CHAPTER
5

Thermodynamics

CLASS 11TH

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. **ΔU^o of combustion of methane is -X kJ mol^{-1}. The value of ΔH^o is:**

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

ANSWER:-

The correct option is c

Q. 5. **The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are $-890.3 kJmol^{-1}$, $-393.5 kJmol^{-1}$, $-285.8 kJmol^{-1}$ respectively. Enthalpy of formation of CH_{4g} will be:**

(a) **-74.8 kJ mol^{-1}**

(b) **-52.27 kJ mol^{-1}**

(c) **+52.26 kJ mol^{-1}**

(d) **+74.8 kJ mol^{-1}**

ANSWER:-

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

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O; \Delta H_1 = -890 kJmol^{-1} \ldots$ (i)

$C + O_2 \rightarrow CO_2; \Delta H_2 = -393.5 kJmol^{-1} \ldots$ (ii)

$2H_2 + O_2 \rightarrow 2H_2O; \Delta H_3 = 2 \times (-285.8) kJmol^{-1} \ldots$ (iii)

Required reaction $\rightarrow$ $C + 2H_2 \rightarrow CH_4$ (g) ΔH_f = ?

From equation (ii) − (i) + (iii)

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

Hence option a is correct.

Q. 6. **A reaction, A + B $\longrightarrow$ C + 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:-

The correct option is iv.

A reaction, A + B $\longrightarrow$ C + D + q is found to have a positive entropy change. The reaction will be possible at anytemperature.

Explanation:

For a reaction to be spontaneous, should be negative.

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

According to the question, for the given reaction,

ΔS = positive

ΔH = 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, ΔU 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, $Q = +701J$ (since heat is absorbed, it is positive).

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

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

$\Delta U = 701J - 394J = 307J$

The change in internal energy of the process is:

$\Delta U = +307J$

Q. 8. **The reaction of cyanamide, NH_2CN (s), with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be –742.7 kJ mol^{-1} at 298 K. Calculate enthalpy change for the reaction at 298 K.**

$NH_2CN(g) + + 3/2\ O_2\ (g) \rightarrow N_2(g) + CO_2(g) + H_2O(l)$

ANSWER:-

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

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

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

$= -742.7 + 1.2 = -741.5$ 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 J mol^{-1} K^{-1}.**

ANSWER:-

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

$= 2.22$ mol

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

Rise in temperature $\Delta T = 55 - 35$

$= 20$ K

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

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

$= 1065.7$ J

$= 1.061$ kJ

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

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

$$C_P\left[H_2O(l)\right] = 75.3\text{Jmol}^{-1}\text{K}^{-1}$$

$$C_P\left[H_2O(s)\right] = 36.8\text{Jmol}^{-1}\text{K}^{-1}$$

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° to 1 mol of ice at 0°C.

(c) Energy change involved in the transformation of 1 mol of ice at to 1 mol of ice at −1C.

$$\text{Total } \Delta H = C_p\left[H_2O(l)\right]\Delta T + \Delta H_{\text{freezing}} + C_p\left[H_2O(s)\right]\Delta T$$

$$= \left(75.3 \text{ J mol}^{-1}\text{K}^{-1}\right)(0-10)\text{K} + \left(-6.03\times10^{3} \text{ J mol}^{-1}\right) + \left(36.8 \text{ J mol}^{-1}\text{K}^{-1}\right)(-10-0)\text{K}$$

$$= -753 \text{ J mol}^{-1} - 6030 \text{ J mol}^{-1} - 368 \text{ J mol}^{-1}$$

$$= -7151 \text{ J mol}^{-1}$$

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

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

Q. 11. **Enthalpy of combustion of carbon to CO_2 is –393.5 kJ mol^{-1}. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.**

ANSWER:-

The combustion of carbon to form carbon dioxide (CO_2) can be represented by the following balanced chemical equation**:**

$C + O_2 \rightarrow CO_2$

The enthalpy change (ΔH) for this reaction is given as -393.5 kJ/mol. This means that when 1 mole of carbon combusts, 393.5 kJ of heat is released.

$$\text{Moles of } CO_2 = \frac{\text{mass of } CO_2}{\text{molar mass of } CO_2}$$

$$= \frac{35.2\text{g}}{44.01\text{g}/\text{mol}} \approx 0.799\text{moles}$$

$$\text{Heat released} = \text{ moles of } CO_2 \times \Delta H$$

$$= 0.799\text{moles} \times (-393.5\text{kJ}/\text{mol}) \approx -314.8\text{kJ}$$

The heat released upon the formation of 35.2 g of CO_2 from carbon and dioxygen gas is approximately -314.8 kJ.

Q. 12. **Enthalpies of formation of CO(g), CO_2(g), N_2O(g) and N_2O_4(g) are –110, – 393, 81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_f H$ for the reaction:**

$N_2O_4(g) + 3CO \rightarrow N_2O(g) + 3CO_2(g)$.

ANSWER:-

$$\Delta H_f^\circ(N_2O_4) = +9.7 Jmol^{-1} \Delta H_f^\circ(CO) = -110 kJmol^{-1}$$

$$\Delta H_f^\circ(N_2O) = +81.0 kJmol^{-1}$$

$$\Delta H_f^\circ(CO_2) = -393 kmol^{-1}$$

$$\Delta H_f^\circ = \sum \Delta H_f^\circ(\text{ products}) - \sum \Delta H_f^\circ(\text{ reactants}) = \left[\Delta H_f^\circ(N_2O) + 3\Delta H_f^\circ CO_2\right] - \left[\Delta H_f^\circ(N_2O_4) - 3\Delta H_f^\circ(CO)\right]$$

$$= [81 + 3(-393)] - [9.7 + 2(-110)]$$

$$= -777.7 KJ$$

Q. 13. **Given,**

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$: $\Delta_f H\Theta = -92.4$ kJ mol^{-1}

What is the standard enthalpy of formation of 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 $NH_{3(g)}$

$$\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightarrow NH_{3(g)}$$

Standard enthalpy of formation of

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

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

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

Q. 14. **Calculate the standard enthalpy of formation of CH_3OH_1 from the following data:**

(i) $$CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}\ \Delta H^\circ = -726 \text{ kJ mol}^{-1}$$

(ii) $$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \Delta_c H^\circ = -393 \text{ kJ mol}^{-1}$$

(iii) $$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}\ \Delta_f H^\circ = -286 \text{ kJ mol}^{-1}$$

ANSWER:-

Required equation

$$C_{(s)} + 2H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow CH_3OH_{(l)}\ \Delta_f H^\circ = ?$$

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

Equation (i) + (ii) +2 × (iii)

$CO_{2(g)} + 2H_2O_{(l)} \rightarrow CH_3OH_{(l)} + 32O_{2(g)}\ \Delta H^{\circ} = -726\ kJ\ mol^{-1}$

$C_{(s)} + O_{2(g)} \rightarrow CO_{(g)}, \Delta_c H^{\circ} = -393\ kJ\ mol^{-1}$

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}, \Delta_f H^{\circ} = -572\ kJ\ mol^{-1}$

$C_{(s)} + 2H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow CH_3OH_{(l)}, \Delta H = -239\ kJ\ mol^{-1}$

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

$\mathbf{CCl_4(g) \rightarrow C(g) + 4Cl(g)}$

and calculate bond enthalpy of C − Cl in CCl_4 (g)

$\mathbf{\Delta_{vap}H^{\ominus}_{(CCl_4)} = 30.5\ kJ\ mol^{-1}}$

$\mathbf{\Delta_f H^{\ominus}_{(CCl_4)} = -135.5\ kJ\ mol^{-1}}$

$\mathbf{\Delta_a H^{\ominus}_{(C)} = 715.0\ kJ\ mol^{-1}}$

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

$\mathbf{\Delta_a H^{\ominus}_{(Cl_2)} = 242\ kJ\ mol^{-1}}$

ANSWER:-

The given chemical reactions are:

$CCl_4(l) \rightarrow CCl_4(g)\ \Delta_{vap}H^{\ominus} = 30.5\ kJ\ mol^{-1}$

$C(g) + 2Cl_2(g) \rightarrow CCl_4(g)\ \Delta_f H^{\ominus} = -135.5\ kJ\ mol^{-1}$

$C(s) \rightarrow C(g)\ \Delta_a H^{-1}.$

$Cl_2(g) \rightarrow 2Cl(g)\ \Delta_a H^{\ominus} = 242.0\ kJ\ mol^{-1}$

Now for calculating enthalpy change for the process CCl_4 (g) → C(g) + 4Cl(g), we have to follow following algebric process

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

$\Delta H = \Delta_a H^{\ominus} + 2\Delta_a H^{\ominus} Cl_2 - \Delta_{vap} H^{\ominus} - \Delta_f H^{\ominus}$

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

$\Delta H = 1304 kJmol^{-1}$

The bond enthalpy of C-Cl in $CCl_4 = \frac{1304}{4} = 326\ kJ\ mol^{-1}$.

Q. 16. **For an isolated system, $\Delta U = 0$, what will be ΔS?**

ANSWER:-

ΔS will be positive i.e., greater than zero Since $\Delta U = 0$, ΔS will be positive and the reaction will be spontaneous

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

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

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range?

ANSWER:-

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

$\Delta G = 0$

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

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

For the reaction to be spontaneous ΔG must be negative.

Therefore, temprature should be greater than 2000 K.

Q. 18. **For the reaction, $2\ Cl(g) \rightarrow Cl_2(g)$, what are the signs of ΔH and ΔS?**

ANSWER:-

ΔH and ΔS 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, ΔH is negative. Also, two moles of atoms have more randomness than one mole of a molecule. Since spontaneity is decreased, ΔS is negative for the given reaction.

Q. 19. **For the reaction, $2\ A(g) + B(g) \rightarrow 2D(g)$, $\Delta U = -10.5KJ$ and $\Delta S = -44.10JK^{-1}$. Calculate $\Delta G^\ominus$ for the reaction and reaction and predict whether the reaction may occur spontaneously**

ANSWER:-

For the given reaction,

$2A_{(g)} + B_{(g)} \rightarrow 2D_{(g)}$

$\Delta n_g = 2 - (3)$

$= -1$ mole

Substituting the value of $\Delta U^\ominus$ in the expression of ΔH:

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

$$-10.5\text{kJ} - (-1)\left(8.314\times10^{-3}\,\text{kJK}^{-1}\text{mol}^{-1}\right)(298\text{K})$$

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

Substituting the values of ΔH^{θ} and ΔS^{θ} in the expression of ΔG^{θ} :

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

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

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

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

Since ΔG^{θ} 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 ΔG^0 ? R = 8.314 JK^{-1} mol^{-1}, T = 300 K.**

ANSWER:-

From the expression,

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

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

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

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

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

Q. 21. **Comment on the thermodynamic stability of NO(g) given**

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g);\ \Delta_r H^{\ominus} = 90\ KJ\ mol^{-1}$$

$$NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g):\ \Delta_r H^{\ominus} = -74\ KJ\ mol^{-1}$$

ANSWER:-

The enthalpy of formation of NO has positive value. Hence, NO is unstable.
During formation of NO_2, energy is released. Hence, NO_2 is formed.

Q. 22. **Calculate the entropy change in surroundings when 1.00 mol of $H_2O(l)$ is formed under standard conditions. $\Delta_f H^{\ominus} = -286$ kJ mol^{-1}.**

ANSWER:-

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}\ \Delta_f H^{\ominus} = -286\ KJ\ mol$$

From the above equation,

At 298 K, when 1 mole of H_2O is formed, 286 KJ of heat is released. The same amount of heat is absorbed by the surroundings.

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

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 kJ mol^{-1} K^{-1}.