

Department of Chemistry
Indian Institute of Technology Madras

CY 102 Chemistry II Assignment II

All Batches
5th February 2004

1. Find the melting point of ice at 100 atm if $\Delta H_{\text{fusion}} = 79.7 \text{ cal gm}^{-1}$.
 $\rho = 0.917 \text{ gm cm}^{-3}$ for ice at 0°C and 1 atm and
 $\rho = 1.00 \text{ gm cm}^{-3}$ for water at 1 atm. (Ans : 272.4 K)

$$\Delta H_{\text{fusion}} = 79.7 \text{ cal gm}^{-1}$$

$$\begin{aligned}\Delta V_{\text{fusion}} &= V_{\text{liq}} - V_{\text{solid}} \\ &= -0.091 \text{ cm}^3\end{aligned}$$

$$\ln T_2/T_1 = (P_2 - P_1) (\Delta V_{\text{fusion}}) / \Delta H_{\text{fusion}}$$

After substitution, $T_2 \approx 272.4 \text{ K}$.

2. What is the change in the boiling point of H₂O at 100⁰C per m.m change in the atmospheric pressure?. The heat of vapourisation is 539.7 cal gm⁻¹. The molar volume of H₂O (l) is 18.78 ml and that of H₂O (g) is 30.199 lit. (at 100⁰C and 1 atm)
(Ans : = .037 K mm¹)

$$\begin{aligned} dP/dT &= \Delta H_{\text{vap}}/TC (V_v - V_l) \\ &= 27.1 \text{ mm Hg K}^{-1}. \end{aligned}$$

$$\therefore dT/dP = 0.037 \text{ K mm Hg}^{-1}$$

3. The internal energy change (ΔU) for the combustion of ZrC(s) was -310863 cal/mol at 25°C . Calculate the enthalpy of combustion for
(Ans : $-311.5 \text{ K cal mol}^{-1}$)

$$\Delta H = \Delta U + (\Delta n) RT$$

$$\Delta U = \Delta H - (\Delta n) RT$$

$$= -310863 - (-1) \times 2 \times 298$$

$$\simeq -310.2 \text{ K cal mol}^{-1}.$$

4. Nitrobenzene was steam distilled at 98.7°C when the atmospheric pressure was 99.56 KPa. Calculate the % composition by the mass of the distillate given that the vapour pressure of H_2O and nitrobenzene are 96.63 and 2.93 kPa respectively.

(Ans : 17.2 % Nitrobenzene)

$$p_w/p_e = W_w/M_w / W_e/M_e$$

Consider 100 gms of the distillate.

Let x be the weight of nitrobenzene.

$$x/100 - x = 2.93 \times 123/96.63 \times 18$$

$$\therefore x = 17.2$$

17.2 wt % Nitrobenzene

5. The normal boiling point of C_6H_6 at 1 atm pressure is 353.2 K. Estimate the pressure at which C_6H_6 would boil at 330 K.
(Ans : 0.47 atm)

To obtain ΔH_v , employ Trouton's rule ($\Delta S_v = 88 \text{ J/K}$ is the normal value)

$$\therefore \Delta H_v \simeq 31800 \text{ J/mol}$$

$$\ln P_2/P_1 = 31800 (330 - 353.2) / (8.314) (353.2) (300)$$

$$\therefore P_2 \simeq 0.432 \text{ atm.}$$

Note: Depending upon the value of ΔH_v employed, the answer for P_2 may vary slightly.

6. Evaluate ΔG^0 , ΔH^0 , and ΔS^0 at 298 K for the reaction $\text{SOCl}_2(\text{l}) + \text{H}_2\text{O} \rightarrow \text{SO}_2(\text{g}) + 2\text{HCl}(\text{g})$ from the following data

Quantity	$\text{SOCl}_2(\text{l})$	$\text{H}_2\text{O}(\text{l})$	$\text{SO}_2(\text{g})$	$\text{HCl}(\text{g})$
$S_{298}^0 (\text{J mol}^{-1}\text{K}^{-1})$	215.7	69.9	248.1	186.8
$\Delta H_f^0 \text{ at } 298 \text{ K } (\text{KJ mol}^{-1})$	-245.6	-241.8	-296.8	-92.3

(Ans : $\Delta S_{298}^0 = 336.1 \text{ J mol}^{-1} \text{ K}^{-1}$;

$\Delta H_{298}^0 = 49.4 \text{ KJ mol}^{-1}$; $\Delta G_{298}^0 = -50.8 \text{ KJ / mol}$)

ΔG^0 , ΔH^0 , ΔS^0 for the reaction

$$\Delta H_{298}^0 = [- (296.8) + 2 (-92.3)] - [-245.6 - 241.8]$$

$$= 6 \text{ kJ / mol.}$$

$$\Delta S_{298}^0 = 336.1 \text{ Jk}^{-1} \text{ mol}^{-1}; \Delta G_{298}^0 = 6000 - (298) (336.1) = -94.15 \text{ kJ}$$

7. Calculate the change in the free energy of 1 mole of acetylene when it is heated from 500K to 600 K at constant pressure.

The average entropy of acetylene in this temperature change is 230 J/K/mol

(Ans : 23KJ/mol).

$$dG = VdP - SdT$$

$$\Delta G = -S(T_2 - T_1)$$

$$= -230 (600 - 500) = -2300 \text{ J/mol.}$$

8. From the given data predict whether the reaction $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$ is spontaneous.

	ΔH_f° (KJ/mol)	S° (J/K/mol)
$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-277.69	160.7
$\text{H}_2\text{O}(\text{l})$	-285.83	69.91
$\text{C}_2\text{H}_4(\text{g})$	52.26	291.56

(Ans: -5.75 KJ. Spontaneous)

$$\begin{aligned}\Delta S^\circ &= 160.7 - (69.91 + 291.56) \\ &= -200.77 \text{ Jk}^{-1}\text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta H^\circ &= -277.69 - (-285.83 + 52.26) \\ &= -44.12 \text{ KJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= -44120 - (298)(-200.77) \\ &= 15.709 \text{ J mol}^{-1}\end{aligned}$$

= +ve \therefore non-spontaneous in the direction specific.

9. The change in the Gibbs free energy values, under standard conditions, (ΔG^0) for a reaction at 500 K and 510 K are -122 KJ and -124 KJ respectively. Calculate the values of ΔH and ΔS assuming that they do not vary with the temperature.

(Ans : $\Delta H = -22$ KJ & $\Delta S = -200$ J/K)

Ans: $T_1 = 500$ K; $T_2 = 510$ K.

$$\Delta G^0_{T_2} = -124 \text{ kJ}$$

$$\Delta G^0_{T_1} = -122 \text{ kJ}$$

$$\Delta G^0_{T_2}/T_2 - \Delta G^0_{T_1}/T_1 = \Delta H^0 [1/510 - 1/500]$$

$$-124/510 + 122/500 = \Delta H^0(-10)/500 \times 510$$

$$-0.2431 + .244 = \Delta H^0 (-3.921 \times 10^{-5})$$

$$\Delta H^0 = 9 \times 10^{-4} / -3.921 \times 10^{-5}$$

$$\simeq -90/3.92 \simeq -22.96 \text{ kJ.}$$

$$\therefore \Delta G^0_{500 \text{ k}} = -22.96 - (500) \text{ kJ}$$

$$\therefore \Delta S^0 \text{ at } 500 \text{ K} \simeq 0.198 \text{ kJ}$$

10. For an equilibrium process, a plot of $\ln K$ against $1/T$ gave a straight line with a negative slope, equal to 7040 K^{-1} .

Find the value of ΔH^0 .

(Ans : 58.53 kJ/mol)

Ans: $d \ln K/d(1/T) = -\Delta H^0/R$

$\therefore \Delta H^0 = 58.53 \text{ kJ mol}^{-1}$

11. At 25°C the distribution ratio of H₂S between water and benzene is 0.17 (a) what is the minimum volume of benzene necessary at 25°C to extract in one step 90% of H₂S present in one litre of a 0.1 M aq. solution ? b) using 100 cc of benzene every time, how many extractions will be required to complete 90% extraction ?

(Ans : a = 1530 CC ; b = 5 extractions)

Ans: $K = \frac{[\text{H}_2\text{S}]_{\text{H}_2\text{O}}}{[\text{H}_2\text{S}]_{\text{C}_6\text{H}_6}} = 1/5.88$ i.e., 0.17

$$\begin{aligned} \text{a) } W_1 &= 10 = 100 (0.17/0.17 + y) \\ 100 (0.17/0.17 + y) &= 10 \\ \therefore y &= 1.53 \text{ litres for 90\% extraction.} \end{aligned}$$

$$\begin{aligned} \text{b) For what value of } n, \\ 10 = 100 (0.17/0.17 + 0.1)^n \text{ is valid?} \\ n \simeq 5 \\ \therefore 5 \text{ extractions.} \end{aligned}$$

12. When aniline (M.Wt= 93 gm mol⁻¹) is steam distilled at 1 atm, the distillate is found to contain 26.5 % by wt.of aniline. What is the vapour pressure of aniline at the temperature of distillation ?

(Ans : 0.0652 atm / 49.57 mm.Hg)

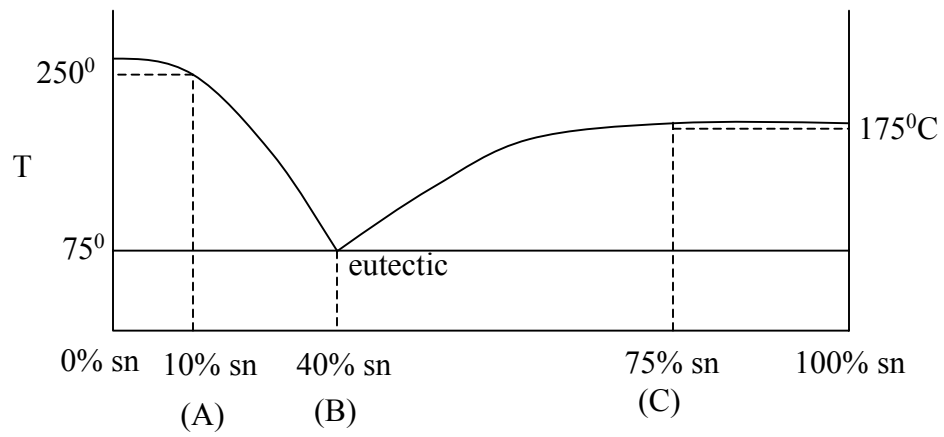
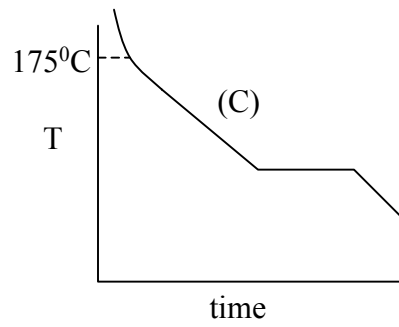
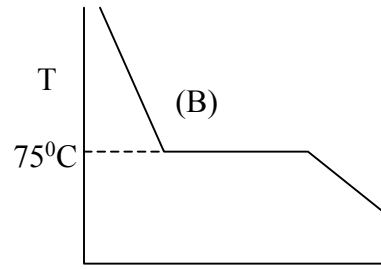
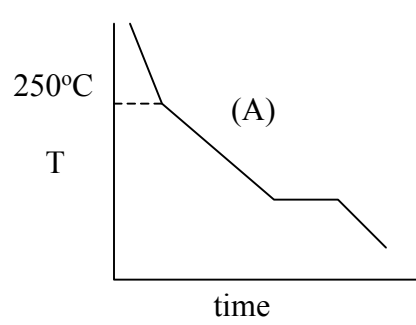
$$\text{Ans: } 26.5/73.5 = p_e / 93 \times 18 / (760 - p_e)$$

$$p_e / 760 - p_e = 18 \times 26.5 / 93 \times 73.5 = 0.06978$$

$$\therefore p_e = 49.57 \text{ mm Hg.}$$

13. Construct the phase diagram of a two component system forming simple eutectic. Apply the phase rule in each region. Draw the cooling curve for pure A, at eutectic composition and another one in between these two compositions.

Ans: Phase diagram of a two - component system forming a simple eutectic.



14. The equilibrium constant of the reaction
 $\text{C (graphite)} + 2 \text{H}_2(\text{g}) = \text{CH}_4(\text{g})$, at 35°C is 3.036×10^8 and
 ΔH^0 for the reaction in the temperature range $25 - 35^\circ\text{C}$ is 179 K cal .
 Calculate ΔG^0 at 25°C

(Ans : - 5754 Cals)

K_p at $308 \text{ K} = \text{given}$

$$\begin{aligned} \Delta G^0_{308} &= -RT \ln (3.036 \times 10^8) \\ &= -2 \times 308 \times 19.5312 \text{ cal mol}^{-1}. \\ &= -12.031 \text{ K cal mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G^0_{308} / 308 - \Delta G^0_{298} / 298 &= \Delta H^0 (1/308 - 1/298) \\ -12.031/308 - \Delta G^0_{298} / 298 &= 179 (-10)/(298) (308) \\ \therefore \Delta G^0_{298} &\simeq -5.82 \text{ k. cal.} \end{aligned}$$

15. The vapour pressure in torr for ice and liq. water are given by the equations. (energy in joules)

$$\ln P (\text{ice}) = 24.00 - \frac{6140.1}{T}$$

$$\ln P (\text{H}_2\text{O}) = 21.41 - \frac{5433}{T}$$

Calculate the triple point temperature and pressure. Determine the molar enthalpies of vapourisation, sublimation and fusion of H₂O at its triple point

(Ans : 273.01 K & 4.55 torr; 45.2, 51.1 & 5.9 KJ/mol)

Ans: At the triple point temperature,

$$24.00 - 6140.1 / T = 21.41 - 5433 / T$$

$$\therefore 6140.1/T - 5433 / T = 2.59$$

$$707.1 / T = 2.59$$

$$\therefore T = 273.01 \text{ K.}$$

Substituting in any of the equations,

we obtain the triple point pressure as

$$\begin{aligned}\ln P &= 24.00 - 6140.1/273.01 \\ &= 1.509 \\ \therefore P &\simeq 4.52 \text{ Torr.}\end{aligned}$$

From the first eqn, $d \ln p/dT = 6140.1/T^2 = \Delta H^0 (\text{sublimation})/RT^2$

$$\therefore \Delta H^0_{\text{sub}} = 6140.1 \times 8.314 = 51.05 \text{ kJ/mol}^{-1}.$$

From the second eqn, $d \ln p/dT = 5433 /T^2 = \Delta H^0_{\text{vap}}/RT^2$

$$\therefore \Delta H^0_{\text{vap}} = 45.17 \text{ kJ/mol}$$

$$\therefore \Delta H^0_{\text{fusion}} = 51.05 - 45.17 = 5.88 \text{ kJ/mol}^{-1}.$$

16. Calculate the change in entropy of a mole of aluminium (at.wt .27) which is heated from 600 to 700⁰ C. The m.pt .of Al is 660⁰ C, the heat of fusion is 393 Jg⁻¹ and the heat capacities of the solid and liquid may be taken as 31.8 amd 34.3 JK⁻¹ mol respectively.

(Ans : 14.92 JK⁻¹ mol⁻¹)

$$\Delta S = C_p^s \ln T_m/T_1 + \Delta H_f/T_m + C_p^l \ln T_2/T_m$$

$$\Delta H_f = 393 \text{ J gm}^{-1} = 10.611 \text{ kJ mol}^{-1}.$$

$$\therefore \Delta s = 31.8 \ln 933/873 + 10611/933 + 34.4 \ln 973/933$$

$$\simeq 14.93 \text{ JK}^{-1} \text{ mol}^{-1}.$$

17. Based on the Trouton's rule, calculate the molar heat of vapourisation of benzene at its boiling point of 353 K (Ans: 31 KJ)

$$\Delta H^0 = 90 \text{ J mol}^{-1} \quad \therefore \Delta H^0_{\text{v}} = 90 \times 353 \approx 31.77 \text{ kJ}$$

18. Calculate the molar heat capacity of a non – linear triatomic gas assuming that the principle of equipartition is valid

$$(\text{ Ans : } 49.9 \text{ J mol}^{-1} \text{ deg}^{-1})$$

$$\text{Ans: } C_{\text{v}} = 3R/2 + 3R/2 + 3R \simeq 49.88 \text{ Jk}^{-1} \text{ mol}^{-1}.$$

19. For the reaction $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$ K_p is 0.63 at 700°C and 1.66 at 100°C . a) What is the average value of K_p in this temperature range? b) What is the value of K_p at 800°C ?

(Ans : $\Delta H = 8 \times 10^3 \text{cal}$, $K_p = 0.93$)

$$\ln K_p(T_2)/K_p(T_1) = \Delta H^0(T_2 - T_1)/R T_1 T_2$$

$$K_p(973 \text{ K}) = 0.63; K_p(373 \text{ K}) = 1.66$$

$$\Delta H^0 = -1.17 \times 10^3 \text{ cal}$$

$$\ln K_p(T_2 - 1073\text{k})/0.63 = \Delta H^0/R (1073 - 973)/(1073 \times 973)$$

$$\therefore K_p \text{ at } 1073 \text{ K} \simeq 0.67$$