

CHAPTER - 05

THERMODYNAMICS & CHEMICAL ENERGETICS

1. 3 Mass, volume – extensive; Density – Intensive

2. 2 $q_p = \Delta H$

3. 3 $W = -P_{\text{ex}} \Delta V = -10^5 (10^{-2} - 10^{-3}) = -900 \text{ J or } -0.9 \text{ kJ}$

4. 3 $q + w = \Delta U$ and $H - TS = G$ are state functions

5. 3 $\text{C}_7\text{H}_6(\ell) + 11\text{O}_2(\text{g}) \longrightarrow 7\text{CO}_2(\text{g}) + 8\text{H}_2\text{O}(\ell)$

$$\Delta n_g = n_p - n_r = 7 - 11 = -4$$

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

$$\therefore \Delta H - \Delta U = -4RT$$

6. 2 $2\text{Al} + \frac{3}{2}\text{O}_2 \rightarrow \text{Al}_2\text{O}_3, \Delta H = -1596 \text{ kJ} \quad \dots\dots(\text{i})$

$2\text{Cr} + \frac{3}{2}\text{O}_2 \rightarrow \text{Cr}_2\text{O}_3, \Delta H = -1134 \text{ kJ} \quad \dots\dots(\text{ii})$

By (i) – (ii)

$$2\text{Al} + \text{Cr}_2\text{O}_3 \rightarrow 2\text{Cr} + \text{Al}_2\text{O}_3, \Delta H = -462 \text{ kJ}.$$

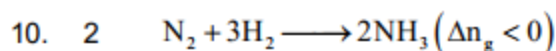
7. 1 $2\text{C}(\text{graphite}) + 3\text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g})$

$$\Delta_f H(\text{C}_2\text{H}_6) = 2\Delta_{\text{comb}} H(\text{C}_{\text{graphite}}) + 3\Delta_{\text{comb}} H(\text{H}_2) - \Delta_{\text{comb}} H(\text{C}_2\text{H}_6)$$

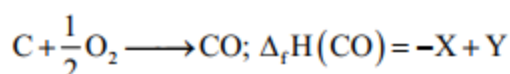
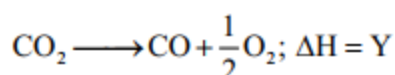
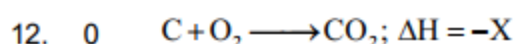
$$= -(286 \times 2) - (393.5 \times 3) - (-1560) = -572 - 1180.5 + 1560 = -192.5 \text{ kJ / mole}$$

8. 1 $\Delta_{\text{sol}} H = \Delta_{\text{lattice}} H + \Delta_{\text{hyd}} H = 788 - 784 = 4 \text{ kJ mol}^{-1}$

9. 2 $T_{\text{eq}} = \frac{\Delta H}{\Delta S} = \frac{491.1 \times 1000}{198} = 2480.3 \text{ K}$



11. 300 $\Delta u = q + w = (+600) + (-300) = 300 \text{ J}$



Clearly, $a = -1$ and $b = 1$

Thus, $a + b = 0$ and $|a + b| = 0$

13. 178

Heat liberated $= 890 \times \frac{3.2}{16} = 178 \text{ kJ}$

14. A $W_{ABCD} = W_{AB} + W_{BC} + W_{CD} = -P_o(2V_o - V_o) - nRT \ln \frac{4V_o}{2V_o} - \frac{P_o}{2}(2V_o - 4V_o)$
 $= -2P_o V_o \ln 2$

15. B $q_{\text{isoth}} = -W = 4 \text{ Nm}^{-2} \times (1 - 5 \text{ m}^3) = -16 \text{ Nm}$

Now, $q_{\text{Al}} = nC_m \Delta T \Rightarrow \Delta T = \frac{q_{\text{Al}}}{nC_m} = \frac{16}{1 \times 24} = \frac{2}{3} \text{ K}$

16. A $W = 0$ for free expansion; $q = 0$ for isothermal free expansion; $\Delta T = 0$ is possible in adiabatic expansion of ideal gas

17. D $q_A = -W_A (\because \text{isothermal expansion})$

$= nRT_1 \ln \frac{V_2}{V_1}$

18. D $\Delta S_{D+E} = \frac{q_{\text{rev}, A}}{T_1} = nR \ln \frac{V_2}{V_1}$

19. ABC Radius of circle $= \frac{V_2 - V_1}{2}$ or $\frac{P_2 - P_1}{2}$

$$\text{Thus magnitude of work done} = \pi \left(\frac{V_2 - V_1}{2} \right)^2 \text{ OR } \pi \left(\frac{P_2 - P_1}{2} \right)^2 \text{ OR } \pi \left(\frac{V_2 - V_1}{2} \right) \left(\frac{P_2 - P_1}{2} \right)$$

20. A Heat supplied by the electric heater = $250 \times 55 = 13.75 \text{ kJ}$

$$\text{Heat capacity of calorimeter} = \frac{13.75 \text{ kJ}}{4.22 \text{ K}} = 326 \text{ kJ K}^{-1}$$

$$\text{Now, enthalpy of oxidation of methanol} = -C_{p, \text{calorimeter}} \times \Delta T_{\text{calorimeter}}$$

$$= -3.26 \times (26.77 - 22.49) = -13.9 \text{ kJ}$$

21. BC ΔG° is positive for $\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{O}_{(g)}$ at 1 atm and 298K; Entropy is the contributory factor for spontaneity of diffusion of two gases

22. BCD Reference state of sulphur is S_{rhombic}

23. BD ΔG° for the reaction, $2\text{Fe}_2\text{O}_3 + 6\text{CO} \rightarrow 4\text{Fe} + 6\text{CO}_2$ is given by,

$$\frac{1487 + (-15432)}{2} = -28.1 \text{ kJ mol}^{-1}$$

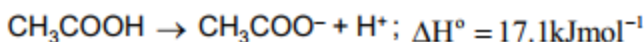
Thus, reduction of Fe_2O_3 with CO is spontaneous at this temperature

24. 327.37



$$\Delta H = \Delta u + \Delta n_g RT = -327 + (-0.15) \times 8.314 \times 300 \times 10^{-3} \text{ S}$$

25. 4.80



$$\text{For } 0.12 \text{ mol, energy required is } 17.1 \times 0.12 = 2.052 \text{ kJ}$$

$$\text{Now, enthalpy change for the neutralisation of } 0.12 \text{ mol } \text{CH}_3\text{COOH} \text{ is, } -57.1 \times 0.12 = -6.852 \text{ kJ}$$

26. 21.97 - 21.98

$$\Delta S = \frac{\Delta H}{T} = \frac{6000}{273} = 21.978 \text{ J K}^{-1} \text{ mol}^{-1}$$

27. 57.85 - 57.86

$$\Delta_r H = \sum \text{BE (reactants)} - \sum \text{BE (products)}$$

$$= (4x + y) - (3x + 84 + 103) = x + y - 187 = -25$$

$$x + y = 162 \Rightarrow \frac{9}{5}y + y = 162 \Rightarrow y = 57.857 \text{ kcal mol}^{-1}$$

28. 191.00

$$\Delta_r H = \sum \text{BE}(\text{reactants}) - \sum \text{BE}(\text{products})$$

$$= (435 + 240) - (2 \times 430) = -185 \text{ kJ mol}^{-1}$$

$$\Delta_r S = 2S_{\text{HCl}} - (S_{\text{H}_2} + S_{\text{Cl}_2}) = 20 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{Now, } \Delta_r G = \Delta_r H - T\Delta_r S = -185 - 300 \times 20 \times 10^{-3} = -191 \text{ kJ}$$

29. A Reversible isothermal expansion: $\Delta S_{\text{sys}} > 0 \Rightarrow \Delta S_{\text{sur}} < 0$

Reversible adiabatic compression: $\Delta S_{\text{sys}} = \Delta S_{\text{sur}} = 0$

Adiabatic free (Irreversible) expansion: $\Delta S_{\text{sys}} > 0$ & $\Delta S_{\text{sur}} = 0$

Irreversible isothermal compression: $q_{\text{sys}} < 0 \Rightarrow \Delta S_{\text{sur}} > 0$