



Eastern University, Sri Lanka

Third Examination in Science

Special degree Examination in Chemistry -2012/2013

CHS 03 Physical Chemistry -I



Answer all questions

Time: 02 hours

Velocity of Light ( $c$ ) =  $2.99 \times 10^8 \text{ m s}^{-1}$  Planck's constant ( $h$ ) =  $6.626 \times 10^{-34} \text{ J s}$   
Boltzmann's constant ( $k$ ) =  $1.38 \times 10^{-23} \text{ J K}^{-1}$  Mass of electron ( $m_e$ ) =  $9.1 \times 10^{-31} \text{ kg}$   
Gas constant ( $R$ ) =  $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

1. a) i) For a dilute solutions, show that the depression of boiling point ( $\Delta T$ ) between the solvent vapour and solvent in solution in terms of molality of the solution is,

$$\Delta T = \left( \frac{RT^2 M}{\Delta H_{vap}} \right) m_B,$$

where  $M$  is the molecular weight of the solvent,  $m_B$  is the molality of the solution and other symbols have their usual meanings

(20 marks)

- ii) The osmotic pressure of a solution of hormone adrenaline in  $\text{CCl}_4$  at  $30^\circ \text{C}$  is 120 kPa. Calculate the boiling point elevation of the solution. Boiling point elevation coefficient ( $k_b$ ) and density of  $\text{CCl}_4$  are  $4.68^\circ \text{C kg mol}^{-1}$  and  $1465 \text{ kg m}^{-3}$  respectively.  
[Use Van't Hoff equation ]

(40 marks)

- b) i) Show that the Gibbs energy change of mixing ( $\Delta_{mix}G$ ) of two perfect gases A and B in amounts of  $n_A$  and  $n_B$  at temperature  $T$  is,

$$\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B)$$

where  $x_A$  and  $x_B$  are mole fraction of gases A and B in the mixture, respectively.

(15 marks)

Contd.

- ii) A container is divided into two compartments. One contains 3 moles of  $H_2$  gas at 1.5 atm and  $25^\circ C$ , the other contains 2 moles  $N_2$  gas at 3 atm and  $25^\circ C$ . Calculate  $\Delta_{mix}G$  when the partition is removed.

(25 marks)

2. a) The quantum mechanical energy levels  $\epsilon_n$  and degeneracies  $g_n$  of a **doubly-degenerate** bending vibration are given within the harmonic normal mode approximation by  $\epsilon_n = (n + 1)h\nu$  and  $g_n = (n + 1)$  where  $n = 0, 1, 2, \dots$

- i) Write the expression for molecular partition function ( $q$ )

- ii) Show that the sum of the molecular partition function

$$q = e^{-\beta h\nu} (1 - e^{-\beta h\nu})^{-2}$$

[Use the fact that  $1 + 2x + 3x^2 + \dots = (1 - x)^{-2}$  for  $x < 1$ ]

- iii) Compare your result obtained in (ii) with the partition function of a non-degenerate oscillator,  $q = e^{-\beta h\nu/2} (1 - e^{-\beta h\nu})^{-1}$

- iv) Show that the contribution to the average energy per molecule in a system of  $N$  non-interacting molecules is,

$$\frac{E}{N} = -\frac{1}{q} \frac{dq}{d\beta}$$

- v) Show that, for a **doubly-degenerate** oscillator,

$$\frac{E}{N} = h\nu \left[ 1 + \frac{2e^{-\beta h\nu}}{1 - e^{-\beta h\nu}} \right]$$

(80 marks)

- b) The first electronically excited state of  $O_2$   ${}^1\Delta_g$  (doubly degenerate) lies  $7918 \text{ cm}^{-1}$  above the ground state, which is  ${}^3\Sigma_g$  (triply degenerate). Calculate the electronic contribution to the molar Gibbs energy of  $O_2$  at 400 K. Use the relation  $G_m - G_m^{(0)} = -RT \ln q$ .

(20 marks)

Using the first order perturbation theory, the real wave function could be written in the form  $\psi_{n,real} = \psi_n^{(0)} + \sum_m a_m \psi_m^{(0)}$  where  $\psi_n^{(0)}$  and  $\psi_m^{(0)}$  are ideal wave functions and  $a_m$  is  $m^{\text{th}}$  expansion coefficient for the perturbation to the  $n^{\text{th}}$  real wave function

- i) Write an expression for the expansion coefficient  $a_m$
- ii) Electrons in the bond  $CN^-$  act as a particle in a 1-D box that has a slightly higher potential energy on one side than the other. Assume a first order perturbation Hamiltonian  $\hat{H} = kx^2$  for the ground state wave function  $\psi_1$  of a particle in a box system and the correction to the real ground state wave function is the second particle in a box of wave function  $\psi_2$ .

The wave function of particle in a box is  $\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$ .

Calculate the expansion coefficient ( $a_2$ ) and hence show that the first order corrected wave function ( $\psi_{1,real}$ ) is,

$$\psi_{1,real} = \psi_1 + \left(\frac{128kma^4}{27\pi^2 h^2}\right) \psi_2$$

$$[\sin ax \cdot \sin bx = 1/2[\cos(a-b)x - \cos(a+b)x]]$$

$$[\int x^2 \cos ax \, dx = \left(\frac{2x}{a^2}\right) \cos ax + \left(\frac{a^2 x^2 - 2}{a^3}\right) \sin ax]$$

(100 marks)

- a)
  - i) Write the expression which relates the variation of fugacity with pressure at constant temperature.
  - ii) For a gas that obeys the equation of state  $PV_m = RT + bP - \frac{aP}{T}$ , show that

$$\ln \gamma = (b - a/T)P/RT$$

where  $\gamma$  is the fugacity coefficient and  $a$  and  $b$  are constants.

(50 marks)

- b)
  - i) Write the expression of rotational partition function ( $q_{rot}$ ) for nonlinear asymmetric top polyatomic molecule XYZ.

Contd.

- ii) Hence show  $q_{rot} = \frac{1}{\sigma} \left( \frac{kT}{hc} \right)^{3/2} \left( \frac{\pi}{B_x B_y B_z} \right)^{1/2}$ , where  $B_x, B_y$  and  $B_z$  are rotational constants of atoms X, Y and Z respectively.

[Rotational constant  $B = h/8\pi^2 I c$ ]

- iii) The NOF molecule is a nonlinear molecule with rotational constants 3.1752  $\text{cm}^{-1}$ , 0.3951  $\text{cm}^{-1}$  and 0.3505  $\text{cm}^{-1}$ . Calculate the rotational partition function of the molecule at 298 K ( $\sigma = 1$ )

(50 marks)

End of paper