJ}$$

Thus,  $\Delta H = -314.8 \text{ kJ}$

7.  $\text{N}_2\text{O}_{4(g)} + 3\text{CO}_{(g)} \rightarrow \text{N}_2\text{O}_{(g)} + 3\text{CO}_{2(g)}$

$$\begin{aligned} \Delta_r H &= \{\Delta_f H[\text{N}_2\text{O}_{(g)}] + 3\Delta_f H[\text{CO}_{2(g)}]\} - \{\Delta_f H[\text{N}_2\text{O}_{4(g)}] \\ &\quad + 3\Delta_f H[\text{CO}_{(g)}]\} \end{aligned}$$

$$= 81 + 3 \times (-393) - \{9.7 + 3(-110)\}$$

$$= 81 - 1179 - 9.7 + 330 = -777.7 \text{ kJ mol}^{-1}$$

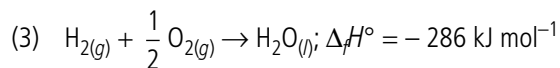
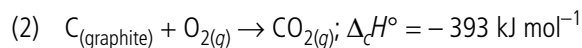
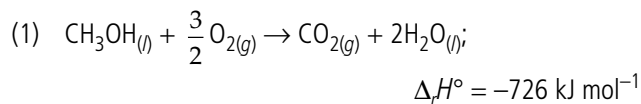
8.  $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$ ;  $\Delta_f H^\circ = -92.4 \text{ kJ mol}^{-1}$

$\therefore$  Standard enthalpy of formation of  $\text{NH}_3(g)$

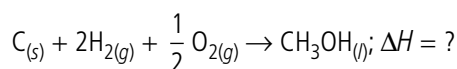
$$= \frac{-92.4}{2} = -46.2 \text{ kJ/mol}$$

## Topic 3

9. The given thermochemical equations are



The required thermochemical equation is



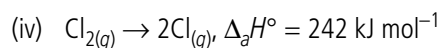
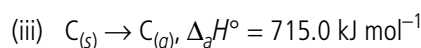
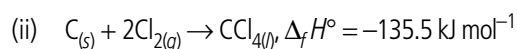
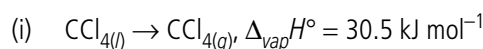
$2 \times \text{eqn. (3)} + \text{eqn. (2)} - \text{eqn. (1)}$  gives the desired equation.

$$\Delta H = (-286 \times 2) + (-393) - (-726)$$

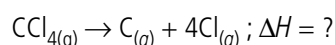
$$= -572 - 393 + 726 = -239 \text{ kJ}$$

$$\therefore \Delta_f H^\circ \text{ for } \text{CH}_3\text{OH}_{(l)} = -239 \text{ kJ mol}^{-1}$$

10. Given :



Required equation is :



From Hess's law,

$\text{eqn. (iii)} + 2 \times \text{eqn. (iv)} - \text{eqn. (i)} - \text{eqn. (ii)}$  gives required equation :

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

$$\text{Bond enthalpy of C - Cl in } \text{CCl}_4 \text{ (average value)} = \frac{1304}{4}$$

$$= 326 \text{ kJ mol}^{-1}$$

1. (d) :  $A + B \rightarrow C + D + q$ ,  $\Delta S = +ve$

Here,  $\Delta H = -ve$

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

For reaction to be spontaneous,  $\Delta G$  should be  $-ve$ .

As  $\Delta H = -ve$  and  $\Delta S$  is  $+ve$ ,  $\Delta G$  will be  $-ve$  at any temperature.

2. When energy factor has no role to play, for the process to be spontaneous  $\Delta S$  must be  $+ve$  i.e.,  $\Delta S > 0$ .

3. According to Gibbs-Helmholtz equation,

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

At equilibrium,  $\Delta G = 0$

$$\therefore T = \frac{\Delta H}{\Delta S} = \frac{400}{0.2} = \frac{4000}{2} = 2000 \text{ K}$$

Thus, the reaction will be spontaneous at temperature above 2000 K. [ $\therefore$  Above 2000 K,  $\Delta G = -ve$ ]

4.  $\Delta H$  is negative because bond energy is released and  $\Delta S$  is negative because there is less randomness among the molecules than among the atoms.

$$5. \Delta H^\circ = \Delta U^\circ + \Delta n_g RT$$

$$\Delta U^\circ = -10.5 \text{ kJ mol}^{-1}, R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}, T = 298 \text{ K}$$

$$\Delta n_g = 2 - (2 + 1) = -1$$

$$\therefore \Delta H^\circ = -10.5 - (1) \times 8.314 \times 10^{-3} \times 298$$

$$= -10.5 - 2.48 = -12.98 \text{ kJ mol}^{-1}$$

$$\text{Now } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -12.98 - 298 \times (-44.1 \times 10^{-3})$$

$$= -12.98 + 13.14 = 0.16 \text{ kJ mol}^{-1}$$

Since  $\Delta G^\circ$  is positive hence, the reaction is non spontaneous.

6. We know that  $\Delta G^\circ = -2.303RT \log K$

$$= -2.303 \times 8.314 \times 300 \times \log 10 = -5744.14 \text{ J/mol}$$

7.  $\Delta H_f^\circ[\text{H}_2\text{O}_{(l)}] = -286 \text{ kJ/mol}$

$$\therefore q_{\text{surroundings}} = +286 \text{ kJ/mol}$$

$$\Delta S_{(\text{surr})} = \frac{q}{298} = \frac{286 \times 1000}{298} = 959.73 \text{ J K}^{-1} \text{ mol}^{-1}$$

