



# SHIKSHA CLASSES

Subject : Chemistry

BOARD ANSWER PAPER

Total Marks : 20

Class : XII

Topic : 4. Chemical Thermodynamics

## Section (A)

**Q.1 : a) Select and write the most appropriate answer from the following alternatives of each sub question. (05)**

**i) Which of the following is not a state function?**

**Ans : (b) heat**

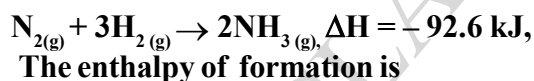
**ii) For which of the following substance enthalpy of formation is not equal to zero?**

**Ans. : (d)  $\text{CH}_3\text{OH}_{(l)}$**

**iii) For which of the following reaction entropy is negative?**

**Ans. : (a)  $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(s)}$**

**iv) Given reaction is**



**Ans.: (c)  $-46.3 \text{ kJ mol}^{-1}$**

**v) The correct thermodynamic conditions for the spontaneous reaction at all temperatures are**

**Ans.: (a)  $\Delta H < 0$  and  $\Delta S > 0$**

**(b) Very short answer type Question (02)**

**i) Write any two factors which affects the enthalpy of solution.**

**Ans. : 1) Solute - solute interaction :**

More solute - solute interaction, more is the enthalpy of solution.

**2) Solute - solvent interaction :**

More solute - solvent interaction less is

the enthalpy of solution.

**3) Solvent - solvent interaction :**

More solvent - solvent interaction, more is the enthalpy of solution.

**ii) Write any one condition for  $\Delta H = \Delta U$**

**Ans. :** The equation of second law of thermodynamic is

$$\Delta H = \Delta U + P\Delta V \text{ or } \Delta H = \Delta U + \Delta n RT$$

(1) In vacuum :-

$$P = 0$$

$$\therefore \Delta H = \Delta U$$

(2) When number of moles of gaseous reactants equal to gaseous products

$$\text{Then } \Delta n = 0$$

$$\therefore \Delta H = \Delta U$$

## Section (B)

**Q.2 : Answer the following questions. (Any three) (06)**

**i) Prove that  $\Delta H = \Delta U + \Delta nRT$**

**Ans. :**  $\Delta H$  and  $\Delta U$  are related by equation

$$\Delta H = \Delta U + P\Delta V$$

$$\Delta H = \Delta U + P(V_2 - V_1)$$

$$= \Delta U + PV_2 - PV_1$$

Where  $V_1$  is initial volume,  $V_2$  is final volume, if assuming reactants & products are ideal then applying ideal gas equation  $PV = nRT$

$$PV_1 = n_1RT \text{ and } PV_2 = n_2RT$$

$$\Delta H = \Delta U + n_2RT - n_1RT$$

$$= \Delta U + RT(n_2 - n_1)$$

$$\Delta H = \Delta U + \Delta nRT$$

ii) Write the sign conventions of q and W.

Ans : Sign Conventions :

Q (heat)

+ve = For endothermic reaction when heat is absorbed by system.

-ve = For exothermic reaction when heat is evolved by system.

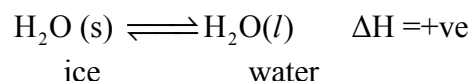
W (Work)

+ve = When work is done on system by surroundings (work of compression).

-ve = When work is done by system on surroundings (work of expansion).

iii) Is it possible for a reaction to be spontaneous yet endothermic. Comment with example.

Ans. : Some endothermic reactions are also spontaneous. For Ex. Melting of ice is endothermic process but it is spontaneous.



iv) 2 moles of an ideal gas are expanded isothermally and reversibly from 20 L to 30 L at 300 K. Calculate the work done ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )

$$\text{Ans : } W_{\max} = -2.303 nRT \log_{10} \frac{V_2}{V_1}$$

$$n = 2 \text{ mol. } T = 300 \text{ K, } V_1 = 20 \text{ L, } V_2 = 30 \text{ L}$$

$$R = 8.314 \text{ J/Kmol}$$

Substitutes all the value in above equation.

$$W_{\max} = -2.303 \times 2 \times 8.314 \times 300 \times \log_{10} 1.5$$

$$= -2022 \text{ J}$$

$$W_{\max} = -2.022 \text{ kJ}$$

### Section (C)

Q.3 : Answer the following question.

(Any One) (03)

i) Derive the expression for maximum work done during the expansion of an ideal gas in isothermal and reversible process.

Ans : 1) Consider ideal gas expands isothermally and reversibly. If  $P_{\text{ext}}$  is external pressure.

Smaller than pressure p of gas by infinitesimally.

It is consider that process occurs in number of steps dV is small change in volume.

2) Then small work done is  $dw = -P_{\text{ext}} dv$ .

3) If pressure of gas is greater by a small amount dP that  $P_{\text{ext}}$ . Hence  $P - P_{\text{ext}} = dp$  or

$$P_{\text{ext}} = p - dp.$$

4)  $dw = -(P - dp) dv = -Pdv + dpdv$  (neglecting  $dp dv$ )

$$\therefore dw = -pdv$$

5) Total work done obtained by integrating

$$\int_1^2 dw = - \int_{V_1}^{V_2} p dv$$

$$W_{\max} = - \int_{V_1}^{V_2} p dv$$

ideal gas equation for n-moles is  $PV = nRT$

$$\text{or } P = \frac{nRT}{V}$$

$$W_{\max} = - \int_{V_1}^{V_2} nRT \frac{dv}{V}$$

$$6) W_{\max} = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= -nRT \ln (V)_{V_1}^{V_2}$$

$$= -nRT (\ln V_2 - \ln V_1)$$

$$= -nRT \left( \ln \frac{V_2}{V_1} \right)$$

$$= -2.303 nRT \log_{10} \frac{V_2}{V_1}$$

At constant pressure, according to Boyle's law

$$P_1 V_1 = P_2 V_2$$

$$\text{or } \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$W_{\max} = -2.303 nRT \log_{10} \frac{P_1}{P_2}$$

ii) What is Enthalpy (H)? Derive relation between change in Enthalpy and heat transfer.

**Ans :** Enthalpy of a system is sum of internal Energy of a system and the energy equivalent to PV work

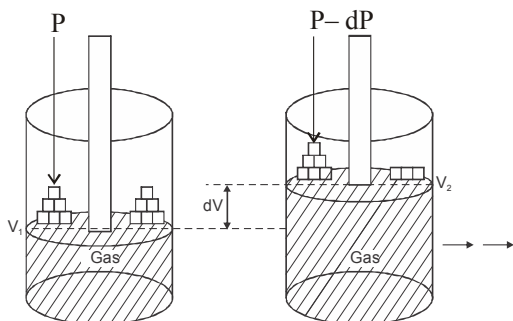
$$H = U + PV \quad \dots\dots (1)$$

Change in Enthalpy  $\Delta H$  is also state function

$$\Delta H = H_2 - H_1$$

Where  $H_1$  and  $H_2$  are the enthalpies of initial and final states, respectively

From eq<sup>n</sup>. (1)



$$H_1 = U_1 + P_1 V_1 \text{ and } H_2 = U_2 + P_2 V_2$$

$$\Delta H = U_2 + P_2 V_2 - (U_1 + P_1 V_1)$$

$$= (U_2 - U_1) + (P_2 V_2 - P_1 V_1)$$

At constant pressure

$$P_1 = P_2 = P$$

$$\therefore \Delta H = \Delta U + P\Delta V \quad \dots\dots (1)$$

According to first law of thermodynamics

$$\Delta U = q_p + w$$

$$\Delta U = q_p - P\Delta V$$

$$q_p = \Delta U + P\Delta V \quad \dots\dots (2)$$

From (1) and (2)

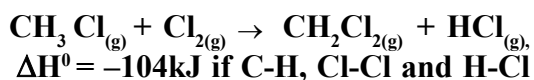
$$q_p = \Delta H$$

Thus change in Enthalpy of system is equal to heat transferred from it at constant pressure.

### Section (D)

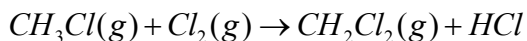
**Q.4 :** Answer the following question. (Any one) (04)

i) a) Calculate C-Cl bond enthalpy from following reaction



**bond enthalpies are 414, 243 and 431 kJ mol<sup>-1</sup> respectively.**

**Ans : Given :-**



$$\Delta H^0 = -104\text{kJ}$$

$$\Delta H^0(\text{C-H}) = 414\text{kJ}$$

$$\Delta H^0(\text{H-Cl}) = 431\text{kJ}$$

$$\Delta H^0(\text{C1-C1}) = 243\text{kJ}$$

$$\Delta H^0 = \sum \Delta H^0 (\text{reactants bonds})$$

$$- \sum \Delta H^0 (\text{product bonds})$$

$$= [3 \times \Delta H^0(\text{C-H}) + 1 \times \Delta H^0$$

$$(\text{C-C1}) + 1 \times \Delta H^0 (\text{C1-C1})]$$

$$(\text{C-C1}) + 1 \times \Delta H^0 (\text{C1-C1})]$$

$$- [2 \times \Delta H^0 (\text{C-H}) + 2 \times \Delta H^0$$

$$(\text{C-C1}) + \Delta H^0 (\text{H-Cl})]$$

$$-104 = [3 \times 414 + \text{C-C1} + 243]$$

$$- [2 \times 414 + 2(\text{C-C1}) + 431]$$

$$-104 = [1242 + 243 + \text{C-C1}]$$

$$- [828 + 2(\text{C-C1}) + 431]$$

$$= [1485 + \text{C-C1}] - [1259 + 2(\text{C-C1})]$$

$$-104 = 1485 - 1259 - (\text{C-C1})$$

$$\text{C-C1} = 1485 - 1259 + 104$$

$$= 1589 - 1259$$

$$\text{C-C1} = 334\text{kJ}$$

**b) Write the expression for enthalpy of reaction when enthalpies of all components are given and enthalpy of formation of all components are given.**

**Ans :** 1) The enthalpy of reaction when enthalpies of all components are given

$$\Delta H = \sum H \text{ products} - \sum H \text{ reactants}$$

Consider a reaction  $aA + bB \rightarrow cC + dD$

$$\therefore \Delta H^0 = (cH_C + dH_D) - (aH_A + bH_B)$$

2) The enthalpy of reaction when enthalpies of formations of all components are given

$$\Delta H^0 = \sum \Delta_f H^0 \text{ products} - \sum \Delta_f H^0$$

reactants

For reaction  $aA + bB \rightarrow cC + dD$

$$\Delta H^0 = (c\Delta_f H^0(C) + d\Delta_f H^0(D)) - (a\Delta_f H^0(A) + b\Delta_f H^0(B))$$

**ii) a) Write the expressions of first law of thermodynamics for**

**Ans : First law of thermodynamics is**

$$\Delta U = q + w$$

$$\Delta U = q + p\Delta v$$

i) Process take place in vacuum :-

$$P = 0$$

$$\therefore \Delta U = q \text{ or } -\Delta U = -q$$

ii) Adiabatic process :-

$$q = 0$$

$$\Delta U = q + w$$

$$\Delta U = w \text{ or } -\Delta U = -w$$

iii) Isothermal process :-

$$\Delta U = q + w$$

$$\Delta U = 0$$

$$\therefore q = -w \text{ or } -q = w$$

**b) What is spontaneous process? State second law of thermodynamics in terms of entropy.**

**Ans :** A process that takes place on its own without the continuous help of external agency is called spontaneous process.

**Second law :**

Total entropy of a system and surroundings (universe) increases in a spontaneous process.

$$\Delta S_T = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

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