Department of Chemistry
Indian Institute of Technology Madras
CY 101 Assignment I

All Batches August 2005

1.Find the melting point of ice at 100 atm if ΔH_{fusion} = 79.7 cal gm^{-1}. ρ = 0.917 gm cm^{-3} for ice at 0^0 C and 1 atm and ρ = 1.00 gm cm^{-3} for water at 1 atm.

(Ans : 272.4 K)

Ans: ΔH_{fusion} = 79.7 cal gm^{-1}

$\Delta V_{fusion} = V_{liq} - V_{solid}$

= - 0.091 cm^3

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

After substitution, $T_2 \simeq 272.4$ K.

2.What is the change in the boiling point of H_2O at 100^0C per m.m change in the atmospheric pressure?. The heat of vapourisation is 539.7 cal gm^{-1}. The molar volume of H_2O (l) is 18.78 ml and that of H_2O (g) is 30.199 lit. (at 100^0C and 1 atm) (Ans : $\frac{dT}{dP}$ = .037 K mm^1)

Ans: $dP/dT = \Delta H_{vap}/T (V_v - V_l)$

= 27.1 mm Hg K^{-1}.

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

3.The internal energy change (ΔU) for the combustion of ZrC(s) was –310863 cal/mol at 25^0C. Calculate the enthalpy of combustion for

$[ZrC(s) + 2O_2(g) \rightarrow ZrO_2(s) + CO_2(g)]$ (Ans : -310.2 K cal mol^{-1})

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

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

= -310863 – (-1) x 2 x 298

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

4.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 : 0.432 atm)

Ans: To obtain ΔH_v, employ Trouton's rule

$\therefore \Delta H_v \simeq$ 31800 J/mol

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

$\therefore P_2 \simeq$ 0.432 atm.

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

5.Evaluate $\Delta G^0, \Delta H^0, and\ \Delta S^0$ at 298 K for the reaction $SOCl_2(l)$ + $H_2O \rightarrow SO_2(g) + 2HCl\ (g)$ from the following data

Quantity	$SOCl_2(l)$	$H_2O(l)$	$SO_2\ (g)$	$HCl\ (g)$
$S^0_{298}(J\ mol^{-1}K^{-1}$	215.7	69.9	248.1	186.8
$\Delta H_f^0 at$ 298 K kJ mol^{-1}	- 245.6	- 241.8	- 296.8	- 92.3

(Ans : ΔS_{298}^0 = 336.1 J mol^{-1} K^{-1};

ΔH^o_{298K} = 6 kJ mol^{-1}, ΔG^o_{298K} = -94.15 kJ mol^{-1}

Ans: ΔG^0, ΔH^0, ΔS^0 for the reaction

ΔH^0_{298} = [- (296.8) + 2 (-92.3)] – [-245.6 – 241.8]

= 6 kJ / mol.

ΔS^0_{298} = 336.1 Jk^{-1} mol^{-1}; ΔG^0_{298} = 6000 – (298) (336.1) = -94.15 kJ mol^{-1}

6. 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 : 23 kJ/mol).

Ans: dG = VdP – SdT

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

= -230 (600 – 500) = -2300 J/mol.

7. From the given data predict whether the reaction

$C_2H_4(g) + H_2O(l) \rightarrow C_2H_5OH\ (l)$

is spontaneous.

	ΔH^0_f (kJ/mol)	S^0 (J/K/mol)
C_2H_5OH (l)	-277.69	160.7
H_2O(l)	-285.83	69.91
C_2H_4(g)	52.26	291.56

(Ans: 15.7 kJ. nonspontaneous)

Ans: ΔS^0 = 160.7 – (69.91 + 291.56)

= -200.77 JK^{-1}mol^{-1}

ΔH^0 = -277.69 – (-285.83 + 52.26)

= - 44.12 kJ mol^{-1}

ΔG^0 = -44120 – (298) (-200.77)

= 15.709 J mol^{-1}

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

8. 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 temperature.

(Ans : ΔH = -23 kJ & ΔS = -200J)

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

ΔG^0_{T2} = -124 kJ

ΔG^0_{T1} = -122 kJ

$\Delta G^0_{T2}/T_2 - \Delta G^0_{T1}/T_1 = \Delta H^0$ [1/510 – 1/500]

-124/510 + 122/500 = ΔH^0(-10)/500 x 510

-0.2431 + .244 = ΔH^0 (-3.921 x 10^{-5})

ΔH^0 = 9 x 10^{-4} / -3.921 x 10^{-5}

$\simeq$ -90/3.92 $\simeq$ -22.96 kJ.

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

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

9. 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(l/I) = $-\Delta H^0/R$

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

10. The equilibrium constant of the reaction C (graphite) + 2 H_2(g) = CH_4(g), at 35^0C is 3.036 X 10^8 and ΔH^0 for the reaction in the temperature range 25 – 35^0C is 179 k cal. Calculate ΔG^0 at 25^0C. (Ans : - 5820 cal)

Ans: K_p at 308 K = given

ΔG^0_{308} = - RT ln (3.036 x 10^8)

= -2 x 308 x 19.5312 cal mol^{-1}.

= -12.031 kcal mol^{-1}

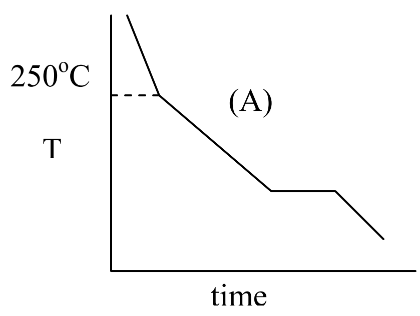
$^{\Delta G0}{}_{308}$ / 308 - $^{\Delta G0}{}_{298}$ / 298 = ΔH^0 (1/308 – 1/298)

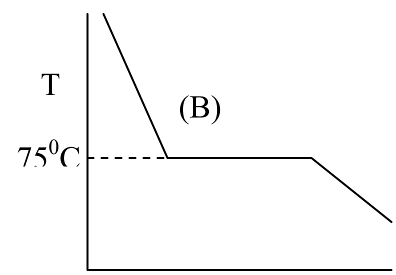
-12.031/308 - $^{\Delta G0}{}_{298}$ / 298 = 179 (-10)/(298) (308)

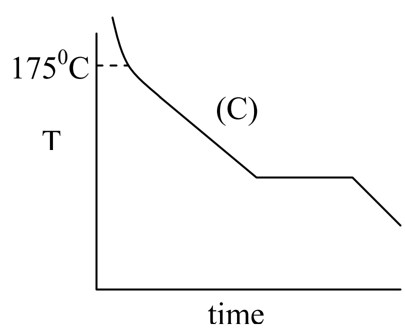
$\therefore \Delta G^0_{298} \simeq$ -5.82 k.cal.

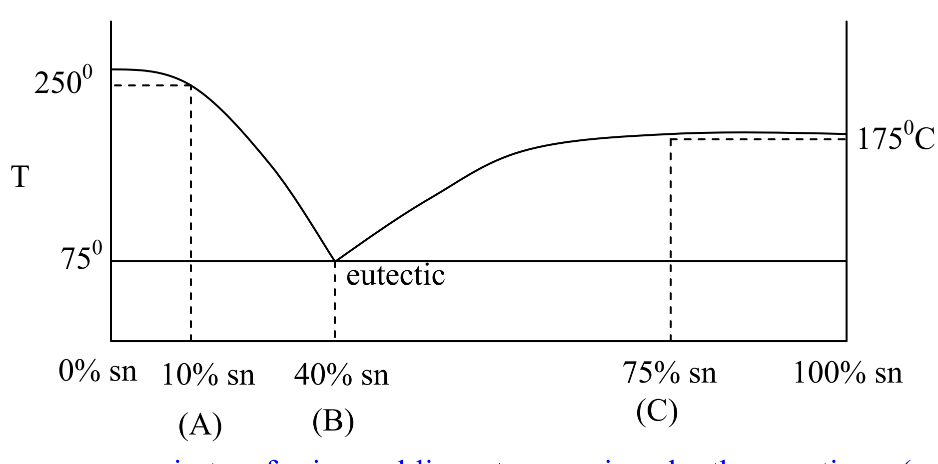
11. Construct the phase diagram of a two component system forming simple eutectic. Apply the phase rule in each region. Draw the cooling cure for pure A, at eutectic composition and another one in between these two compositions.

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









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

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

$$\ln P\,(H_2O) = 21.41 - \frac{5433}{T}$$

Calculate the triple point temperature and pressure. Determine the molar enthalpies of vapourisation, sublimation and fusion of H_2O at its triple point

(Ans : 273.01 K & 4.52 torr; 45.2, 51.1 & 5.9 kJ mol^{-1})

Ans: At the triple point temperature,

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

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

$707.1 / T = 2.59$

$\therefore T = 273.01$ K.

Substituting in any of the equations, we obtain the triple point pressure as

$\ln P = 24.00 - 6140.1/273.01$

$= 1.509$

$\therefore P \simeq 4.52$ Torr.

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

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

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

$\therefore \Delta H^0_{vap} = 45.17$ kJ mol^{-1}

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

13.Calculate the change in entropy of a mole of aluminium (at.wt .27) which is heated from 600 to 700^0 C. The m.pt .of Al is 660^0 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})

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

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

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

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

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

Ans: $\Delta H^0 = 90$ J mol^{-1} $\therefore \Delta H^0_v = 90 \times 353$ □ 31.77 kJ

15. Calculate the molar heat capacity of a non – linear triatomic gas assuming that the principle of equipartition is valid (Ans : 49.9 J mol^{-1} deg^{-1})

Ans: $C_v = 3R/2 + 3R/2 + 3R \simeq 49.88$ JK^{-1} mol^{-1}.

16. For the reaction CO_2 (g) + H_2 (g) □□□ CO_2(g) + H_2O (g) K_p is 0.63 at 700^0 C and 1.66 at 100^0 C. a) What is the average value of ΔH in this temperature range ? b) What is the value of K_p at 800^0C ?

(Ans : $\Delta H = 1.17 \times 10^3$cal, K_p= 0.67)

Ans: $\ln K_p(T_2)/K_p(T_1) = \Delta H^0(T_2 - T_1)/R\ T_1T_2$
$K_p(973K) = 0.63$; $K_p\ (373\ K) = 1.66$
$\Delta H^0 = -1.17 \times 10^3$ cal
$\ln [K_p(1073K)/0.63] = \Delta H^0/R\ (1073 - 973)/(1073 \times 973)$
$\therefore K_p$ at 1073 K $\simeq 0.67$

17. 100 g N_2 at 300 K were held by a piston at 30 atm. Pressure was released suddenly to become 10 atm, adiabatically. Calculate ΔS. C_V= 20.8 $JK^{-1}mol^{-1}$.

$\Delta S = n(C_v \ln T_2/T_1 + R \ln V_2/V_1)$

Sudden adiabatic expansion, T_2 is unknown.
$V_2/V_1 = T_2P_1/T_1P_2 = 217.8$
$\Delta S = -0.692\ JK^{-1}$

18. Calculate entropy change when 0.5 L ideal gas, C_V = 12.6 $JK^{-1}mol^{-1}$, at 300 K and 1 atm was allowed to expand to double its volume while heated simultaneously to 373 K.

$\Delta S = n(C_v \ln T_2/T_1 + R \ln V_2/V_1)$
$\Delta S = 0.17\ JK^{-1}$

19. 10 g ice at 0 oC are added to 20 g water at 90 oC, in a thermally insulated flask of negligible heat capacity. Heat of fusion of ice is 6 kJ mol^{-1}. Calculate the final temperature and the entropy change of the system. C_P = 75.42 $JK^{-1}mol^{-1}$.

10 g H_2O (s), 273 K → H_2O(l) 273 K → H_2O(l), T K , Two entropy changes, ΔS_1, ΔS_2
90 g H_2O(l) 363 K → H_2O(l), T K, ΔS_3

Heat balance equation, nL_f+ Cp(T-273) = nCp(363-T); T = 306.5

$\Delta S1 = nL_f/T = 12.2\ JK^{-1}$
$\Delta S2 = n(C_p \ln T_2/T_1) = 4.85\ JK^{-1}$
$\Delta S3 = n(C_p \ln T_2/T_1) = -14.31\ JK^{-1}$
ΔS = sum = 2.75 JK^{-1}, corresponds only to the system

20. In an open beaker held at 27 oC and 1 at pressure containing dilute sulphuric acid, 100 g zinc were added. Calculate the work done by the liberated gas. Calculate the work done if the reaction was carried out in a closed container.

Zn + H2SO4 → ZnSO4 + H2
Wirr = ΔnRT = 100/65 x 8.314 x 300 = 3.84 kJ
Closed container, no volume change, no work.

21. A balloon containing air at 1 atm pressure is 0.5 m in diameter. It was isothermally filled with air so that the pressure is 5 atm. Assuming the pressure is proportional to the diameter of the balloon, calculate the (a) final diameter and (b) work done in the process.

$P \alpha d$

d final = 2.5 m

$P = kd = k = 2$ atm m^{-1}

$dW = P\,dV = kd\,.\,3\,(4\pi)\,(d/2)^2\,dd = k\pi/2\,d^3\,dd$

$W = k\pi/2 \int_{0.5}^{2.5} d^3\,dd = k\pi/8\,[2.5^4 - 0.5^4] = [2\text{atm m}^{-1} \times \pi/8] \times 39 = 30.63$ atm m^3

$= 3.1 \times 10^6$ J

22. The entropy change of argon is given to a good approximation by the expression, S JK^{-1} mol^{-1} = 36.36 + 20.79 ln T

Calculate change in Gibb's free energy of one mole of argon gas if it is heated at constant pressure from 25 °C to 50 °C.

$dG = VdP - SdT$, at constant P, $dG = -SdT$

$\int dG = -[36.36\int dT + 20.79\int \ln T dT] = -36.36\,(T2-T1) - 20.79[T\ln T - T]_{T1}^{T2}$

$= -999 - 20.79\,(1543.18 - 1399.73) = -3891.33$ J

23. 1 mole of ideal gas initially at 10 atm and 300 K was expanded adiabatically against a constant pressure of 4 atm so as to reach equilibrium. $C_P = 28.48 + 1.76 \times 10^{-2}$ T $Jmol^{-1}$. Calculate ΔU, ΔH and Δ S.

$C_V = 20.17 + 1.76 \times 10-2$ T

$dU = C_V\,dT = PdV$

$\Delta U = 20.17\,(T_2 - T_1) + 1.76/2\,10^{-2}\,(T_2^2 - T_1^2) = P_2\,(V_2 - V_1) = P_2\,(RT_1/P_1 - RT_2/P_2) =$

$R\,(P_2T_1/P_1 - T_2)$

We can now solve for T_2.

$T_2 = 255.3$ K

$dS = C_P\,dT/T - R\,dP/P = (28.58 + 1.76 \times 10^{-2}\,T)\,dT/T - R\,dP/P$

$\Delta S = 28.58 \ln T_2/T_1 + 1.76 \times 10^{-2}\,(T_2 - T_1) + R \ln P_1/P_2 = 2.22\ JK^{-1}$

$\Delta U = \int C_V\,dT = -1124.3$ J

$\Delta H = \int C_P\,dT = -1496$ J

24. One mole of ideal gas was subjected to the following change. A (5 atm, 500K) → (reversible isothermal expansion) B → (isochoric cooling) C (300K) -→ (reversible adiabatic compression) → A. Depict the above process in a P-V diagram, determine the net work done in the cyclic process. $C_V = 1.5R$.

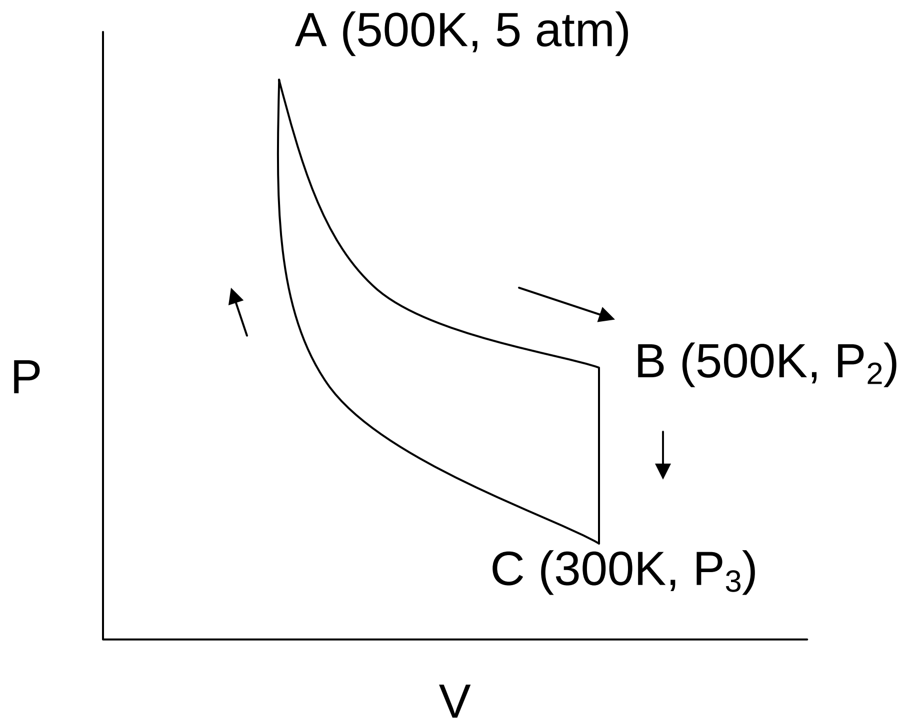
$P_3/P_1 = (T_1/T_3)^{-Cp/R}$

$P_3 = (T_1/T_3)^{-Cp/R}\,P_1$

$P_3 = (500/300)^{-2.5}\,5 = 1.39$ atm

$P_2V_2/P_3V_3 = T_2/T_3$ (V_3 and V_2 are the same)
$P_2 = (T_2/T_3) \times P_3 = (500/300) \times 1.39 = 2.32$ atm

$W_{A\ to\ B} = -RT \ln P_1/P_2 = 8.314 \ln 5/2.32 = 3192$ J
$W_{B\ to\ C} = 0$
$W_{C\ To\ A} = -\ n\ C_V\,(T_2\text{-}T_1) = -1.5 \times 8.314 \times 200 = -\ 2494.2$ J
$W_{Total} = -697.8$ J



(Question 17 to 24 are from Problems in Chemistry, Ranjeet Shahi, Arihant Prakashan)