# **Exercise-1**

## Section (A) : Basic definition

A-2. Sol. Extensive properties : The properties of the system which depends upon the quantity of matter contained in it are called extensive properties e.g., mass, volume, energy, heat capacity etc. Intensive properties : The propoerties which are indepedent of the quantity of matter present in it are called intensive properties e.g., temprature, pressure, refractive index, viscosity, specific heat, density, surface tension etc.

## Section (B) : First law of thermodynamics, calculations of $\Delta E$ , W & Q.

**B-1.** Sol. According to first law of thermodynamics "Energy can neither be created nor be destroyed, it can only be converted from one form to another"

Mathematically

 $\Delta E \text{ or } \Delta U = q + W$ 

 $\Delta U$  = change in internal energy

q = heat absorbed

W = work done

NOTE: Heat absorbed by the system  $\rightarrow$  q = + ve

Heat given out by the system  $\rightarrow$  q = – ve Work done on the system  $\rightarrow$  W = + ve

Work done by the system W = -ve

- B-2. Sol. Change in internal energy = 0; and the process is reversible. Hence, Work done = heat supplied
- **B-3. Sol.** PV = constant for isothermal proces

 $PV^{\gamma}$  = constant for adiabatic process so more

value of  $\boldsymbol{\gamma},$  more decrease in pressure as volume increases.

- **B-4.** Sol. First law of thermodynamics is the law of conservation of energy.
- **B-5.** Sol. Work done by the gas in the cyclic process = Area bounded (ABCA) =  $5P_1V_1$

# Section (C) : Calculation of $\Delta E$ , $\Delta H$ , w and q in different type of physical processes on an idel gas, solid and on liquids

- **C-1. Sol.** The heat exchanged in a chemical reaction at the constant temprature and pressure is known as enthalpy of the reaction.
- **C-2.** Sol. The total heat content of a system is equivalent to the internal energy and work done, at constant pressure

 $\Delta \mathsf{H} = \Delta \mathsf{E} + \mathsf{W}$ 

**C-3.** Sol. The fixed quantity of any substance is associated with a definite amount of energy which depends upon chemical nature of the substance and its state of energy. This energy is called Internal energy or intrinic energy( $\mu$ ).  $\mu$  is a state function and increases with increase in temprature .

C-4. Sol. From 1st law of thermodynamics  $\Delta U = q + W$ Q = +800 J $W = -P(V_2 - V_1)$  $10 dm^3 \times 8.314 J/K mol$  $= -1 (20 - 10) = -10 \text{ dm}^3 \text{ atm} = - \frac{0.08206 \text{ dm}^3/\text{K} \text{ mol}}{1000 \text{ m}^3/\text{K}}$ W = -1013 J $\Delta U = 800 \text{ J} + (-1013 \text{ J}) = -213 \text{ J}$ C-5. Sol. When both P and V are changing  $\Delta H = \Delta U + \Delta (PV) = \Delta U + (P_2V_2 - P_1V_1) = 40 + (20 - 3) = 57 \text{ L-atm}$ From I law of thermodynamics  $\Delta E = Q + W$ C-6. Sol. where Q = 0 for adiabatic process. C-7.  $Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(q)$ Sol. this reaction takes place at constant pressure and leads to expansion (release of H<sub>2</sub>(g)). C-8. Sol. When ideal gases mix : temperature remain constant ; no work is done ; process is irreversible

- **C-9. Sol.** When an ideal gas expands in vaccum the work done is zero as in vaccum there is no force of attraction or repulsion.
- **C-10. Sol.** The process carried out in perfect insulation is adiabatic because in this process no heat enters or comes out from the system.
- **C-11.** Sol. In adiabatic process Q = 0 because in this case neither heat enters nor eliminate out from the system hence no heat exchange.

Section (D) : IInd Law of thermodynamics : Basics of entropy, Entropy calculation for different types of physical process on an ideal gas, solid and liquid, chemical reaction

**D-1.** Sol.  $\Delta n_g$  is + ve

- **D-2.** Sol.  $\Delta n_g < 0$  for  $3C_2H_2(g) \longrightarrow C_6H_6(\ell)$
- D-3. Sol.

$$n_{C_6H_6} = \frac{117}{78} = 1.5$$

 $\Delta S_{\text{system fudk}} = 1.5 \times 85 \text{ J/K}$ 

 $\therefore \qquad \Delta S_{surrounding} \ {}_{ifjos'k} = - \ 1.5 \times 85 \ J/K$ 

# Section (E) : $\Delta G$ calculation, Spontanity of chemical reaction significance of $\Delta G$ and III<sub>rd</sub> Law of thermodynamics

**E-3.** Sol.  $\Delta G = (\Delta H) - T(\Delta S)$ 

-ve +ve

Hence spontaneous at all temperatures.

## **CHEMISTRY FOR JEE**

## Section (F) : Thermochemistry : Enthalpy contents and Kirchoff's equation

**F-1.** Sol. Enthalpy of reaction ( $\Delta$ H) is defined as heat exchanged during any chemical reaction  $\Delta H = H_P - H_R$ 

for exothermic reaction  $H_{\text{P}} < H_{\text{R}}$ 

- ∴ ∆H is -ve.
- **F-4.** Sol. Enthalpy of formation NH<sub>3</sub> (g) is enthalpy change of the following reaction,  $\frac{1}{2} \sum_{N_2} \frac{3}{(g)} + \frac{3}{2} \sum_{H_2} (g) \longrightarrow NH_3 (g)$
- **F-5.** Sol. When one mole of NH<sub>3</sub> is formed from its constituent elements the enthalpy change = -46.0 kJTherefore when one mole of NH<sub>3</sub> decompose to give its constituent elements enthalpy change = 46.0 kJ $\Rightarrow$  When 2 mole NH<sub>3</sub> decompose, enthalpy change =  $2 \times 46 = 92.0 \text{ kJ}$
- F-6. Sol.  $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$   $\Delta n_g = 1 - 3 = -2$  $\Delta H - \Delta E = \Delta n_g RT = -2 RT$
- **F-7** Sol. From Kirchoff's equation :  $y x = (C_{P, water} C_{P, ice}) (T_2 T_1) < 0$ .

#### Section (G) : Enthalpy of combustion and neutralisation

**G-1. Sol.** Combustion reaction of solid boron

$$\begin{split} &\mathsf{B}(\mathsf{s}) + \frac{3}{4} \operatorname{O}_2(\mathsf{g}) \longrightarrow \frac{1}{2} \operatorname{B}_2 \operatorname{O}_3 \\ &\Delta \mathsf{H}^\circ_\mathsf{r} = \Delta \mathsf{H}^\circ_\mathsf{c} \ = \ \frac{1}{2} \Delta \mathsf{H}^\circ_\mathsf{f} \left( \mathsf{B}_2 \operatorname{O}_3, \, \mathsf{s} \right) - \Delta \mathsf{H}^\circ_\mathsf{f} \left( \mathsf{B}, \, \mathsf{s} \right) - \ \frac{3}{4} \Delta \mathsf{H}^\circ_\mathsf{f} \left( \operatorname{O}_2, \, \mathsf{g} \right) \end{split}$$

 $\Delta H_{f}^{\circ}$  of element in stable state of aggregation is assumed to be zero.

$$\Delta H^{\circ}_{c} = \frac{1}{2} \Delta H^{\circ}_{f} (B_{2}O_{3})$$

G-2. Sol. Combustion of benzene can be represented as follows

 $C_6H_6 \, + \, O_2 \, \rightarrow \, 6CO_2 \, + \, H_2O \, + \, 3250 \; kJ$ 

78 g of  $C_6H_6$  produce 3250 kJ heat

1 g will produce 
$$\frac{3250}{78}$$
 kJ heat

3250

 $39 \text{ g will produce} = \frac{78}{30} \times 0.39 \text{ kJ}$ 

= 16.25 kJ heat is librated

NOTE: Enthalpy of combustion is the amount of heat libreated when one mole of a substance is burnt in excess of air.

**G-3. Sol.** Enthalpy of neutralization is defined as amount of heat liberated when one mole of a strong acid is completely neutralized by one mole of a strong base. Its value is less in case of weak acid or weak base because small amount of heat is utilized in ionising the weak acid/base.

 $\Delta H$  for ionisation of CH<sub>3</sub>COOH = Heat of neutralization for CH<sub>3</sub>COOH – Heat of neutralization of strong acid

= - 50.6 - (- 55.9) kJ / mol = + 5.3 kJ / mol

## Section (H) : Bond Enthalpies and Resonance Energy

H-1. Sol. Given  $H_2(g) \longrightarrow HCl(g);$ ∆H = 104 kcal ...(1)  $Cl_2(g) \longrightarrow 2Cl(g);$  $\Delta H = 58 \text{ kcal}$ ...(2)  $HCl(g) \longrightarrow H(g) + Cl(g);$ ∆H = 103 kcal ...(3) Heat of formation for HCI  $\frac{1}{2}$  H<sub>2</sub> (g) +  $\frac{1}{2}$  Cl<sub>2</sub> (g)  $\longrightarrow$  HCl (g) ;  $\Delta$ H = ? Divide equation (1) and (2) by 2, and then add 1  $\frac{1}{2}$  H<sub>2</sub>(g) +  $\frac{1}{2}$  Cl<sub>2</sub>(g)  $\longrightarrow$  H(g) + Cl(g) ;  $\Delta$ H = 81 kcal ...(4) Subtracting equation (3) from equation (4)  $HCI (g) \longrightarrow H(g) + CI(g);$ ∆H = 103 kcal ...(3) \_ 1  $\frac{1}{2} \frac{1}{H_2(g)} + \frac{1}{2} \frac{1}{Cl_2(g)} \longrightarrow HCl(g); \qquad \Delta H = -22.0 \text{ kcal}$ 1 Enthalpy of formation of HCl gas = – 22.0 kcal *.*..  $\dot{\overline{2}}$  A - A +  $\dot{\overline{2}}$  B - B  $\rightarrow$  AB  $\Delta$ H = - 100 KJ/mole Sol. H-2. 1  $\frac{1}{2} x + \frac{1}{2} (0.5x) - x = -100 \implies \frac{2}{2} + 0.25x - x = -100$  $\Rightarrow$  $\Rightarrow$ 0.75 x = - 100 0.25 x = -100100  $x = \frac{25}{100} \times 100$  $\Rightarrow$  $\Rightarrow$ x = 400 kJ/mol Exercise-2 1. Sol.  $\Delta G$  for  $3Fe(s) + 2O_2(g) \longrightarrow Fe_3O_4(s)$  can be obtained by taking  $[(2) + 4 \times (1)] \times \frac{3}{3}$ Hence we get  $\Delta G_f = [-19 + 4 \times (-177)] \times \frac{3}{2} = -242.3 \text{ k cal for 1 mole Fe}_{3}O_4$ 

- 2. Sol.  $CS_2(\ell) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$   $\Delta H = -256$  Kcal Let  $\Delta H_f(CO_2, g) = -4 \times \text{and} \Delta H_f(SO_2, g) = -3 \times$   $\Delta H_{reaction} = \Delta H_f(CO_2, g) + 2 \Delta H_f(SO_2.g) - \Delta H_f(CS_2, \ell)$   $-265 = -4 \times -6 \times -26$   $\times = + 23.9$ ∴  $\Delta H_f(SO_2, g) = 3 \times = -71.7$  Kcal / mol.
- **3. Sol.** For freezing of water the temperature should be kept below freezing point to absorb latent heat of fusion of water.
- $S + O_2 \longrightarrow SO_2$ Sol.  $\Delta H = -298.2 \text{ KJ/mole}$ 4.  $SO_2 + 2 O_2 \longrightarrow SO_3 \qquad \Delta H = -98.7 \text{ KJ/mole}$ ΔH = – 130.2 KJ/mole  $SO_3 + H_2O \longrightarrow H_2SO_4$  $H_2 + \overline{2} O_2 \longrightarrow H_2O$ ΔH = – 287.3 KJ/mole 5. Sol. Given energy = 1560 $1560 \times 50$ <sup>100</sup> = 7800 kJ Utilised energy = 44 kJ Utilised energy = 18 gram 18 780 kJ Utilised energy =  $44 \times 780$  = 319 am *:*. 6.  $AB_2(\ell) + 3X_2(g) \rightleftharpoons AX_2(g) + 2BX_2$ Sol. ΔH = - 270 Kcal  $\Delta H_{F^{\circ}}(AX_{2}) + 2 \Delta H_{F^{\circ}}(BX_{2}) - \Delta H_{F^{\circ}}(AB_{2}) = -270$  $\Delta H_{F^{\circ}}(AX_{2}) + 2 \Delta H_{F^{\circ}}(BX_{2}) = -240$  $\Rightarrow$ 4x - 6x = -240 $\Rightarrow$  -2x = -240 $\Rightarrow$ x = 120  $\Delta H_{F^{\circ}}$  (AX<sub>2</sub>) = 4 × 120 = **480 Kcal/mole**  $K_p = K_c (RT)^{\Delta ng}$  $\Delta n_g = 0$  So  $K_p = K_c$  $nCH_2 = CH_2 \longrightarrow (-CH_2 - CH_2 -)_n \qquad \Delta H = -100 \text{ KJ/mole}$ 7. Sol.  $n [C = C] + n[C - H]4 - n [C - H]4 - n[C - C] \times 2 = -100$ n[C = C] - 2n[C - C] = -100 $\Rightarrow$ [C = C] - 2[C - C] = -100+ 600 - 2[C - C] = - 100  $\Rightarrow$  - 2 [C - C] = - 700 KJ/mole  $\Rightarrow$  (C - C) = - 350  $\Rightarrow$ (1)  $\Delta G^{200} = \Delta H^{200} - T \Delta S^{200}$ 8. Sol.  $\Delta H^{200} = 20 - 4 = 16 \text{ kJ/mol}$  $\Delta H^{T_2} = \Delta H^{T_1} + \Delta C_p [T_2 - T_1]$

	$20 \times 200$	
	$\Delta H^{400} = \Delta H^{200} + 1000$ kJ/ mol = 16 + 4 = 20 kJ/mol.	
9.	<b>Sol.</b> $W = - Pext (V_2 - V_1) = -1 atm (1 L)$	
10.	<b>Sol.</b> $\Delta n_g = 0 \Rightarrow \Delta H^o = \Delta U^o$	
	For 2 mole $\Delta U^{\circ} = -370$ kJ.	
11.	<b>Sol.</b> A (g) $$ B (g) $P_B = \overline{4} P_A$ $P_A = 4P_B$	
	$\frac{P_{B}}{P_{A}} = \frac{P_{A}/4}{P_{A}} = \frac{1}{4}$	
	$K_p = \Lambda = \Lambda = 4$ At equilibrium $\Delta G = 0$ .	
	$\Delta G^{o} = -RT \ell n K_{P} = -RT l n K_{P}$	
12	<b>Sol</b> AS = nCy ln $\left(\frac{I_f}{T_i}\right)_+$ nB ln $\left(\frac{V_f}{V_i}\right)$	
12.		
13	Solution $C_{2}$ $(C_{2}, C_{2}) \rightarrow C_{2}(q) \rightarrow AH = -0.4.0 \text{ km/s}$	
10.	<b>301.</b> CDiamond + $O_2$ / $CO_2(g)$ , $\Delta H = -94.0$ Real	
10.	$C_{\text{Graphite}} + O_2 \longrightarrow CO_2(g) ; \Delta H = -97.6 \text{ kcal}$	
10.	$C_{\text{Graphite}} + O_2 \longrightarrow CO_2(g) ; \Delta H = -97.6 \text{ kcal}$ $C_{\text{Diamond}} \longrightarrow C_{\text{Graphite}} \Delta H = 3.6 \text{ kcal}$	
10.	$C_{Graphite} + O_2 \longrightarrow CO_2(g) ; \Delta H = -97.6 \text{ kcal}$ $C_{Diamond} \longrightarrow C_{Graphite} \Delta H = 3.6 \text{ kcal}$ Heat required to convert 12 gram diamond to graphite = 3.6	
10.	<b>Sol.</b> CDiamond + O <sub>2</sub> $\rightarrow$ CO <sub>2</sub> (g) ; $\Delta H = -97.6$ kcal C <sub>Graphite</sub> + O <sub>2</sub> $\longrightarrow$ CO <sub>2</sub> (g) ; $\Delta H = -97.6$ kcal C <sub>Diamond</sub> $\longrightarrow$ C <sub>Graphite</sub> $\Delta H = 3.6$ kcal Heat required to convert 12 gram diamond to graphite = 3.6 $\frac{3.6}{12}$	
10.	Sol. CDiamond + O <sub>2</sub> $\rightarrow$ CO <sub>2</sub> (g); $\Delta H = -97.6$ kcal C <sub>Graphite</sub> + O <sub>2</sub> $\longrightarrow$ CO <sub>2</sub> (g); $\Delta H = -97.6$ kcal C <sub>Diamond</sub> $\longrightarrow$ C <sub>Graphite</sub> $\Delta H = 3.6$ kcal Heat required to convert 12 gram diamond to graphite = 3.6 $\therefore$ Heat required to convert 1 gm diamond to graphite = $\frac{3.6}{12} = 0.3$	
10.	Graphite + O <sub>2</sub> → CO <sub>2</sub> (g); ΔH = - 97.6 kcal C <sub>Graphite</sub> + O <sub>2</sub> → CO <sub>2</sub> (g); ΔH = - 97.6 kcal C <sub>Diamond</sub> → C <sub>Graphite</sub> ΔH = 3.6 kcal Heat required to convert 12 gram diamond to graphite = 3.6 ∴ Heat required to convert 1 gm diamond to graphite = $\frac{3.6}{12} = 0.3$	
10.	Sol. $C(s) C(g) \longrightarrow cover 1 gm diamond to graphite = \frac{3.6}{12} = 0.3$ Sol. $C(s) C(g) \longrightarrow can be obtained as \Delta H = \Delta H_1 - \Delta H_2 - \frac{1}{2} \Delta H_3 + \Delta H_3$	.H4
14.	Sol. $C(s) C(g) \rightarrow CO_2(g)$ ; $\Delta H = -97.6$ kcal $C_{Graphite} + O_2 \longrightarrow CO_2(g)$ ; $\Delta H = -97.6$ kcal $C_{Diamond} \longrightarrow C_{Graphite} \Delta H = 3.6$ kcal Heat required to convert 12 gram diamond to graphite = 3.6 $\therefore$ Heat required to convert 1 gm diamond to graphite = $\frac{3.6}{12} = 0.3$ Sol. $C(s) C(g) \longrightarrow$ can be obtained as $\Delta H = \Delta H_1 - \Delta H_2 - \frac{1}{2} \Delta H_3 + \Delta \frac{1}{2}$	<b>\H</b> 4
14.	Sol. $C(s) C(g) \longrightarrow CO_2(g)$ ; $\Delta H = -97.6$ kcal $C_{Graphite} + O_2 \longrightarrow CO_2(g)$ ; $\Delta H = -97.6$ kcal $C_{Diamond} \longrightarrow C_{Graphite} \Delta H = 3.6$ kcal Heat required to convert 12 gram diamond to graphite = $3.6$ $\therefore$ Heat required to convert 1 gm diamond to graphite = $\frac{3.6}{12} = 0.3$ Sol. $C(s) C(g) \longrightarrow$ can be obtained as $\Delta H = \Delta H_1 - \Delta H_2 - \frac{1}{2} \Delta H_3 + \Delta$ Sol. $H_2(g) + \frac{1}{2}O_2 \longrightarrow H_2O(g)$ ; $\Delta H_f = -\epsilon_1$ ,(i)	١H4
14. 15.	Sol. C(s) C(g) $\longrightarrow$ CO <sub>2</sub> (g); $\Delta H = -97.6$ kcal C <sub>Graphite</sub> + O <sub>2</sub> $\longrightarrow$ CO <sub>2</sub> (g); $\Delta H = -97.6$ kcal C <sub>Diamond</sub> $\longrightarrow$ C <sub>Graphite</sub> $\Delta H = 3.6$ kcal Heat required to convert 12 gram diamond to graphite = 3.6 $\therefore$ Heat required to convert 1 gm diamond to graphite = $\frac{3.6}{12} = 0.3$ Sol. C(s) C(g) $\longrightarrow$ can be obtained as $\Delta H = \Delta H_1 - \Delta H_2 - \frac{1}{2} \Delta H_3 + \Delta$ Sol. H <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> $\longrightarrow$ H <sub>2</sub> O(g) ; $\Delta H_f = -\epsilon_1$ ,(i) H <sub>2</sub> O(g) $\longrightarrow$ H <sub>2</sub> O(l) ; $\Delta H_f = -\epsilon_2$ ,(ii)	١H4
14. 15.	Sol. C(s) C(g) $\rightarrow$ CO <sub>2</sub> (g); $\Delta H = -97.6$ kcal C <sub>Graphite</sub> + O <sub>2</sub> $\longrightarrow$ CO <sub>2</sub> (g); $\Delta H = -97.6$ kcal C <sub>Diamond</sub> $\longrightarrow$ C <sub>Graphite</sub> $\Delta H = 3.6$ kcal Heat required to convert 12 gram diamond to graphite = 3.6 $\therefore$ Heat required to convert 1 gm diamond to graphite = $\frac{3.6}{12} = 0.3$ Sol. C(s) C(g) $\longrightarrow$ can be obtained as $\Delta H = \Delta H_1 - \Delta H_2 - \frac{1}{2}\Delta H_3 + \Delta$ Sol. H <sub>2</sub> (g) + $\frac{1}{2}O_2 \longrightarrow H_2O(g)$ ; $\Delta H_f = -\epsilon_1$ ,(i) H <sub>2</sub> O(g) $\longrightarrow$ H <sub>2</sub> O(l) ; $\Delta H_f = -\epsilon_2$ ,(ii) and (i) and (ii).	١H4
14. 15.	Sol. Clamond + O <sub>2</sub> $\rightarrow$ CO <sub>2</sub> (g); $\Delta H = -94.0$ Kdai $C_{Graphite} + O_2 \longrightarrow CO_2(g)$ ; $\Delta H = -97.6$ kcal $C_{Diamond} \longrightarrow C_{Graphite} \Delta H = 3.6$ kcal Heat required to convert 12 gram diamond to graphite = $3.6$ $\therefore$ Heat required to convert 1 gm diamond to graphite = $\frac{3.6}{12} = 0.3$ Sol. C(s) C(g) $\longrightarrow$ can be obtained as $\Delta H = \Delta H_1 - \Delta H_2 - \frac{1}{2} \Delta H_3 + \Delta$ Sol. H <sub>2</sub> (g) + $\frac{1}{2}O_2 \longrightarrow H_2O(g)$ ; $\Delta H_f = -\epsilon_1$ ,(i) H <sub>2</sub> O(g) $\longrightarrow$ H <sub>2</sub> O(l) ; $\Delta H_f = -\epsilon_2$ ,(ii) and (i) and (ii). H <sub>2</sub> (g) + $\frac{1}{2}O_2(g)$ H <sub>2</sub> O(l) $\Delta H_f = -\epsilon_2$ ,(ii)	١H4

 Sol. Heat of neutralisation for strong acid and strong base combination is constant is equal to - 13.7 Kcal or - 57.1 KJ.

Exercise-3

## PART - I : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

### **OFFLINE JEE-MAIN**

1. Sol. In an isolated system, there is no exchange of energy or matter between the system and surrounding. For a spontaneous process in an isolated system, the change in entropy is positive, i.e.  $\Delta S > 0$ .

Most of the spontaneous chemical reactions are exothermic. A number of endothermic reaction are spontaneous e.g melting of ice (an endothermic process) is a spontaneous reaction.

The two factors which are responsible for the spontaneity of process are

(i) tendency to acquire minimum energy

(ii) tendency to acquire maximum randomness.

**2. Sol.**  $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$ 

for a spontaneous process  $\Delta G^{\circ} < 0$ 

- $\Rightarrow \qquad \Delta H^{\circ} T \Delta S^{\circ} < 0$
- $\Rightarrow$  T $\Delta$ S° >  $\Delta$ H°

$$\Rightarrow \qquad \mathsf{T} > \frac{\Delta \mathsf{H}^{\circ}}{\Delta \mathsf{S}^{\circ}} \Rightarrow \mathsf{T} > \frac{179.1 \times 1000}{160.2}$$

- ⇒ T > 1117.9 K ≈ 1118 K.
- 3. Sol.  $\Delta U = \Delta H \Delta nRT$ = 41000 - 1 x 8.314 x 373 = 41000 - 3101.122 = 37898.878 J mol<sup>-1</sup> = 37.9 kJ mol<sup>-1</sup>.

4. Sol.  $C + 2H_2 \rightarrow CH_4$ ;  $\Delta H^\circ = -74.8 \text{ kJ mol}^{-1}$ In order to calculate average energy for C - H bond formation we should know the followng data.  $C(\text{graphite}) \rightarrow C(g)$ ;  $\Delta H_f^\circ = \text{enthalpy of sublimation of carbon}$  $H_2(g) \rightarrow 2H(g)$ ;  $\Delta H^\circ$  bond dissociation energy of  $H_2$ .

5. Sol.  $\Delta S^{\circ}$  reaction  $= 50 - \frac{1}{2}(60) - \frac{3}{2}(40) = -40 \text{ JK}^{-1}$ For reaction to be at equilibrium  $\Delta G = 0$  $\Delta H - T\Delta S = 0 \Rightarrow T = \frac{\Delta H}{\Delta S} = \frac{30000}{40} = 750 \text{ K}$ 

6. Sol.  $H_2(g) + \frac{1}{2}O_2(g) - \rightarrow H_2O(\ell)$   $\Delta H = -286.20 \text{ kJ}$   $\Delta H_r = \Delta H_f (H_2O, \ell) - \Delta H_f (H_2, g) \Delta H_f (O_2, g)$   $-286.20 = \Delta H_f (H_2O(\ell))$ So  $\Delta H_f (H_2O, \ell) = -286.20 \text{ KJ/mole}$  $H_2O(\ell) \longrightarrow H^+ (aq) + OH^- (aq) \Delta H = 57.32 \text{ kJ}$ 

 $\Delta H_r = \Delta H^{o_f} (H^+, aq) + \Delta H^{o_f} (OH^-, aq) - \Delta H^{o_f} (H_2O, \ell)$  $57.32 = 0 + \Delta H^{o_f} (OH^-, aq) - (-286.20)$  $\Delta H^{0}_{f}(OH^{-}, aq) = 57.32 - 286.20 = -228.88 \text{ kJ}.$ 7. Sol.  $CH_3OH(\ell) + O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$ 3  $\Delta G_{r} = \Delta G_{f} (CO_{2}, g) + 2\Delta G_{f} (H_{2}O_{1}, (\ell)) - \Delta G_{f} (CH_{3}OH_{1}, (\ell)) - \frac{1}{2} \Delta G_{f} (O_{2}, g)$  $= -394.4 + 2(-237.2) - (-166.2) - 0 = -394.4 - 474.4 + 166.2 = -868.8 \times 166.2$  $\Delta G_{\rm r} = -702.6 \, \rm kJ$ % efficiency =  $\frac{702.6}{726} \times 100$ = 97%. 3  $N_2(g) + \frac{1}{2}H_2(g) \longrightarrow NH_3(g)$ ;  $\Delta H_1^0 = -46.0 \text{ kJ mol}^{-1}$ 8. Sol. ;  $2H(q) \longrightarrow H_2(q)$  $\Delta H_{f^0} = -436 \text{ kJ mol}^{-1}$  $2N(g) \longrightarrow N_2(g)$ ;  $\Delta H_{f^0} = -712 \text{ kJ mol}^{-1}$  $NH_3(g) \longrightarrow \frac{1}{2} \frac{1}{N_2(g)} + \frac{3}{2} \frac{3}{H_2(g)}$ :  $\Delta H = +46$ 3 3  $\overline{2}_{H_2} \longrightarrow 3 H$  ;  $\Delta H = + 436 \times \overline{2}$ 1 ; ΔH = + 712 × <sup>\_\_</sup>2  $\overline{2}_{N_2} \longrightarrow N$  $NH_3(g) N (g) + 3H (g)$ ;  $\Delta H = + 1056 \text{ kJ mol}^{-1}$ 1056 Average bond enthalpy of N–H bond =  $3 = +352 \text{ kJ mol}^{-1}$ 9. Sol.  $\Delta G = \Delta H - T\Delta S$ 

For spontaneous reaction  $\Delta G$  must be negative At equilibrium temperature  $\Delta G = 0$ to maintain the negative value of  $\Delta G$ T should be greater than T<sub>e</sub>.

**10.** Sol. 
$$\Delta S = nR \ln \frac{V_2}{V_1}$$
  
= 2.303 nR log  $\frac{V_2}{V_1}$   
= 2.303 x 2 x 8.314 x log  $\frac{100}{10}$   
= 38.3 J mol<sup>-1</sup> K<sup>-1</sup>

11.  $C_2H_5OH(\ell) + 3O_2(g) - \rightarrow 2CO_2(g) + 3H_2O(\ell)$ Sol.

$$\Delta n_g = 2 - 3 = -1$$
  

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

$$= -1366.5 - (-1) \times \frac{8.314}{10^3} \times 300$$
  

$$= -1366.5 + 0.8314 \times 3 = -1364 \text{ KJ}$$

12. Ans. (4)  

$$4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(g), \Delta H = -111 \text{ kg}$$
  
 $\Delta H' \longrightarrow -54$   
Sol.  
 $-111 - 54 = \Delta H'$ 

ΔH' = - 165 KJ

13. Negative  $\Delta_r G^o$  value indicates that + 2 oxidation state is more stable for Pb<sup>2+</sup>. Also it is supported Sol. by inert pair effect that +2 oxidation state is more stable for Pb and + 4 oxidation state is more stable for Sn.

#### 14.

Sol.  $\Delta G^{o} = \Delta H^{o} - T \Delta S^{o}$  $-RTInK = \Delta H^{\circ} - T\Delta S^{\circ}$  $\Delta H^{\circ} - T \Delta S^{\circ}$ RT lnK = –

15. Sol. The process is isothermal expansion Hence, q = - w  $\Delta u = 0$ q = + 208 J w = - 208 J(expansion work)

**16.** Sol. 
$$C_2H_5OH(\ell) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(\ell)$$
  
 $\Delta U = -1364.47 \text{ KJ/mol.}$   
 $\Delta H = \Delta U + \Delta n_g \text{ RT}$   
 $\Delta n_g = -1$   
 $\Delta H = -1364.47 + \left[\frac{-1 \times 8.314 \times 298}{1000}\right]_{=} - 1364.47 - 2.4776 = -1366.94 \text{ KJ/mol.}$ 

17. Sol.  $2\Delta G^{o_{f}}(NO2) - [2\Delta G^{o_{f}}(NO) + \Delta G^{o_{f}}(O2)] = \Delta G^{o_{r}} = - RT\ell n K_{p}$ 

 $2\Delta G^{0}_{f}$  (NO2) - [2 × 86,600 + 0] = - RT $\ell$ n K<sub>p</sub>

 $\Delta G^{o}_{f (NO2)} = 0.5[2 \times 86,600 - R (298) \ln(1.6 \times 10^{12})]$ 

- **18.** Sol.  $C(s) + \frac{1}{2}O_{2}(g) \rightarrow CO_{2}(g)$ ;  $\Delta H = -393.5 \text{ kJ/mol.}$   $CO(g) + O_{2}(g) \rightarrow CO_{2}(g)$ ;  $\Delta H = -283.5 \text{ kJ/mol.}$  $\frac{1}{2}O_{2}(g) \rightarrow CO(g)$ ;  $\Delta H = -393.5 + 283.5 \text{ kJ/mol} = -110 \text{ kJ/mol.}$
- **19.** Sol. For Adiabatic process Q = 0Now,  $\Delta U = Q + W$  $\Rightarrow \qquad \Delta U = W$
- 20. Sol.  $C_{(graphite)} + O_2(g) \longrightarrow CO_2(g)$   $\Delta H_r = -393.5 \text{ kJ/mol} = \Delta H_f CO_2(g)$   $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$   $\Delta H_r = -285.8 \text{ kJ/mol} = \Delta H_f H_2O(\ell)$   $CO_2(g) + 2H_2O(\ell) \longrightarrow CH_4(g) + 2O_2(g)$   $\Delta H_r = \Delta H_f (CH_4) - \Delta H_f CO_2(g) - 2\Delta H_f H_2O(\ell) = 890.3$   $\Rightarrow \Delta H_f CH_4 + 393.5 + 2 \times 285.8 = 890.3$  $\Rightarrow \Delta H_f CH_4(g) = -74.8 \text{ kJ/mol}$

## **ONLINE JEE-MAIN**

5. Sol.  $CH_4(g) \longrightarrow C(g) + 4H(g)$  $\Rightarrow$  $4 \times E_{C-H} = 360 \text{ KJ/Mol.}$  $\Rightarrow$ Ес-н = 90 KJ/Mol.  $C_2H_6(g) \longrightarrow 2C(g) + 6H(g)$ and  $E_{C-C} + 6 \times 90 = 620$  $E_{c-c} = 80 \text{ kJ/mol}$ ⇒ ⇒ hc  $N_A \times \lambda = 80 \times 1000 \text{ J}$ ⇒  $6.02\!\times\!10^{^{23}}\!\times\!6.62\!\times\!10^{^{-34}}\!\times\!3\!\times\!10^{^8}$ 80000  $= 14.9 \times 10^{-7} \text{ m} = 1.49 \times 10^{-6} \text{ m} = 1.49 \times 10^{3} \text{ nm}.$ λ= 6. Sol.  $\Delta G^{\circ} = \Delta H^{\circ} - T.\Delta S^{\circ} = -29.8 + 298 \times (0.1) = -29.8 + 29.8$  $\Delta G^{0} = 0$ ÷ apply relation between  $\Delta G^{\circ} \& K_{eq}$  $\Delta G^{\circ} = -RT \ell n K_{eq}$  $K_{eq} = 1$ *.*..

7. Sol.  $\Delta G = \Delta H - T \Delta S$ 

If  $\Delta H \& \Delta S$  are both positive, then  $\Delta G$  may be negative at high temperature hence reaction becomes spontaneous at high temperature.

8. Sol.  $2H_2O_2(l) = 2H_2O(l) + O_2(g)$ 

 $W = -P_{ext} (\Delta V) = -\frac{(n_{O_2})}{RT}$ 

- $\therefore$  100 mol H<sub>2</sub>O<sub>2</sub> on decomposition will give 50 mol O<sub>2</sub>
- ⇒ W = -(50)(8.3)(300)J = -124500 JW = -124.5 kJ
- $\Rightarrow$  Work done by O2(g) = 124.5 kJ Ans.

9. Sol.  $\Delta H = \Delta U + \Delta n_g RT$   $\therefore \Delta ng = -1$  $-3RT = \Delta U - 1RT$ 

 $\Delta U = -2P$ So  $|\Delta H| > |\Delta U|$ 

**10.** Sol.  $\Delta H = {}^{\Delta H_{H_2O_{(\lambda)}}} + \Delta H_{fus} + {}^{\Delta H_{H_2O_{(S)}}}$ =  ${}^{n_{C_P\Delta T}} + \Delta H_{fus} + n_{CP\Delta T}$ = 1×75.3×5 + 6000 + 1× 36.8×5 = 6560.5 J mole<sup>-1</sup> or 6.56 kJ mol<sup>-1</sup>

11. Sol. 
$$A \longrightarrow B$$
:  
 $q = +5$ ;  $W = -8 \therefore \Delta E = -3$   
 $B \longrightarrow A$ :  
 $\Delta E = 3$ ;  $q = -3 \therefore W = +6J$   
 $\Rightarrow 6J$  of the work will be done by the surrounding on gas.

**12. Sol.**  $\Delta H = nC_P\Delta T = O$ 

 $\Delta S = nR \ \ell n \left( \frac{V_f}{V_i} \right)$ 

 $\left( \mathbb{I} \quad V_f > V_i \right)$ 

: Entahalpy remains constant but entropy increases.

## PART - II : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

**1. Sol.** In a reversible process, the driving and the opposite forces are nearly equal, hence the system and the surroundings always remain in equilibrium with each other.

2.

**Sol.** Work is not a state function becuase it depends upon the path followed.

- 3. Sol.  $\Delta H = \Delta U + \Delta (PV)$  $\Rightarrow \Delta H = 30 + (P_2V_2 - P_1V_1) = 30 + (4 \times 5 - 2 \times 3) = 30 + 14 = 44$  L atm.
- Sol. The amount of heat either evolved or absorbed when one gram mole of a substance is formed from its constituent elements, is known as the standard heat of formation (ΔH°<sub>f</sub>). Standard state temperature is 25C° or 298K and pressure of gaseous substance is one atmosphere. Thus in given thermochemical equation '(B)' represents the standard heat of formation of HF.
   1

$$\overline{2}_{H_{2(g)}} + \overline{2}_{F_{2}(g)} \longrightarrow HF(g)$$
,  $\Delta H^{\circ}_{f} = ?$  (Standard heat of formation of HF(g))

**5. Sol.**  $\therefore$  H = E + PV and  $\Delta$ H =  $\Delta$ E + P $\Delta$ V

 $P\Delta V = nRT.$ 

 $\Delta H = \Delta E + nR\Delta T$ 

For isothermal and reversible process

 $\Delta T = 0.$ 

$$\therefore \quad \Delta H = \Delta E + 0.$$

 $\therefore \quad \Delta E = 0.$ 

*:*..

 $\therefore$   $\Delta H$  is also equal to zero.

6. Sol. Given that,  $\Delta H_{vaps} = 30 \text{ kJ/mol} = 30 \times 10^3 \text{ J/mol}.$   $\Delta S_{vaps} = 75 \text{ J/mol}.$ We know that,  $\Delta S = \frac{\Delta H_{vap}}{T_{B,P}}$  $\therefore \qquad \Delta H = T\Delta S \implies 30 \times 10^3 = T \times 75.$ 

T = 400 K.

- **7. Sol.** In adsorption there in bond formation between the gases and solid surface which decrease the entropy.
- $\Delta U = W$ 8. Sol.  $nCv (T_2 - T) = -P \times (V_2 - V_1)$ 2 3  $\frac{3}{2}$  R (T<sub>2</sub>-T) = -1  $T_2 = T - 3 \times 0.0821$ ⇒ :. 9. Sol. From first law of Thermodynamics,  $\Delta E = q + w \Rightarrow nC_v dT = nCdT - PdV$ .....(1) Now according to process, P = V and according to ideal gas equation, PV = nRT We have,  $V^2 = nRT$

On differentiating, 2VdV = nRdT and  $PdV = VdV = \frac{nRdT}{2}$ So, from first equation we have,  $nC_vdT = nCdT - \frac{nRdT}{2}$ 

So, 
$$C_v = C - \frac{R}{2}$$
 Hence,  $C = \frac{4R}{2}$ 

**10.** Sol.  $A \longrightarrow C$ ;  $\Delta S = 50$ ;  $C \longrightarrow D$ ;  $\Delta S = 30$ ;  $D \longrightarrow B$ ;  $\Delta S = -20$ For  $A \longrightarrow B$ :  $\Delta S = 50 + 30 - 20 = 60$ 

- **11. Sol.** When nitrogen is added at equilibrium condition, the equilibrium will shift according to Le-chatelier principle at equilibrium  $\Delta G = 0$  and catalyst changes the rate of forward and backward reactions by equal extent. K<sub>P</sub> of reaction is a function of temperature only.
- 12. Sol.  $\Delta G^{\circ} = \Delta H^{\circ} T\Delta S^{\circ} = -54.07 \times 1000 298 \times 10 = -54070 2980 = -57050$   $\Delta G^{\circ} = -2.303 \text{ RT} \log_{10} \text{ K}$   $-57050 = -2.303 \times 298 \times 8.314 \log_{10} \text{K} = -5705 \log_{10} \text{ K}$  $\log_{10} \text{ K} = 10$
- **13.** Sol. H<sub>2</sub>O(ℓ,1bar, 373K) → H<sub>2</sub>O(g, 1bar, 373 K) ΔS > 0 ;ΔH > 0 ;ΔG = 0
- **14.** Sol. At equilibrium  $\Delta G$  (Gibbs energy) = 0 but  $\Delta G^{\circ}$  (standard Gibbs energy)  $\neq 0$ As  $\Delta G$  (Gibbs energy) is more negative reaction will be more spontaneous.
- **15. Sol.** Statement 2 is II<sup>nd</sup> law of thermodynamics which concludes that total heat can never be converted into equivalent amount of work.
- **16.** Sol.  $\Delta H_{f^{\circ}}(Cl_{2},g) = 0$ , As  $\Delta H_{f^{\circ}}$  of elements in their standard state is taken to be zero.
- **17. Sol.** E<sub>C-C</sub> 100 KCal/mole.

18.  

$$2C(s) + H_{2}(g) \longrightarrow C_{2}H_{2}(g) \Delta H = 225 \text{ KJ/mol}$$

$$1410 \downarrow 330 \downarrow f - (2\varepsilon_{C-H} + \varepsilon_{C=C})$$
Sol.  

$$2C(g) + 2H(g) - (2\varepsilon_{C-H} + \varepsilon_{C=C})$$

$$\therefore \Delta H = +1410 + 330 - (350 \times 2) - \varepsilon_{C=C} = +225$$

$$\therefore \varepsilon_{C=C} = 1740 - 700 - 225 = +815 \text{ KJ/mol}.$$

**19.** Sol. 
$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(\mathcal{X})$$
  
 $\Delta_C H = 6 \times \Delta_f H (CO_2) + 6 \Delta_f H (H_2O) - \Delta_f H (C_6H_{12}O_6) - 6\Delta_f(O_2,g)$   
 $= 6 \times (-400 - 300) - (-1300) - 0$ 

= - 4200 + 1300 = - 2900 KJ/ mol

For one gram of glucose, enthalpy of combustion =  $-\frac{180}{-16.11}$  KJ/g.

**20.** Sol. For  $H_2O(\ell) \rightarrow H_2O(g)$  at T = 100°C, 1 atm equilibrium exists.

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

 $\Delta H = T\Delta S > 0$  for system, since evaporation is endothermic

 $-\frac{\mathsf{q}_{\mathsf{surr}}}{\mathsf{T}_{\mathsf{surr}}}$ 

 $\therefore$  ( $\Delta$ S)<sub>system</sub> > 0, also ( $\Delta$ S)<sub>surrounding</sub> =  $I_{surr}$ 

Heat gained by system = heat lost by surroundings

 $\therefore q_{surr.} < 0 \therefore (\Delta S)_{surr.} < 0$ 

**Sol.**  $\Delta S_{Surr} = \frac{q_{Surr}}{T} = -\frac{q_{Sys}}{T} = \frac{vv_{Sys}}{T}$  (:: Isothermal process  $\Rightarrow \Delta U = 0$ )

$$\Delta S_{Surr} = \frac{-P_{ext}(V_f - V_i)}{T} = \frac{-3(2-1)}{300} \times 101.3 = -1.013 \text{ J/K}$$

## Additional Problems For Self Practice (APSP)

## PART - I : PRACTICE TEST PAPER

$$(125 + 8) \times 4.2 \times 6$$

6. Sol.  $\Delta H_{solution} = \frac{7}{8} \times 80 = 33516 \text{ J/mol or } 33.51 \text{ kJ/mol.}$ 7. Sol.  $\Delta_r C_p = 0$ ,  $\therefore \Delta H_{300} = \Delta H_{310}$ 8. Sol.  $C_2 H_5 OH(\ell) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2 O(\ell)$   $\Delta n_g = 2 - 3 = -1$ so  $\Delta U = \Delta H - \Delta n_g RT$ = -q + RT

9. Sol. 
$$H_2C_2O_4(\ell) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell) + 2CO_2(g);$$

 $\Delta n_g = 3/2$   $\Delta U_c = -\frac{0.312 \times 8.75}{1} \times 90 = -245.7 \text{ kJ/mol}$   $\Delta H = \Delta U + \Delta n_g RT$   $= -245.7 + \frac{3}{2} \times \frac{8.314 \times 300}{1000} = -241.947 \text{ kJ/mol}.$ 

**10.** Sol. From given reaction  $\Delta n_g = 12 - 15 = -3$ 

so  $\Delta E^{\circ} = \Delta H^{\circ} - \Delta n_{g} RT = -6542 + 3RT$ for 1.5 mole,  $\Delta E^{\circ} = \frac{1.5}{2} \{-6542 + 3RT\} = 4900.9 \text{ kJ}$ 

- **11.** Sol.  $\Delta n_g = 1-2 = -1$   $\Delta E = \Delta H - \Delta n_g RT = \Delta H - RT = -72.3 + 8.314 \times 300 \times 10^{-3}$  = -69.806 kJ/moleso for 3 mole we will get  $\Delta E = -69.806 \times 3 \text{ kJ/mole} = 209.42 \text{ kJ/mole}$
- 12. Sol. For same amount of gas at constant temperature, lesser is the volume, lower will be the entropy.

**13.** Sol. 
$$W = -P_{ext}(\Delta V) = -(1 \text{ atm}) \times 500 \times 50 \times 10^{-3} \text{ L}$$
  
= - 25 L atm = - 25 × 101.3 × 10<sup>-3</sup> kJ = -2.53 kJ

- 14. Sol.  $C_2H_4 + H_2 \longrightarrow C_2H_6$ 50 ml 50 ml 0 X X 50 ml  $\Delta H = \Delta U + P (\Delta V)$   $- 0.31 = \Delta U + 1.5 \times 1.01 \times 10^5 (-50 \times 10^{-6}).$  $\Delta U = - 0.3024 \text{ kJ}.$
- **15.** Sol.  $H_2O(s) H_2O(l), \Delta H = 1440$  cal.  $\Delta H \cong \Delta U \longrightarrow$  for solids and liquids.

16. Sol. 
$$\Delta E = q + w$$
  
 $W_{BC} = \frac{1}{2} (2V^{\circ} - V^{\circ}) (P^{\circ} - 3P^{\circ}) + (2V^{\circ} - V^{\circ}) (0 - P^{\circ}) = -2P^{\circ}V^{\circ}$   
 $\Delta E = nC_{V}\Delta T = 1 \times R \left(\frac{P^{\circ}2V^{\circ}}{R} - \frac{3P^{\circ}V^{\circ}}{R}\right)_{=} -P^{\circ}V^{\circ}$   
 $q_{BC} = \Delta E - W = -\frac{3}{2}P^{\circ}V^{\circ} + 2P^{\circ}V^{\circ} = \frac{1}{2}P^{\circ}V^{\circ}$ 

17. Sol. Beaker is open and in open beaker external pressure remains constant.  $Zn + H_2SO_4 - \rightarrow ZnSO_4 + H_2 (g)$   $\frac{130}{65} = 2 \text{ mole}$  PV = nRT $P\Delta V = n_gRT$ 

 $W = -n_g RT = 2 \times 2 \times 300 = -1200 cal.$ 

**18.** Sol.  $C_3H_8(g) + 5O_2 \rightarrow 3CO_2(g) + 4H_2O(\ell)$ 

$$\begin{bmatrix} 8 \times BE. (C - H) \\ +2 \times BE. (C - C) \\ +5 \times BE. (O = 0) \end{bmatrix}_{=}^{1} \begin{bmatrix} 6 \times BE. (C - C) \\ +8 \times BE(O - H) \\ +3 \times [RE] \text{ of } CO_{2} \\ +4 \times \Delta_{eqp} \quad H(H_{2}O) \end{bmatrix}$$
19. Sol.  $H_{2}(g) + \frac{1}{2}O_{2}(g) \longrightarrow H_{2}O(l)$  :  $\Delta H_{comb,}H_{2}$   
 $\Delta H_{comb} = \Delta H_{H-H} + \frac{1}{2}\Delta H_{0=0} - 2\Delta H_{0-H} - \Delta H_{eqp} = x_{1} + \frac{x_{2}}{2} - 2x_{3} - x_{4}$ 
20. Sol.  $\frac{1}{2}N_{2}(g) + \frac{3}{2}Cl_{2}(g) \longrightarrow NCl_{3}(g)$   
 $\Delta H = -\Delta H_{1} + \frac{1}{2} - \frac{3}{2}\Delta H_{3}$ 
21. Sol.  $H^{*}(q) + OH^{*}(q) \longrightarrow H_{2}O(l)$   
so  $\Delta H^{\circ} = -57.3 = -285.5 - \Delta H^{*}(H+, aq) - \Delta H^{\circ}(OH^{*}, aq)$   
so  $\Delta H^{\circ}(OH^{*}, aq) = -228.5 \text{ kJ/mole} (as \Delta H^{*}(H+, aq) = 0)$ 
22. Sol.  $\Delta H = \frac{8}{9} \times 45.54 + \frac{1}{9} \times 68.91 = 48.137 \text{ kJ}.$ 
23. Sol.  $\Delta H = \Delta U + \Delta ng RT$   
 $= 2.1 + \frac{2 \times 2 \times 300}{1000} = 1.2$   
 $\Delta G = \Delta H - T\Delta S$   
 $= 3.3 - 300 \times \frac{26}{1000} = 3.3 - 6 = -2.7 \text{ K cal}$ 
24. Sol.  $\Delta H^{\circ} = 2 \times \Delta H^{\frac{1}{2}} + 2 \times \Delta H^{\frac{1}{2}} - \Delta H^{\frac{1}{3}}$ 
25. Sol.  $\Delta G = \Delta H - T\Delta S$   
 $= -2808 - 310 \times 182.4 \times 10^{-3}$   
 $= -2864.5 \text{ kJ}$ 
26. Sol.  $\Delta S = 10.13 = 31.2 + 51.1 - 47.3 - \frac{S_{10}O}{S_{10}O} = \frac{S_{10}O + 10.23 \times 10^{-3}}{S_{10}O + 10.23 \times 10^{-3}} = -2864.5 \text{ kJ}$ 
27. Sol.  $\Delta G = 29.3 \times 10^{3} - (2 \times 239.7 - 152.3 - 223) \times 298 = -1721.8 \text{ Joule.}$ 
28. Sol. Since, expansion occurred at constant temperature,

$$\Delta S = nR \ln \frac{V_2}{V_1} = \frac{1}{32} \times 8.314 \ln \frac{3.0}{0.75} = 0.36 \text{ JK}^{-1}$$

Since, this is case of free expansion,  $P_{ext} = 0$ .  $\Rightarrow$   $-W = P_{ext} \Delta V = 0$ , q = 0Also, since,  $\Delta T = 0 \Rightarrow \Delta H = \Delta E = 0$ .

**29.** Sol. (2)  $Cu_2O(s) + \frac{1}{2}O_2(g) \rightleftharpoons 2CuO(s)$   $\Delta G^{0}_{reaction} = [2 \times (-30.4)] - [-34.98] = -25.82 \text{ kcal}$ and  $-25.82 \times 10^3 = 2.303 \times 2 \times 298 \text{ logK}$  $\therefore \qquad K \approx 10^{19}$ , a very high value, hence reaction will be almost complete with a trace of Cu<sub>2</sub>O.

30. Sol. 
$$\Delta_{f}S^{\circ}(NH_{4}CI,s)$$
 at 300 K (300 K ij  $\Delta_{f}S^{\circ}(NH_{4}CI,s)$ )  

$$= S^{NH_{4}CI(s)} - \left[\frac{1}{2}S^{\circ}_{N_{2}} + 2S^{\circ}_{H_{2}} + \frac{1}{2}S^{\circ}_{CI_{2}}\right]$$

$$= -374 \text{ JK}^{-1} \text{ mol}^{-1}$$
 $\Delta_{f}C_{P} = 0$ 
 $\therefore \quad \Delta_{f} \frac{S^{\circ}_{310}}{S^{\circ}_{310}} = \Delta_{f}S^{\circ}_{300}$ 
 $= -374 \text{ JK}^{-1} \text{ mol}^{-1}$ 
 $\Delta_{f}H^{\circ}_{310} = \Delta_{f}H^{\circ}_{300} = -314.5$ 
 $\Delta_{f}G^{\circ}_{310} = \Delta_{f}H^{\circ} - 310 \Delta S^{\circ} = -314.5 - \frac{310(-374)}{1000} = -198.56 \text{ kJ/mol.}$ 

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## **PART - II : PRACTICE QUESTIONS**

**1. Sol.** For endothermic reactions standard heat of reaction ( $\Delta H$ ) is positive because in these reactions total energy of reactants is lower than that of products. i.e.,

Er < Ep

So,  $\Delta H = E_P - E_R = +ve$ 

- **2.** Sol. (i)  $S(s) + \overline{2}O_2(g) \rightarrow SO_3(g) + 2x \text{ kcal}$

3

(ii) By inverting second equation  $SO_3(g) \rightarrow SO_2(g) + O_2(g) - y$  kcal,

On addition Eq. (i) and (ii)

 $S(s) + O_2(g) - \rightarrow SO_2(g) + (2x - y)$  kcal Hence, heat of formation of  $SO_2$  is (2x - y) kcal.

3. Sol. We known that

 $\Delta H = \Delta E + \Delta nRT$ 

where,  $\Delta n$  = number of moles of gaseous product – number of moles of gaseous reactant

$$= 2 - 3 = -1$$
So,  $\Delta H = \Delta E - RT$ 

 $\Delta H_{f}$ 

4. Sol.  $\Delta S_f = \overline{T_f}$ 

 $\Delta S_{f} = \frac{\frac{2930 \text{ J mol}^{-1}}{300 \text{ K}}}{300 \text{ K}} = 9.77 \text{ JK}^{-1} \text{ mol}^{-1}$ 

**5. Sol.**  $\Delta G$  of formation of different substances are as :

$$\begin{split} 2SO_2 &= -544 \text{ kJ} \\ 2ZnS &= -293 \text{ kJ} \\ ZnO &= -480 \text{ kJ} \end{split}$$
 For the reaction,  $2ZnS + 3O_2 (g) \to 2ZnO (s) + 2 \text{ SO}_2 (g) \\ \Delta G &= [(\Delta G_{(\text{products})} - \Delta G (\text{reactants})] \\ &= [(-480) + (-544) - (-293)] \\ &= -1024 + 293 = -731 \text{ kJ} \end{split}$ 

6. Sol.  $2H_2O_2(\ell) \rightarrow 2H_2O(\ell) + O_2(g) \Delta H = ?$ 

 $\Delta H = [(2 \times \Delta H_f \text{ of } H_2O(\ell) + (\Delta H_f \text{ of } O_2)] - (2 \times \Delta H_f \text{ of } H_2O_2(\ell))]$  $= [(2 \times -286) + (0) - (2 \times -188)] = [-572 + 376] = -196 \text{ kJ / mol}$ 

7. Sol. We know that  $\Delta H = \Delta E + p\Delta V$ When  $\Delta V = 0 \therefore \Delta H = \Delta E$ From the law of thermodynamics

$$\begin{split} \Delta E &= q - W \\ \text{In given problem } \Delta H &= 500 \text{ J} \\ &-W &= -p \Delta V, \ \Delta V &= 0 \\ \text{So,} \qquad \Delta E &= q = 500 \text{ J} \end{split}$$

8. Sol.  $CH_4 + \frac{1}{2}O_2$ 

$$CH_4 + 2 O_2 - \rightarrow CH_3OH(\ell)$$

 $\therefore \Delta H = -[(\Delta H \text{ of combustion of } CH_3OH)]$ 

 $-(\Delta H \text{ of combustion of } CH_4)]$ 

$$= - [(-y) - (-x)]$$
  
= - [ - y + x] = y - x  
∴ x < y

9. Sol.

 $\Delta S = \frac{q}{T}$ Sol. q = required heat per mol

T = constant absolute temprature

Thus unit of entropy is JK<sup>-1</sup> mol<sup>-1</sup>

$$\Delta S = \frac{q}{T}$$

Sol. In closed insulated contianer a liquid is stirred with a paddle to increase the temprature, therefore No heat exchange with surrounding, so for it q = 0.
 Hence, from first law of thermodynamics

 $\Delta E = q + W$ 

 $\therefore \Delta E = W$  but not equal to zero.

11. Sol. 
$$\Delta S$$
 (Entopy change) = 2.303 nR log10  $\frac{V_2}{V_1} = 2.303 \times 2 \times 2 \times \log_{10} \frac{20}{1}$   
= 2.303  $\times 2 \times 2 \times 1$   
= 9.212 cal

12. Sol. 
$$C(s) + 2H_2(g) \rightarrow CH_4(g), \Delta H^0 = ?$$
  
 $\Delta H^0 = -[(\Delta H^0_c \text{ of } CH_4) - (\Delta H^0_c \text{ of } C + 2 \times \Delta H^0_c, \text{ of } H_2)]$   
 $C + O_2 - \rightarrow CO_2: \Delta H = -94 \text{ kcal .....(i)}$   
 $2H_2 + O_2 - \rightarrow 2H_2O:$   
 $\Delta H = -68 \times 2\text{ kcal ....(ii)}$   
Eq. (i) + (ii) - Eq. (iii)  
 $= -[(-213) - (-94 + 2 \times -68)] \text{ kcal/mol}$   
 $= -[(-213 + 230)] = -17 \text{ kcal/mol}$ 

13. Sol.

$$\frac{1}{2} \xrightarrow{A} \longrightarrow B + 150 \dots (1)$$

$$3B \longrightarrow 2C + D - 125 \dots (2)$$

$$E + A \longrightarrow 2D + 350 \dots (3)$$

$$\overline{B + D \longrightarrow E + 2C}$$

$$2 \times eq.(1) + eq.(2) - eq.(3)$$

$$\Delta H = 300 - 125 - 350 = -175$$

Sol. C =  $\frac{q}{n(T_2 - T_1)}$ Given that C = 75 JK<sup>-1</sup> mol<sup>-1</sup>, q = 1.0 kJ = 1000 J 75 =  $\frac{1000}{5.55 \text{ x } \Delta T}$  (n =  $\frac{100}{18}$  = 5.55) ∴  $\Delta T = \frac{1000}{5.55 \text{ x } 75}$  = 2.4 K

**15.** Sol.  $\Delta S = \frac{\Delta Hf}{T} = \frac{6.0}{273} = 0.02198 \text{ kJ K}^{-1} \text{ mol}^{-1}$ (T = 0°C + 173 = 273 K) = 0.02198 x 1000 JK<sup>-1</sup> mol<sup>-1</sup> = 21.98 JK<sup>-1</sup> mol<sup>-1</sup>

**16. Sol.** When one mole of a substance is directly formed from its constituent elements, then the enthalpy change is called heat of formation.

For the reaction

Xe (g) + 2F<sub>2</sub> (g) 
$$\rightarrow$$
 XeF<sub>4</sub> (g)  
1 mol  
 $\Delta H^{\circ}_{react} = \Delta H^{\circ} f$ 

17. Sol. For the reaction,

 $C_{3}H_{8}(g) + 5O_{2}(g) - \rightarrow 3CO_{2}(g) + 4H_{2}O(\ell)$ 

- $\Delta n$  = number of gaseous moles of products
  - number of gaseous moles of reactants

$$= 3 - 6 = -3$$

 $\therefore$   $\Delta H = \Delta E + \Delta nRT$ 

- or  $\Delta H \Delta E = \Delta nRT$
- $\therefore \qquad \Delta H \Delta E = 3RT$
- **18.** Sol. For the reaction  $H_2(g) + Br_2(g) \rightarrow 2HBr(g) \Delta H^\circ = ?$

$$\begin{split} \Delta H^\circ &= - \left[ (2 \text{ x bond energy of HBr}) - (\text{bond energy of H}_2 + \text{bond energy of Cl}_2) \right] \\ \Delta H^\circ &= - \left[ (2 \text{ x } (364) - (433 + 192) \right] \text{kJ} \\ &= - \left[ 728 - (625) \right] \text{kJ} \end{split}$$

**19. Sol.**  $\Delta G^{\circ} = \Delta H - T \cdot \Delta S^{\circ}$ 

 $\Delta H = -382.64 \text{ kJ mol}^{-1}$   $\Delta S^{\circ} = -145.6 \text{ J K}^{-1} \text{ mol}^{-1}$   $= -145.6 \text{ x } 10^{-3} \text{ kJ K}^{-1}$ or  $\Delta G^{\circ} = -382.64 - (298 \text{ x} - 145.6 \text{ x } 10^{-3})$  $= -339.3 \text{ kJ mol}^{-1}$ 

**20.** Sol. For spontaneous process,  $\Delta S$  must be positive. In reversible process

 $\Delta S_{system} + \Delta S_{surrounding} = 0$ Hence, system is present in equilibrium. (i.e, it is not spontaneous process) While in irreversible process

 $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$ 

Hence, in process  $\Delta S$  is positive.

21. Sol. Work done (W) =  $-P_{ext} (V_2 - V_1)$ = -3 x (6 - 4) = -6 L-atm = -6 x 101.32 J( $\because 1 L$ -atm = 101.32 J) =  $-607.92 \approx 608 J$ 

**22. Sol.** The spotaneously of a reaction is based upon the negative value of  $\Delta G$  and  $\Delta G$  is based upon T,  $\Delta S$  and  $\Delta H$  according to following equation (Gibb's-Helmholtz equation)

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

If the magnitude of  $\Delta H - T\Delta S$  is negative, then the reaction is spontaneous.

When  $T\Delta S > \Delta H$  and  $\Delta H$  and  $\Delta S$  +ve, then  $\Delta G$  is negative.

**23. Sol.** If reaction is exothermic, therefore  $\Delta H$  is -ve and on increasing disorder,  $\Delta S$  is +ve thus, at these condition,  $\Delta G$  is negative according to following equation.

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

 $\Delta G$  = -ve, and for spotaneous reaction  $\Delta G$  must be -ve.

**24. Sol.** Heat of neutralisation of strong acid and strong base is -57.33 kJ MgO is weak base while HCI is strong acid, so the heat neutralisation of MgO and HCI is lower than -57.33 kJ because MgO requires some heat for ionisation, then net released amount of heat is decreased.

### **CHEMISTRY FOR JEE**

- **25.** Sol. If the Gibb's free energy for a system ( $\Delta G_{system}$ ) is equal to zero, then system is present in equilibrium at a constant temprature and pressure.
- 26. Sol. As we know that

 $\Delta H = \Delta E + p \Delta V$ 

or  $\Delta H = \Delta E + \Delta nRT$ 

where  $\Delta n \rightarrow no.$  of gaseous mole of product – no. of gaseous moles of reactant

If  $\Delta n = 0$  (for reactions in which the number of moles of gaseous product are equal to number of moles of gaseous reactants), therefore  $\Delta H = \Delta E$ 

So, for reaction (1)  $\Delta n = 2 - 2 = 0$ 

Hence, for reaction (1) =  $\Delta H = \Delta E$ 

**27.** Sol. At equilibrium Gibb's free energy change ( $\Delta$ G) is equal to zero.

 $\Delta G = \Delta H - T\Delta S$   $0 = 30 \times 10^{3} (J \text{ mol}^{-1}) - T \times 105 (J \text{ K}^{-1} \text{ mol}^{-1})$  $\therefore T = \frac{30 \times 10^{3}}{105} \text{ K} = 285.71 \text{ K}$ 

28.

Sol.

 $\Delta H = [\Delta H \text{ of combustion of cyclohexane} - (\Delta H \text{ of combustion of cyclohexane} + \Delta H \text{ of combustionof } H_2)]$ = -[- 3920 -( - 3800 - 241) ] kJ = -[- 3920 + 4041] kJ = -[ 121] kJ = - 121 kJ

**29. Sol. Enthalpy of formation :** The amount of heat evolved or absorbed during the formation of 1 mole of a compound for its constituent elements is known as heat of formation. So, the correct answer is :

 $H_2(g) + \frac{1}{2}O_2(g) - → H_2O(\ell)$ ,  $\Delta H = + x_2 \text{ kJ mol}^{-1}$ 

**30.** Sol.  $\Delta_{f}H_{(HCI)} = -90 = \frac{1}{2} \times 430 + \frac{1}{2} \times 240 - \Delta H_{BE(HCI)}$