

# CHAPTER 5

# Thermodynamics

VEDA  
ACADEMY

CLASS 11<sup>TH</sup>

## NCERT EXERCISE AND SOLUTIONS - CHEMISTRY



**Q. 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:-**

The correct option is B whose value is independent of path

A thermodynamic state function is a quantity whose value is independent of path. Thus, enthalpy is a state function.

Its value depends on initial and final states and is independent of path followed.

**Q. 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:-**

option (iii) correct

For the process to occur under adiabatic conditions the correct condition is  $q=0$ .

There is no exchange of heat.

**Q. 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 **ii is correct**.

**Q. 4.**  $\Delta U^\circ$  of combustion of methane is  $-X \text{ kJ mol}^{-1}$ . The value of  $\Delta H^\circ$  is:

- (a)  $< \Delta U^\circ$
- (b)  $= \Delta U^\circ$
- (c)  $> \Delta U^\circ$
- (d) 0

**ANSWER:-**

The correct option is c

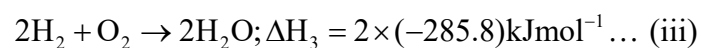
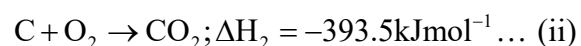
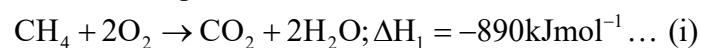


**Q. 5.** The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are  $-890.3\text{kJmol}^{-1}$ ,  $-393.5\text{kJmol}^{-1}$ ,  $-285.8\text{kJmol}^{-1}$  respectively. Enthalpy of formation of  $\text{CH}_4$  will be:

- (a)  $-74.8\text{ kJ mol}^{-1}$
- (b)  $-52.27\text{ kJ mol}^{-1}$
- (c)  $+52.26\text{ kJ mol}^{-1}$
- (d)  $+74.8\text{ kJ mol}^{-1}$

**ANSWER:-**

The correct option is A- $74.8\text{ kJ mol}^{-1}$



Required reaction  $\rightarrow \text{C} + 2\text{H}_2 \rightarrow \text{CH}_4$  (g)  $\Delta H_f = ?$

From equation (ii) - (i) + (iii)

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

Hence option a is correct.

**Q. 6.** A reaction,  $\text{A} + \text{B} \rightarrow \text{C} + \text{D} + \text{q}$  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:-**

The correct option is iv.

A reaction,  $\text{A} + \text{B} \rightarrow \text{C} + \text{D} + \text{q}$  is found to have a positive entropy change. The reaction will be possible at any temperature.

Explanation:

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,

$\Delta S =$  positive

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

$\Rightarrow \Delta G =$  negative

Therefore, the reaction is spontaneous at any temperature.



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:-**

To find the change in internal energy of the process, we can use the first law of thermodynamics, which states:

$$\Delta U = Q + W$$

Where,  $\Delta U$  is the change in internal energy,

$Q$  is the heat absorbed by the system,

$W$  is the work done by the system.

Heat absorbed by the system,  $Q = +701\text{J}$  (since heat is absorbed, it is positive).

Work done by the system,  $W = -394\text{J}$  (since work is done by the system, it is negative).

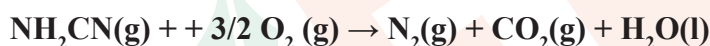
$$\Delta U = 701\text{J} + (-394\text{J})$$

$$\Delta U = 701\text{J} - 394\text{J} = 307\text{J}$$

The change in internal energy of the process is:

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

- Q. 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:-**

For given reaction,  $\Delta n = 1 + 1 - 1.5 = 0.5$ .

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

$$= -742.7 + 0.5 \times 8.314 \times 10^{-3} \times 298$$

$$= -742.7 + 1.2 = -741.5 \text{ kJ mole}^{-1}$$

- Q. 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  $24 \text{ J mol}^{-1} \text{ K}^{-1}$ .

**ANSWER:-**

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

$$= 2.22 \text{ mol}$$

$$2) \text{ Molar heat capacity(c)} = 24.\text{mol}^{-1} \text{ K}^{-1}$$

$$\text{Rise in temperature } \Delta T = 55 - 35$$

$$= 20 \text{ K}$$

$$3) \text{ Heat evolved (q)} = C \times m \times T$$

$$= (24.\text{mol}^{-1} \text{ K}^{-1} \times 2.22 \text{ mol}) \times (20 \text{ K})$$

$$= 1065.7 \text{ J}$$

$$= 1.061 \text{ kJ}$$



**Q. 10.** Calculate the enthalpy change of freezing of 1.0 mol of water at to ice

at  $-10^{\circ}\text{C}$ ,  $\Delta_{\text{fus}}H = 6.03\text{kJmol}^{-1}$  at  $0^{\circ}\text{C}$ .

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

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

**ANSWER:-**

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

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

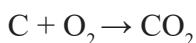
$$\begin{aligned} \text{Total } \Delta H &= C_p [\text{H}_2\text{O(l)}] \Delta T + \Delta H_{\text{freezing}} + C_p [\text{H}_2\text{O(s)}] \Delta T \\ &= (75.3 \text{ J mol}^{-1}\text{K}^{-1})(0 - 10)\text{K} + (-6.03 \times 10^3 \text{ J mol}^{-1}) + (36.8 \text{ J mol}^{-1}\text{K}^{-1})(-10 - 0)\text{K}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

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

**Q. 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.

**ANSWER:-**

The combustion of carbon to form carbon dioxide ( $\text{CO}_2$ ) can be represented by the following balanced chemical equation:



The enthalpy change ( $\Delta H$ ) for this reaction is given as  $-393.5 \text{ kJ/mol}$ . This means that when 1 mole of carbon combusts, 393.5 kJ of heat is released.

$$\begin{aligned} \text{Moles of } \text{CO}_2 &= \frac{\text{mass of } \text{CO}_2}{\text{molar mass of } \text{CO}_2} \\ &= \frac{35.2\text{g}}{44.01\text{g/mol}} \approx 0.799\text{moles} \\ \text{Heat released} &= \text{moles of } \text{CO}_2 \times \Delta H \\ &= 0.799\text{moles} \times (-393.5\text{kJ/mol}) \approx -314.8\text{kJ} \end{aligned}$$

The heat released upon the formation of 35.2 g of  $\text{CO}_2$  from carbon and dioxygen gas is approximately  $-314.8 \text{ kJ}$ .



**Q. 12.** Enthalpies of formation of  $\text{CO}(\text{g})$ ,  $\text{CO}_2(\text{g})$ ,  $\text{N}_2\text{O}(\text{g})$  and  $\text{N}_2\text{O}_4(\text{g})$  are  $-110$ ,  $-393$ ,  $81$  and  $9.7$   $\text{kJ mol}^{-1}$  respectively. Find the value of  $\Delta_r H$  for the reaction:



**ANSWER:-**

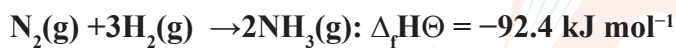
$$\Delta H_f^\circ (\text{N}_2\text{O}_4) = +9.7 \text{ Jmol}^{-1} \quad \Delta H_f^\circ (\text{CO}) = -110 \text{ kJmol}^{-1}$$

$$\Delta H_f^\circ (\text{N}_2\text{O}) = +81.0 \text{ kJmol}^{-1}$$

$$\Delta H_f^\circ (\text{CO}_2) = -393 \text{ kJmol}^{-1}$$

$$\begin{aligned} \Delta H_f^\circ &= \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants}) = [\Delta H_f^\circ (\text{N}_2\text{O}) + 3\Delta H_f^\circ (\text{CO}_2)] \\ &\quad - [\Delta H_f^\circ (\text{N}_2\text{O}_4) + 3\Delta H_f^\circ (\text{CO})] \\ &= [81 + 3(-393)] - [9.7 + 3(-110)] \\ &= -777.7 \text{ KJ} \end{aligned}$$

**Q. 13.** Given,

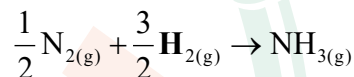


What is the standard enthalpy of formation of  $\text{NH}_3$  gas?

**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  $\text{NH}_3(\text{g})$



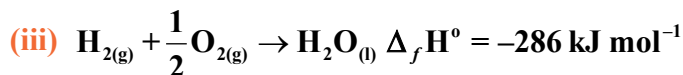
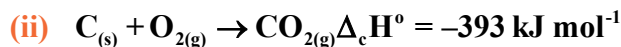
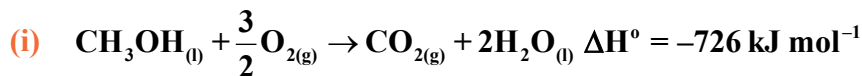
Standard enthalpy of formation of

$$= 1/2 \Delta_r H^\ominus$$

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

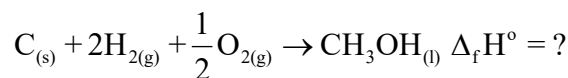
$$= -46.2 \text{ kJ mol}^{-1}$$

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



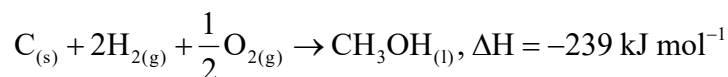
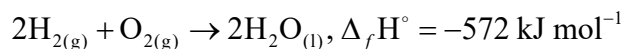
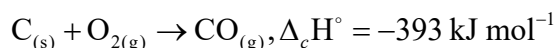
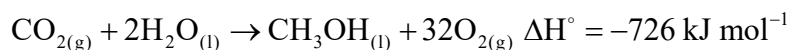
**ANSWER:-**

Required equation



Reversing the equation (i), multiply equation (iii) by (i) and add all equations.

Equation (i) + (ii) + 2 × (iii)



**Q. 15.** Calculate the enthalpy change for the process



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

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

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

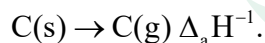
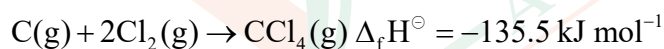
$$\Delta_a H^\ominus_{(\text{C})} = 715.0 \text{ kJ mol}^{-1}$$

where  $\Delta_a H^\ominus$  is enthalpy of atomisation

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

**ANSWER:-**

The given chemical reactions are:



Now for calculating enthalpy change for the process  $\text{CCl}_4(g) \rightarrow \text{C}(g) + 4\text{Cl}(g)$ , we have to follow following algebraic process

Equation(2) + 2 × Equation(3) - Equation(1) - Equation(4)

$$\Delta H = \Delta_a H^\ominus + 2\Delta_a H^\ominus_{\text{Cl}_2} - \Delta_{\text{vap}} H^\ominus - \Delta_f H^\ominus$$

$$= 715 + 2 \times 242 - 30.5 - (-135.5)$$

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

The bond enthalpy of C-Cl in  $\text{CCl}_4 = \frac{1304}{4} = 326 \text{ kJ mol}^{-1}$ .



**Q. 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

**Q. 17.** For the reaction at 298 K,  $2A + B \rightarrow C$

$$\Delta H = 400 \text{ KJ mol}^{-1} \text{ and } \Delta S = 0.02 \text{ KJ K}^{-1} \text{ mol}^{-1}$$

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

**ANSWER:-**

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

$$\Delta G = 0$$

$$\Delta G = \Delta H - T\Delta S = 0$$

$$T = \Delta H / \Delta S = 4000 / 0.2 = 2000 \text{ K.}$$

For the reaction to be spontaneous  $\Delta G$  must be negative.

Therefore, temperature should be greater than 2000 K.

**Q. 18.** For the reaction,  $2 \text{Cl}(g) \rightarrow \text{Cl}_2(g)$ , what are the signs of  $\Delta H$  and  $\Delta S$ ?

**ANSWER:-**

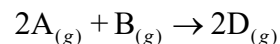
$\Delta H$  and  $\Delta S$  are negative

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.

**Q. 19.** For the reaction,  $2A(g) + B(g) \rightarrow 2D(g)$ ,  $\Delta U = -10.5 \text{ KJ}$  and  $\Delta S = -44.10 \text{ JK}^{-1}$ . 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  $\Delta U^\ominus$  in the expression of  $\Delta H$ :



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

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

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

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

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

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

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

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

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

- Q. 20.** The equilibrium constant for a reaction is 10. What will be the value of  $\Delta G^\ominus$ ?  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $T = 300 \text{ K}$ .

**ANSWER:-**

From the expression,

$$\Delta G^\ominus = -2.303 RT \log k_{\text{eq}}$$

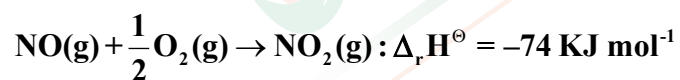
$\Delta G^\ominus$  for the reaction,

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

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

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

- Q. 21.** Comment on the thermodynamic stability of  $\text{NO}(\text{g})$  given



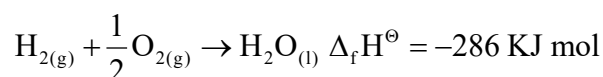
**ANSWER:-**

The enthalpy of formation of  $\text{NO}$  has positive value. Hence,  $\text{NO}$  is unstable.

During formation of  $\text{NO}_2$ , energy is released. Hence,  $\text{NO}_2$  is formed.

- Q. 22.** Calculate the entropy change in surroundings when 1.00 mol of  $\text{H}_2\text{O}(\text{l})$  is formed under standard conditions.  $\Delta_r H^\ominus = -286 \text{ kJ mol}^{-1}$ .

**ANSWER:-**



From the above equation,



At 298 K, when 1 mole of  $\text{H}_2\text{O}$  is formed, 286 KJ of heat is released. The same amount of heat is absorbed by the surroundings.

$$\therefore q_{\text{surr.}} = +286\text{KJ} / \text{mol}; T = 298\text{K}$$

As we know that,

$$\Delta S_{\text{surr.}} = \frac{q_{\text{surr.}}}{T}$$

$$\therefore \Delta S_{\text{surr.}} = \frac{286}{298} = 0.96 \text{ KJ} / \text{mol} - \text{K}$$

Hence the entropy change in surroundings will be  $0.96 \text{ kJ mol}^{-1} \text{ K}^{-1}$ .

