Department of Chemistry, Indian Institute of Technology Madras

CY 1001 Assignment (Physical Chemistry)
September 2010
Batches a, b, c, d and e

1. What is the change in the boiling point of H_2O at 100^0 C per mm change in the atmospheric pressure? The heat of vaporization 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)

$\frac{dT}{dP}$ = .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)

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

$ZrC(s) + 2O_2(g) \rightarrow ZrO_2(s) + CO_2(g)$

$\left[ZrC(s) + 2O_2(g) \square \quad ZrO_2(s) + CO_2(g)\right]$

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}.

3. 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.

4. 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/Kmol.

Ans: dG = VdP – SdT

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

= -230 (600 – 500) = -2300 J/mol.

5. Calculate the change in entropy of a mole of aluminium (at.wt .27) which is heated from 600 to 700^0 C. The m. p. 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 and 34.3 JK^{-1} mol respectively.

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}.

6. 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}

7. 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}

8. 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.

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$
$W_{irr} = \Delta nRT = 100/65 \times 8.314 \times 300 = 3.84$ kJ
Closed container, no volume change, no work.

9. 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 ^oC to 50 ^oC.

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

10. 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.

$C_V = 20.17 + 1.76 \times 10\text{-}2\ T$
$dU = C_V\, dT = PdV$
$\Delta U = 20.17\,(T_2-T_1) + 1.76/2\ 10^{-2}\,(T_2^2-T_1^2) = P_2\,(V_2-V_1) = P_2\,(RT_1/P_1 - RT_2/P_2) =$
$R\,(P_2T_1/P_1 - T_2)$

We can now solve for T_2.
$T_2 = 255.3\ K$

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

$\Delta U = \int C_V\, dT = -1124.3\ J$
$\Delta H = \int C_P\, dT = -1496\ J$

11. The enthalpy of vaporization of a certain liquid is found to be 14.4 kJ mol^{-1} at 180 K, its normal boiling point. The molar volumes of the liquid and the vapour at the boiling point are 115 $cm^3\ mol^{-1}$ and 14.5 $dm^3\ mol^{-1}$, respectively. (a) Estimate dp/dTfrom the Clapeyron equation and (b) the percentage error in its value if the Clausius-Clapeyron equation is used instead.

(Ans.: (a) 5.56 kPa K^{-1} ; (b) 2.5 per cent.)

$$\frac{dP}{dT} = \frac{\Delta H_{vap}}{V_g T} = \frac{14.4x10^3\ J/mol}{14.5 dm^3/molx180K} = 0.0055172x10^6\ J/m^3K \sim 5.2kPa/K$$

12. Consider a system of distinguishable particles having only two non-degenerate energy levels separated by an energy which is equal to the value of kT at 10K. Calculate at 10K, the ratio of populations in the two states.

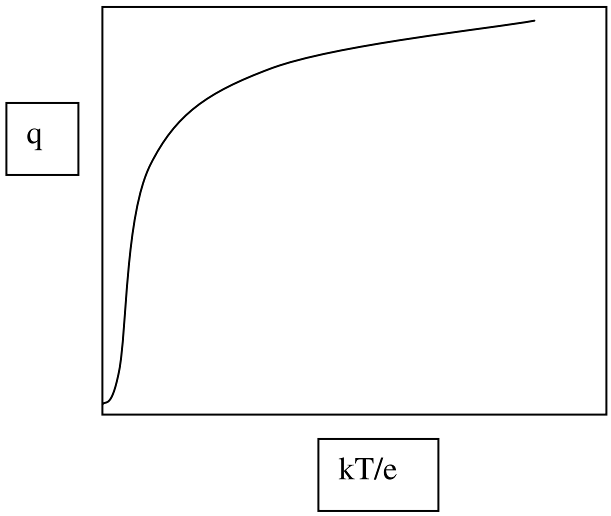
(Ans.: 0.4)

Q2 Energy separation is $\varepsilon = k \times (10K)$

(a) $\frac{n_1}{n_0} = e^{-\beta(\varepsilon_1-\varepsilon_0)} = e^{-\beta\varepsilon} = e^{-10/T}$

$T = 10K$ $\quad \frac{n_1}{n_0} = e^{-1.0} = 0.4$

13. Draw a graph showing the variation in partition function q for a two level system as the system temperature → infinity.



(Atkins, page number 566)

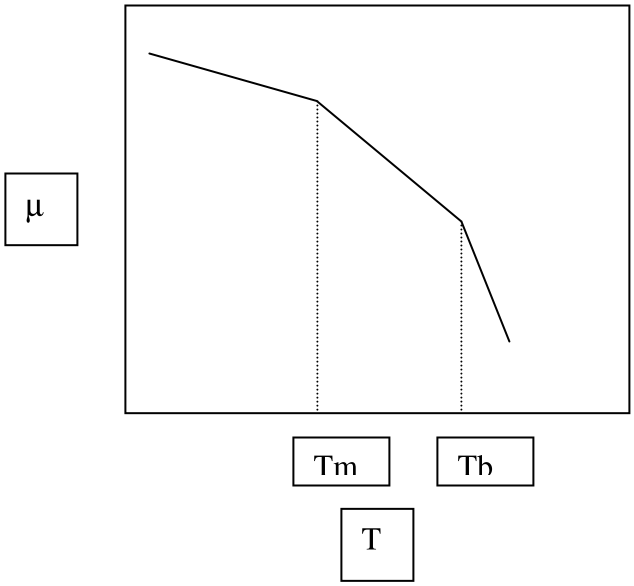
14. Calculate the residual entropy of N2O at absolute zero, assuming that equal mole fractions of NNO and ONN exist in the system.

Entropy of mixing problem.

$$\Delta_{mix}S = -n_t R \sum y_i \ln y_i$$

$n_t = 1$; $yi = ½$.

15. Plot a graph of chemical potential variations with respect to temperature in a system undergoing phase transitions from solid to liquid and to vapor. Indicate the melting and boiling points in the graph.


μ
Tm
Tb
T