



## Chapter – 6

### Thermodynamics

#### NCERT Back Exercises :

**Ques 6.1:** 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.

**Ans 6.1:** A thermodynamic state function is a quantity whose value is independent of a path. Functions like  $p$ ,  $V$ ,  $T$  etc. depend only on the state of a system and not on the path. Hence, alternative (ii) is correct.

**Ques 6.2:** 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 6.2:** A system is said to be under adiabatic conditions if there is no exchange of heat between the system and its surroundings. Hence, under adiabatic conditions,  $q = 0$ . Therefore, alternative (iii) is correct.



**Ques 6.3:** The enthalpies of all elements in their standard states are:

- (i) Unity
- (ii) Zero
- (iii)  $< 0$
- (iv) Different for each element

**Ans 6.3:** The enthalpy of all elements in their standard state is zero.  
Therefore, alternative (ii) is correct.

**Ques 6.4:**  $\Delta U^\theta$  of combustion of methane is  $-X \text{ kJ mol}^{-1}$ . The value of  $\Delta H^\theta$  is

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

**Ans 6.4:** Since  $\Delta H^\theta = \Delta U^\theta + \Delta n_g RT$  and  $\Delta U^\theta = -X \text{ kJ mol}^{-1}$ ,  
 $\Delta H^\theta = (-X) + \Delta n_g RT \Rightarrow \Delta H^\theta < \Delta U^\theta$   
Therefore, alternative (iii) is correct.

**Ques 6.5:** 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  $\text{CH}_{4(g)}$  will be

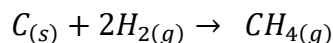
- (i)  $-74.8 \text{ kJ mol}^{-1}$
- (ii)  $-52.27 \text{ kJ mol}^{-1}$
- (iii)  $+74.8 \text{ kJ mol}^{-1}$
- (iv)  $+52.26 \text{ kJ mol}^{-1}$

**Ans 6.5:** According to the Question,

- (i)  $\text{CH}_{4(g)} + 2\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(g)}$   
 $\Delta H = -890.3 \text{ kJ mol}^{-1}$
- (ii)  $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$   
 $\Delta H = -393.5 \text{ kJ mol}^{-1}$
- (iii)  $2\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{H}_2\text{O}_{(g)}$   
 $\Delta H = -285.8 \text{ kJ mol}^{-1}$



Thus, the desired equation is the one that represents the formation of  $\text{CH}_{4(g)}$  i.e.,



$$\Delta_f H_{\text{CH}_4} = \Delta_e H_e + 2\Delta_e H_{\text{H}_2} - \Delta_e H_{\text{CO}_2}$$

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

$$= -74.8 \text{ kJ mol}^{-1}$$

Enthalpy of formation of  $\text{CH}_{4(g)} = -74.8 \text{ kJ mol}^{-1}$

Hence, alternative (i) is correct.

**Ques 6.6:** A reaction,  $\text{A} + \text{B} \rightarrow \text{C} + \text{D} + q$  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

**Ans 6.6 :** For a reaction to be spontaneous,  $\Delta G$  should be negative.

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

According to the Question, for the given reaction,

$\Delta S = \text{positive}$

$\Delta H = \text{negative}$  (since heat is evolved)

$\Rightarrow \Delta G = \text{negative}$

Therefore, the reaction is spontaneous at any temperature.

Hence, alternative (iv) is correct.

**Ques 6.7:** 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?

**Ans 6.7 :** According to the first law of thermodynamics,

$$\Delta U = q + W \quad (i)$$

Where,

$\Delta U$  = change in internal energy for a process

$q$  = Heat

$W$  = Work

Given,

$q = +701 \text{ J}$  (Since heat is absorbed)

$W = -394 \text{ J}$  (Since work is done by the system)



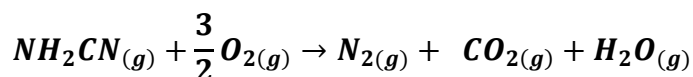
Substituting the values in expression (i), we get

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

$$\Delta U = 307 \text{ J}$$

Hence, the change in internal energy for the given process is 307 J.

**Ques 6.8:** The reaction of cyanamide,  $\text{NH}_2\text{CN}_{(g)}$ , 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 enthalpy change for the reaction at 298 K.



**Ans 6.8 :** Enthalpy change for a reaction ( $\Delta H$ ) is given by the expression,

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

Where,

$\Delta U$  = change in internal energy

$\Delta n_g$  = change in number of moles For the given reaction,

$$\Delta n_g = \sum n_g (\text{products}) - \sum n_g (\text{reactants})$$

$$= (2 - 2.5) \text{ moles}$$

$$\Delta n_g = -0.5 \text{ moles}$$

And,

$$\Delta U = -742.7 \text{ kJ mol}^{-1}$$

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

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

Substituting the values in the expression of  $\Delta H$ :

$$\Delta H = (-742.7 \text{ kJ mol}^{-1}) + (-0.5 \text{ mol})(298 \text{ K})(8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})$$

$$= -742.7 - 1.2$$

$$\Delta H = -743.9 \text{ kJ mol}^{-1}$$

**Ques 6.9:** Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from  $35^\circ\text{C}$  to  $55^\circ\text{C}$ . Molar heat capacity of Al is  $24 \text{ J mol}^{-1} \text{ K}^{-1}$ .

**Ans 6.9 :** From the expression of heat (q),

$$q = m \cdot c \cdot \Delta T$$

Where,

c = molar heat capacity

m = mass of substance

$\Delta T$  = change in temperature



Substituting the values in the expression of  $q$ :

$$q = \left(\frac{60}{27} \text{ mol}\right) (24 \text{ J mol}^{-1} \text{ K}^{-1})(20 \text{ K})$$

$$q = 1066.7 \text{ J}$$

$$q = 1.07 \text{ kJ}$$

**Ques 6.10:** Calculate the enthalpy change on freezing of 1.0 mol of water at  $10.0^\circ\text{C}$  to ice at  $-10.0^\circ\text{C}$ .

(i)  $\Delta_{fus}H = 6.03 \text{ kJ mol}^{-1}$  at  $0^\circ\text{C}$ .

(ii)  $C_p[\text{H}_2\text{O(l)}] = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$

(iii)  $C_p[\text{H}_2\text{O(s)}] = 36.8 \text{ J mol}^{-1} \text{ K}^{-1}$

**Ans 6.10:** Total enthalpy change involved in the transformation is the sum of the following changes:

(i) Energy change involved in the transformation of 1 mol of water at  $10^\circ\text{C}$  to 1 mol of water at  $0^\circ\text{C}$ .

(ii) Energy change involved in the transformation of 1 mol of water at  $0^\circ$  to 1 mol of ice at  $0^\circ\text{C}$ .

(iii) Energy change involved in the transformation of 1 mol of ice at  $0^\circ\text{C}$  to 1 mol of ice at  $-10^\circ\text{C}$ .

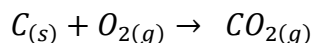
$$\begin{aligned} \text{Total } \Delta H &= C_p[\text{H}_2\text{O(l)}]\Delta T + \Delta H_{\text{freezing}} + C_p[\text{H}_2\text{O(s)}]\Delta T \\ &= (75.3 \text{ J mol}^{-1} \text{ K}^{-1})(0 - 10)\text{K} + (-6.03 \times 10^3 \text{ J mol}^{-1}) + (36.8 \text{ J mol}^{-1} \text{ K}^{-1})(-10 - 0)\text{K} \\ &= -753 \text{ J mol}^{-1} - 6030 \text{ J mol}^{-1} - 368 \text{ J mol}^{-1} \\ &= -7151 \text{ J mol}^{-1} \\ &= -7.151 \text{ kJ mol}^{-1} \end{aligned}$$

Hence, the enthalpy change involved in the transformation is  $-7.151 \text{ kJ mol}^{-1}$ .



**Ques 6.11:** Enthalpy of combustion of carbon to  $\text{CO}_2$  is  $-393.5 \text{ kJ mol}^{-1}$ . Calculate the heat released upon formation of 35.2 g of  $\text{CO}_2$  from carbon and dioxygen gas.

**Ans 6.11 :** Formation of  $\text{CO}_2$  from carbon and dioxygen gas can be represented as:



$$\Delta_f H = -393.5 \text{ kJ mol}^{-1}$$

Heat released on formation of 44 g  $\text{CO}_2 = -393.5 \text{ kJ mol}^{-1}$

$$\begin{aligned} \text{Heat released on formation of 35.2 g CO}_2 &= \frac{-393.5 \text{ kJ mol}^{-1}}{44 \text{ g}} \times 35.2 \text{ g} \\ &= -314.8 \text{ kJ mol}^{-1} \end{aligned}$$

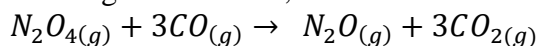
**Ques 6.12:** Enthalpies of formation of  $\text{CO(g)}$ ,  $\text{CO}_2(\text{g})$ ,  $\text{N}_2\text{O(g)}$  and  $\text{N}_2\text{O}_4(\text{g})$  are  $-110 \text{ kJ mol}^{-1}$ ,  $-393 \text{ kJ mol}^{-1}$ ,  $81 \text{ kJ mol}^{-1}$  and  $9.7 \text{ kJ mol}^{-1}$  respectively. Find the value of  $\Delta_r H$  for the reaction:



**Ans 6.12:**  $\Delta_r H$  for a reaction is defined as the difference between  $\Delta_f H$  value of products and  $\Delta_f H$  value of reactants.

$$\Delta_r H = \sum \Delta_f H(\text{products}) - \sum \Delta_f H(\text{reactants})$$

For the given reaction,



$$\Delta_r H = [\{\Delta_f H(\text{N}_2\text{O}) + 3\Delta_f H(\text{CO}_2)\} - \{\Delta_f H(\text{N}_2\text{O}_4) + 3\Delta_f H(\text{CO})\}]$$

Substituting the values of  $\Delta_f H$  for  $\text{NO}_2$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}_4$ , and  $\text{CO}$  from the Question, we get:

$$\Delta_r H = [81 \text{ kJ mol}^{-1} + 3(-393) \text{ kJ mol}^{-1}] - [9.7 \text{ kJ mol}^{-1} + 3(-110) \text{ kJ mol}^{-1}]$$

$$\Delta_r H = -777.7 \text{ kJ mol}^{-1}$$

Hence, the value of  $\Delta_r H$  for the reaction is  $= -777.7 \text{ kJ mol}^{-1}$

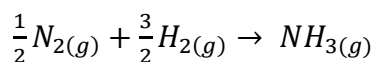


**Ques 6.13:** Given,  $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$ ;  $\Delta_r H^\theta = -92.4 \text{ kJ mol}^{-1}$

**What is the standard enthalpy of formation of  $NH_3$  gas?**

**Ans 6.13 :** Standard enthalpy of formation of a compound is the change in enthalpy that takes place during the formation of 1 mole of a substance in its standard form from its constituent elements in their standard state.

Re-writing the given equation for 1 mole of  $NH_{3(g)}$ ,



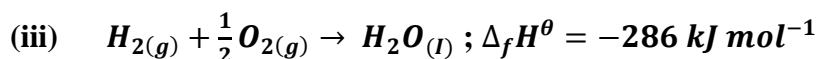
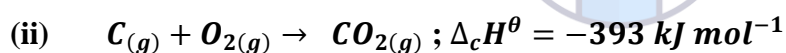
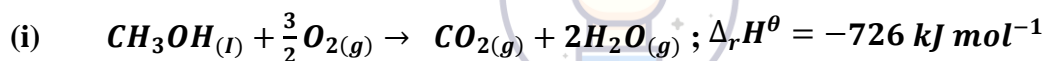
Standard enthalpy of formation of  $NH_3$

$$= \frac{1}{2} \Delta_r H^\theta$$

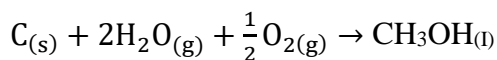
$$= \frac{1}{2} (-92.4 \text{ kJ mol}^{-1})$$

$$= -46.2 \text{ kJ mol}^{-1}$$

**Ques 6.14:** Calculate the standard enthalpy of formation of  $CH_3OH_{(l)}$  from the following data:



**Ans 6.14:** The reaction that takes place during the formation of  $CH_3OH_{(l)}$  can be written as:



The reaction (1) can be obtained from the given reactions by following the algebraic calculations as:

Equation (ii) + 2 × equation (iii) – equation (i)

$$\Delta_f H^\theta [CH_3OH_{(l)}] = \Delta_c H^\theta + 2\Delta_f H^\theta [H_2O_{(l)}] - \Delta_r H^\theta$$

$$= (-393 \text{ kJ mol}^{-1}) + 2(-286 \text{ kJ mol}^{-1}) - (-726 \text{ kJ mol}^{-1})$$

$$= (-393 \text{ kJ mol}^{-1}) + 2(-286 \text{ kJ mol}^{-1}) - (-726 \text{ kJ mol}^{-1})$$



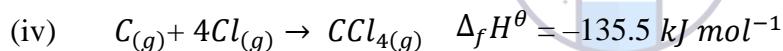
$$= (-393 - 572 + 726) \text{ kJ mol}^{-1}$$

$$\Delta_f H^\theta [\text{CH}_3\text{OH}_{(l)}] = -239 \text{ kJ mol}^{-1}$$

**Ques 6.15:** Calculate the enthalpy change for the process  $\text{CCl}_{4(g)} \rightarrow \text{C}_{(g)} + 4\text{Cl}_{(g)}$  and calculate bond enthalpy of C–Cl in  $\text{CCl}_{4(g)}$ .

- (i)  $\Delta_{\text{vap}} H^\theta (\text{CCl}_{4(g)}) = 30.5 \text{ kJ mol}^{-1}$ .
- (ii)  $\Delta_f H^\theta (\text{CCl}_{4(g)}) = -135.5 \text{ kJ mol}^{-1}$ .
- (iii)  $\Delta_a H^\theta (\text{C}) = 715.0 \text{ kJ mol}^{-1}$ , where  $\Delta_a H^\theta$  is enthalpy of atomisation
- (iv)  $\Delta_a H^\theta (\text{Cl}_2) = 242 \text{ kJ mol}^{-1}$

**Ans 6.15 :** The chemical equations implying to the given values of enthalpies are:



Enthalpy change for the given process  $\text{CCl}_{4(g)} \rightarrow \text{C}_{(g)} + 4\text{Cl}_{(g)}$ , can be calculated using the following algebraic calculations as:

Equation (ii) + 2 × Equation (iii) – Equation (i) – Equation (iv)

$$\Delta H = \Delta_a H^\theta (\text{C}) + 2\Delta_a H^\theta (\text{Cl}_2) - \Delta_{\text{vap}} H^\theta - \Delta_f H^\theta$$

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

$$\Delta H = 1304 \text{ kJ mol}^{-1}$$

Bond enthalpy of C–Cl bond in  $\text{CCl}_{4(g)}$

$$= \frac{1304}{4} \text{ kJ mol}^{-1}$$

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





Ques 6.16: For an isolated system,  $\Delta U = 0$ , what will be  $\Delta S$ ?

Ans 6.16 :  $\Delta S$  will be positive i.e., greater than zero

Since  $\Delta U = 0$ ,  $\Delta S$  will be positive and the reaction will be spontaneous.

Ques 6.17: For the 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?

Ans 6.17: From the expression,

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

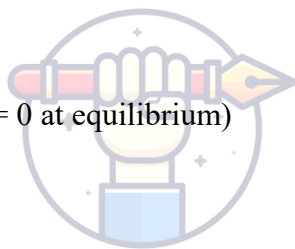
Assuming the reaction at equilibrium,  $\Delta T$  for the reaction would be:

$$T = (\Delta H - \Delta G) \frac{1}{\Delta S}$$

$$= \frac{\Delta H}{\Delta S}$$

$$= \frac{400 \text{ kJ mol}^{-1}}{0.2 \text{ kJ K}^{-1}\text{mol}^{-1}}$$

( $\Delta G = 0$  at equilibrium)



$$T = 2000 \text{ K}$$

For the reaction to be spontaneous,  $\Delta G$  must be negative. Hence, for the given reaction to be spontaneous,  $T$  should be greater than 2000 K.

Ques 6.18: For the reaction,  $2\text{Cl}_{(g)} \rightarrow \text{Cl}_{2(g)}$ , what are the signs of  $\Delta H$  and  $\Delta S$  ?

Ans 6.18 :  $\Delta H$  and  $\Delta S$  are negative.

The given reaction represents the formation of chlorine molecule from chlorine atoms. Here, bond formation is taking place. Therefore, energy is being released. Hence,  $\Delta H$  is negative.

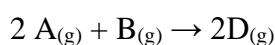
Also, two moles of atoms have more randomness than one mole of a molecule. Since spontaneity is decreased,  $\Delta S$  is negative for the given reaction.



**Ques 6.19:** For the reaction  $2A(g) + B(g) \rightarrow 2D(g)$   
 $\Delta U^\theta = -10.5 \text{ kJ}$  and  $\Delta S^\theta = -44.1 \text{ JK}^{-1}$ .

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

**Ans 6.19:** For the given reaction,



$$\Delta n_g = 2 - (3) = -1 \text{ mole}$$

Substituting the value of  $\Delta U^\theta$  in the expression of  $\Delta H$  :

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

$$= (-10.5 \text{ kJ}) + (-1)(8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})(298 \text{ K})$$

$$= -10.5 \text{ kJ} - 2.48 \text{ kJ}$$

$$\Delta H^\theta = -12.98 \text{ kJ}$$

Substituting the values of  $\Delta H^\theta$  and  $\Delta S^\theta$  in the expression of  $\Delta G^\theta$  :

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

$$= -10.5 \text{ kJ} - (298 \text{ K})(-44.1 \text{ J K}^{-1})$$

$$= -12.98 \text{ kJ} + 13.14 \text{ kJ}$$

$$\Delta G^\theta = +0.16 \text{ kJ}$$

Since  $\Delta G^\theta$  for the reaction is positive, the reaction will not occur spontaneously.

**Ques 6.20:** The equilibrium constant for a reaction is 10. What will be the value of  $\Delta G^\theta$ ?  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ,  $T = 300 \text{ K}$ .

**Ans 6.20 :**

From the expression,

$$\Delta G^\theta = -2.303 RT \log K_{eq}$$

$\Delta G^\theta$  for the reaction,

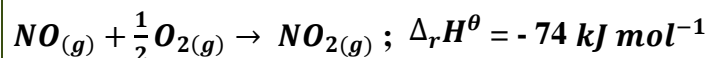
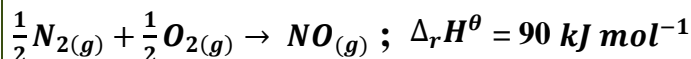
$$= (2.303)(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(300 \text{ K}) \log 10$$

$$= -5744.14 \text{ Jmol}^{-1}$$



$$= -5.744 \text{ kJ mol}^{-1}$$

**Ques 6.21:** Comment on the thermodynamic stability of  $\text{NO}_{(g)}$ , given



**Ans 6.21 :** The positive value of  $\Delta_r H$  indicates that heat is absorbed during the formation of  $\text{NO}_{(g)}$ . This means that  $\text{NO}_{(g)}$  has higher energy than the reactants ( $\text{N}_2$  and  $\text{O}_2$ ). Hence,  $\text{NO}_{(g)}$  is unstable.

The negative value of  $\Delta_r H$  indicates that heat is evolved during the formation of  $\text{NO}_{2(g)}$  from  $\text{NO}_{(g)}$  and  $\text{O}_2(g)$ . The product,  $\text{NO}_2(g)$  is stabilized with minimum energy.

Hence, unstable  $\text{NO}_{(g)}$  changes to unstable  $\text{NO}_{2(g)}$ .

**Ques 6.22:** Calculate the entropy change in surroundings when 1.00 mol of  $\text{H}_2\text{O}_{(l)}$  is formed under standard conditions.  $\Delta_f H^\theta = -286 \text{ kJ mol}^{-1}$ .

**Ans 6.22:** It is given that  $286 \text{ kJ mol}^{-1}$  of heat is evolved on the formation of 1 mol of  $\text{H}_2\text{O}_{(l)}$ . Thus, an equal amount of heat will be absorbed by the surroundings.  $Q_{\text{surr}} = +286 \text{ kJ mol}^{-1}$

Entropy change ( $\Delta S_{\text{surr}}$ ) for the surroundings =  $\frac{q_{\text{surr}}}{T}$

$$= \frac{286 \text{ kJ mol}^{-1}}{298 \text{ K}}$$

$$\Delta S_{\text{surr}} = 959.73 \text{ J mol}^{-1} \text{ K}^{-1}$$