

## (Chapter 6)(Thermodynamics)

### XI

#### Question 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.

Answer

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.

#### Question 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)  $w = 0$

Answer

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.

#### Question 6.3:

The enthalpies of all elements in their standard states are:

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

Answer

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

**Question 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)  $= 0$

Answer

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.

**Question 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

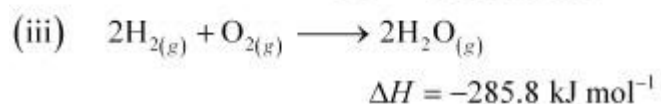
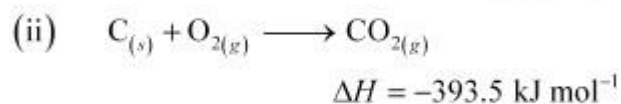
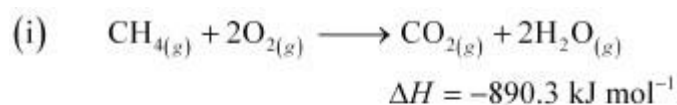
$\text{CH}_{4(g)}$  will be

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

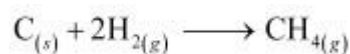
(iii)  $+74.8 \text{ kJ mol}^{-1}$                       (iv)  $+52.26 \text{ kJ mol}^{-1}$ .

Answer

According to the question,



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



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

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

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

∴ Enthalpy of formation of  $\text{CH}_{4(g)} = -74.8 \text{ kJ mol}^{-1}$  Hence, alternative (i) is correct.

#### Question 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

Answer

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.

#### Question 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?

Answer

According to the first law of thermodynamics,

$$\Delta U = q + W \text{ (i)}$$

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

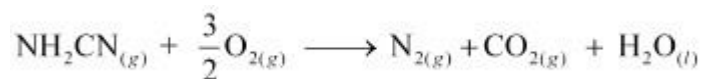
$$\Delta U = 701 \text{ J} + (-394 \text{ J})$$

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

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

#### Question 6.8:

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



Answer

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  $\Delta H$ :

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

$$= -742.7 - 1.2$$

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

**Question 6.9:**

Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 J mol<sup>-1</sup> K<sup>-1</sup>.

Answer

From the expression of heat ( $q$ ),

$$q = m \cdot c \cdot \Delta T \text{ Where,}$$

$c$  = molar heat capacity  $m$

= mass of substance

$\Delta T$  = change in temperature

Substituting the values in the expression of  $q$ :

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

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

$$= 1.07 \text{ kJ}$$

**Question 6.10:**

Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0°C to ice at -10.0°C.  $\Delta_{fus}H = 6.03 \text{ kJ mol}^{-1}$  at 0°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

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

(a) Energy change involved in the transformation of 1 mol of water at 10°C to 1 mol of water at 0°C.

(b) Energy change involved in the transformation of 1 mol of water at 0°C to 1 mol of ice at 0°C.

(c) Energy change involved in the transformation of 1 mol of ice at 0°C to 1 mol of ice at -10°C.

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

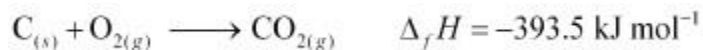
Hence, the enthalpy change involved in the transformation is -7.151 kJ mol<sup>-1</sup>.

**Question 6.11:**

Enthalpy of combustion of carbon to CO<sub>2</sub> is -393.5 kJ mol<sup>-1</sup>. Calculate the heat released upon formation of 35.2 g of CO<sub>2</sub> from carbon and dioxygen gas.

Answer

Formation of CO<sub>2</sub> from carbon and dioxygen gas can be represented as:



(1 mole = 44 g)

Heat released on formation of 44 g CO<sub>2</sub> = -393.5 kJ mol<sup>-1</sup>

∴ Heat released on formation of 35.2 g CO<sub>2</sub>

$$= \frac{-393.5 \text{ kJ mol}^{-1}}{44 \text{ g}} \times 35.2 \text{ g}$$

$$= -314.8 \text{ kJ mol}^{-1}$$

**Question 6.12:**

Enthalpies of formation of CO<sub>(g)</sub>, CO<sub>2(g)</sub>, N<sub>2</sub>O<sub>(g)</sub> and N<sub>2</sub>O<sub>4(g)</sub> are -110 kJ mol<sup>-1</sup>, - 393 kJ mol<sup>-1</sup>, 81 kJ mol<sup>-1</sup> and 9.7 kJ mol<sup>-1</sup> respectively. Find the value of Δ<sub>r</sub>H for the reaction:



Answer

Δ<sub>r</sub>H for a reaction is defined as the difference between Δ<sub>f</sub>H value of products and Δ<sub>f</sub>H value of reactants.

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

For the given reaction,



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

Substituting the values of  $\Delta_f H$  for  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}_4$ , and  $\text{CO}$  from the question, we get:

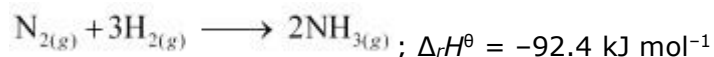
$$\Delta_r H = \left[ \left\{ 81 \text{ kJ mol}^{-1} + 3(-393) \text{ kJ mol}^{-1} \right\} - \left\{ 9.7 \text{ kJ mol}^{-1} + 3(-110) \text{ kJ mol}^{-1} \right\} \right]$$

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

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

#### Question 6.13:

Given

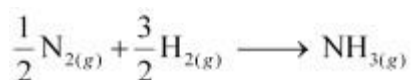


What is the standard enthalpy of formation of  $\text{NH}_3$  gas?

Answer

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.

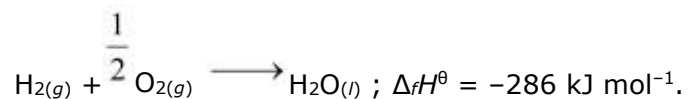
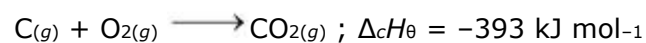
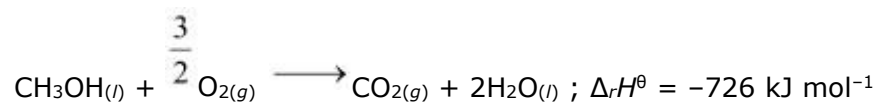
Re-writing the given equation for 1 mole of  $\text{NH}_{3(g)}$ ,



$$\begin{aligned} \therefore \text{Standard enthalpy of formation of NH}_{3(g)} &= \frac{1}{2} \Delta_r H^\theta \\ &= \frac{1}{2} (-92.4 \text{ kJ mol}^{-1}) \\ &= -46.2 \text{ kJ mol}^{-1} \end{aligned}$$

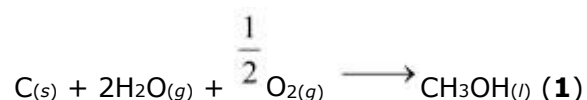
#### Question 6.14:

Calculate the standard enthalpy of formation of  $\text{CH}_3\text{OH}_{(l)}$  from the following data:



Answer

The reaction that takes place during the formation of  $\text{CH}_3\text{OH}_{(l)}$  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)

$$\Delta_f H^\theta [\text{CH}_3\text{OH}_{(l)}] = \Delta_c H^\theta + 2\Delta_f H^\theta [\text{H}_2\text{O}_{(l)}] - \Delta_r H^\theta$$

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

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

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

### Question 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  $\text{CCl}_{4(g)}$ .

$$\Delta_{\text{vap}} H^\theta (\text{CCl}_4) = 30.5 \text{ kJ mol}^{-1}.$$

$$\Delta_f H^\theta (\text{CCl}_4) = -135.5 \text{ kJ mol}^{-1}.$$

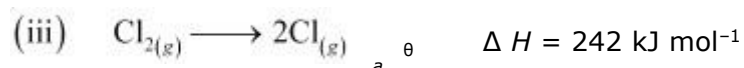
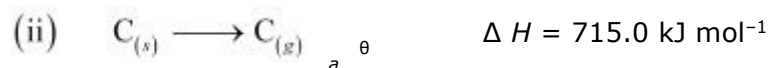
$$\Delta_a H^\theta (\text{C}) = 715.0 \text{ kJ mol}^{-1}, \text{ where } \Delta_a H^\theta \text{ is enthalpy of atomisation}$$

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

Answer

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





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

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

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

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

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

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

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

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

### Question 6.16:

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

Answer

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

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

### Question 6.17:

For the reaction at 298 K,



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

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

Answer

From the expression,

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

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

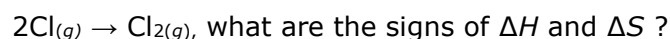
$$\begin{aligned} T &= (\Delta H - \Delta G) \frac{1}{\Delta S} \\ &= \frac{\Delta H}{\Delta S} \quad (\Delta G = 0 \text{ at equilibrium}) \\ &= \frac{400 \text{ kJ mol}^{-1}}{0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

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

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.

**Question 6.18:**

For the reaction,



Answer

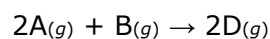
$\Delta H$  and  $\Delta S$  are negative

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.

**Question 6.19:**

For the reaction

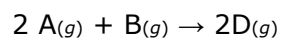


$$\Delta U^\ominus = -10.5 \text{ kJ and } \Delta S^\ominus = -44.1 \text{ JK}^{-1}.$$

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

Answer

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  $\Delta G^\theta$ :

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

$$= -12.98 \text{ kJ} - (298 \text{ K}) (-44.1 \text{ J K}^{-1})$$

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

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

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

#### Question 6.20:

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

Answer

From the expression,

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

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

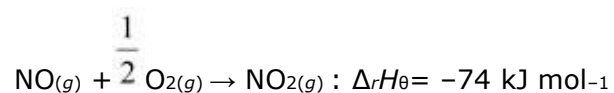
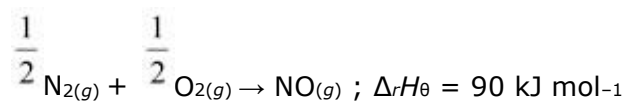
$$= (2.303) (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) (300 \text{ K}) \log 10$$

$$= -5744.14 \text{ J mol}^{-1}$$

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

#### Question 6.21:

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



Answer

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  $\text{NO}_{2(g)}$ .

#### Question 6.22:

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

Answer

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.  $q_{surr} = +286 \text{ kJ mol}^{-1}$

$$\begin{aligned} \text{Entropy change } (\Delta S_{surr}) \text{ for the surroundings} &= \frac{q_{surr}}{T} \\ &= \frac{286 \text{ kJ mol}^{-1}}{298 \text{ K}} \end{aligned}$$

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