



II. Short Answer Type Questions

Question 1. When liquid benzene is oxidised at constant pressure at 300 K, the change in enthalpy is -3728 kJ. What is the change in internal energy at the same temperature?

Answer: The chemical equation representing the oxidation of liquid benzene is:



$$\Delta H = -3728 \text{ kJ}; \quad \Delta n_g = 6 - \frac{15}{2} = -\frac{3}{2} \text{ mol}$$

$$R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}, T = 300 \text{ K}$$

According to the relation, $\Delta H = \Delta U + \Delta n_g RT$

$$(-3728 \text{ kJ}) = \Delta U + \left(-\frac{3}{2} \text{ mol}\right)$$

$$\times (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})$$

$$(-3728 \text{ kJ}) = \Delta U - 3.7413 \text{ kJ}$$

$$\Delta U = -3728 + 3.7413 = -3724.2587 \text{ kJ}$$

Question 2. The enthalpy of formation of methane at constant pressure and 300 K is - 78.84 kJ. What will be the enthalpy of formation at constant volume?

Answer: The equation representing the enthalpy of formation of methane is:



$$\Delta H = -78.84 \text{ kJ}; \quad \Delta n_g = 1 - 2 = -1 \text{ mol}$$

$$R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}; \quad T = 300 \text{ K}$$

According to the relation, $\Delta H = \Delta U + \Delta n_g RT$

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

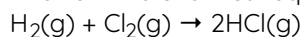
$$= (-78.84 \text{ kJ}) - (1 \text{ mol})$$

$$\times (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times 300 \text{ K}$$

$$= -78.84 - 2.49 = -81.35 \text{ kJ}$$

Question 3. Calculate the enthalpy change for the reaction: $\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g)$. Given that bond energies of H-H, Cl-Cl and H-Cl bonds are 433, 244 and 431 kJ mol⁻¹ respectively.

Answer: The chemical equation for the reaction is:



The enthalpy of reaction is:

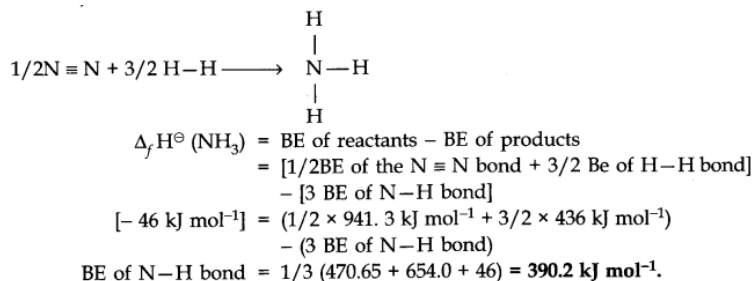
$$\Delta_r H = \sum \text{B.E. of reactants} - \sum \text{B.E. of products} = [\text{B.E. of H-H bond} + \text{B.E. of Cl-Cl bond}]$$

$$- [2 \times \text{B.E. of H-Cl bond}]$$

$$= (433 + 244) - (2 \times 431) = 433 + 244 - 862 = -185 \text{ kJ}$$

Question 4. The bond enthalpy of $\text{H}_2(g)$ is 436 kJ mol⁻¹ and that of $\text{N}_2(g)$ is 941.3 kJ mol⁻¹. Calculate the average bond enthalpy of an N-H bond in ammonia. Given: $\Delta_f H^\circ(\text{NH}_3) = -46 \text{ kJ mol}^{-1}$

Answer:

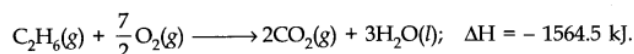


Question 5. When two moles of $\text{C}_2\text{H}_6(\text{g})$ are burnt, 3129 kJ of heat is liberated. Calculate the heat of formation of $\text{C}_2\text{H}_6(\text{g})$. $\Delta_f H^\ominus$ for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -393.5 and -286 kJ mol⁻¹ respectively.

Answer:

The heat of combustion of $\text{C}_2\text{H}_6(\text{g})$ per mole (ΔH) = $\frac{-3129}{2} = -1564.5 \text{ kJ}$.

The combustion equation may be written as :



$$\begin{aligned} \text{Now,} \quad \Delta H &= \sum \Delta_f H^\ominus (\text{products}) - \sum \Delta_f H^\ominus (\text{reactants}) \\ &= [2\Delta_f H^\ominus \text{CO}_2(\text{g}) + 3\Delta_f H^\ominus \text{H}_2\text{O}(\text{l})] \\ &\quad - \left[\Delta_f H^\ominus \text{C}_2\text{H}_6(\text{g}) + \frac{7}{2} \Delta_f H^\ominus \text{O}_2(\text{g}) \right] \end{aligned}$$

On substituting the values in the above equation

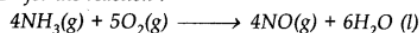
$$-1564.5 = [2 \times (-393.5) + 3 \times (-286)] - [\Delta_f H^\ominus \text{C}_2\text{H}_6(\text{g}) + \text{zero}]$$

$$-1564.5 = -787 - 858 - \Delta_f H^\ominus \text{C}_2\text{H}_6(\text{g})$$

$$\text{or} \quad \Delta_f H^\ominus \text{C}_2\text{H}_6(\text{g}) = -787 - 858 + 1564.5 = \mathbf{-80.5 \text{ kJ}}.$$

Question 6.

Calculate ΔG^\ominus for the reaction :



Given that $\Delta_f G^\ominus$ for the formation of $\text{NH}_3(\text{g})$, $\text{NO}(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -16.8 kJ mol⁻¹, +86.7 kJ mol⁻¹ and -237.2 kJ mol⁻¹ respectively. Predict feasibility of reaction under the conditions.

Answer:

$$\begin{aligned} \Delta G^\ominus &= \sum \Delta_f G^\ominus (\text{products}) - \sum \Delta_f G^\ominus (\text{reactants}) \\ &= \{4 \text{ mol} \times \Delta_f G^\ominus \text{NO}(\text{g}) + 6 \text{ mol} \times \Delta_f G^\ominus \text{H}_2\text{O}(\text{l})\} \\ &\quad - \{4 \text{ mol} \times \Delta_f G^\ominus \text{NH}_3(\text{g}) + 5 \text{ mol} \times \Delta_f G^\ominus \text{O}_2(\text{g})\} \\ &= [4 \text{ mol} \times (86.7 \text{ kJ mol}^{-1}) + 6 \times (-237.2 \text{ kJ mol}^{-1})] \\ &\quad - [4 \text{ mol} \times (-16.8 \text{ kJ mol}^{-1}) + 5 \times \text{zero}] \\ &= (346.8 \text{ kJ} - 1423.2 \text{ kJ}) + 67.2 \text{ kJ} = \mathbf{-1009.2 \text{ kJ}}. \end{aligned}$$

Since ΔG^\ominus is negative, the reaction is feasible in the forward direction.

Question 7.

Determine whether or not it is possible for sodium to reduce aluminium oxide to aluminium at 298 K.

Given: $\Delta_f G^\ominus \text{Al}_2\text{O}_3(\text{s}) = -1582 \text{ kJ mol}^{-1}$; $\Delta_f G^\ominus \text{Na}_2\text{O}(\text{s}) = -377 \text{ kJ mol}^{-1}$.

Answer:

The reaction involved is



$$\begin{aligned} \Delta G^\ominus &= \sum \Delta_f G^\ominus (\text{p}) - \sum \Delta_f G^\ominus (\text{r}) \\ &= [2\Delta_f G^\ominus \text{Al}(\text{s}) + 3\Delta_f G^\ominus \text{Na}_2\text{O}(\text{s})] - [\Delta_f G^\ominus \text{Al}_2\text{O}_3(\text{s}) + 6\Delta_f G^\ominus \text{Na}(\text{s})] \\ &= [2 \times 0 + 3 \times (-377)] - [-1582 + 6 \times 0] \\ &= \mathbf{451 \text{ kJ mol}^{-1}}. \end{aligned}$$

This means that sodium can not reduce aluminium oxide (Al_2O_3) to aluminium metal because ΔG^\ominus comes out to be positive.

Question 8. 1 g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$. During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7 kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm?

Answer: Suppose q is the quantity of heat from the reaction mixture and C_v is the heat capacity of the calorimeter, then the quantity of heat absorbed by the calorimeter.

$$q = C_v / \Delta T$$

Quantity of heat from the reaction will have the same magnitude but opposite sign because the heat lost by the system (reaction mixture) is equal to the heat gained by the calorimeter.

$$q = -C_v \times \Delta T = -20.7 \text{ kJ/K} \times (299 - 298) \text{ K} = -20.7 \text{ kJ}$$

(Here, negative sign indicates the exothermic nature of the reaction). Thus, ΔU for the combustion of the 1g of graphite = -20.7 kJ K⁻¹ For combustion of 1 mol of graphite,

$$\begin{aligned} &= \frac{12.0 \text{ g mol}^{-1} \times (-20.7 \text{ kJ})}{1 \text{ g}} \\ &= -2.48 \times 10^2 \text{ kJ mol}^{-1}. \text{ Since } \Delta n_g = 0, \\ \Delta H &= \Delta U = -2.48 \times 10^2 \text{ kJ mol}^{-1} \end{aligned}$$

Question 9.

Calculate $\Delta_r G^\ominus$ for conversion of oxygen to ozone, $3/2 \text{ O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})$ at 298 K. If K_p for this conversion is 2.47×10^{-29} .

Answer:

$$\begin{aligned} \text{We know } \Delta_r G^\ominus &= -2.303 RT \log K_p \\ \text{and } R &= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \\ \text{Therefore, } \Delta_r G^\ominus &= -2.303 (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) (\log 2.47 \times 10^{-29}) \\ &= 163000 \text{ J mol}^{-1} = 163 \text{ kJ mol}^{-1}. \end{aligned}$$

Question 10. Define the following:

- (i) First law of thermodynamics.
- (ii) Standard enthalpy of formation.

Answer:

(i) First law of thermodynamics: It states that energy can neither be created nor be destroyed. The energy of an isolated system is constant.

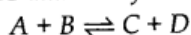
$$\Delta u = q + w$$

(ii) It is defined as the amount of heat evolved or absorbed when one mole of the compound is formed from its constituent elements in their standard states.

Question 11.

(a) Why is the entropy of a substance taken as zero at 0K?

(b) Calculate ΔG and ΔG^\ominus for the reaction.



at 27°C. Equilibrium constant (K) for this reaction = 10^2

Answer:

(a) From third law of thermodynamics, it can be explained that entropy of a perfectly crystalline substance is zero at zero kelvin.

$$\begin{aligned} \Delta G &= 0 \text{ (because the reaction is in equilibrium)} \\ \Delta G^\ominus &= -2.303 RT \log K \\ &= -2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \log 10^2 \\ &= -11.488 \text{ kJ mol}^{-1} \end{aligned}$$

Question 12. Give reason for the following:

- (a) Neither q nor w is a state function but q + w is a state function.
- (b) A real crystal has more entropy than an ideal crystal.

Answer:

$$(a) q + w = \Delta u$$

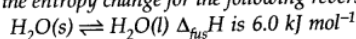
As Δu is a state function hence, q + w is a state function.

(b) A real crystal has some disorder due to the presence of defects in its structural arrangement whereas ideal crystal does not have any disorder. Hence, a real crystal has more entropy than an ideal crystal.

Question 13.

(a) Under what condition, the heat evolved or absorbed in a reaction is equal to its free energy change?

(b) Calculate the entropy change for the following reversible process



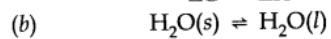
Answer:

$$(a) \quad \Delta G = \Delta H - T\Delta S$$

When the reaction is carried out at 0°k

$$\text{or} \quad \Delta S = 0$$

$$\Delta G = \Delta H$$



$$\Delta_{\text{fus}}H = 6.0 \text{ kJ mol}^{-1}$$

$$= 6000 \text{ J mol}^{-1}$$

$$T_f = 0^\circ\text{C} = (0 + 273) = 273 \text{ K}$$

$$\Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T_f} = \frac{6000 \text{ J mol}^{-1}}{273 \text{ K}} = 21.98 \text{ J K}^{-1} \text{ mol}^{-1}$$

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