UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE SPECIAL DEGREE (LEVEL I) SEMESTER (II) EXAMINATIONS DECEMBER 2016

SUBJECT: Chemistry

COURSE UNIT: CHE 4223

Time: Three (03) hours

Answer **all** questions.

Speed of light (c)	$=2.997 \times 10^8$ m s^{-1}
Universal gas constant (R)	$=8.314510$ J K^{-1} mol^{-1}
Faraday constant (F)	$=9.648530 \times 10^4$ C mol^{-1}
Planck constant (h)	$=6.626 \times 10^{-34}$ J s
Boltzmann constant (k$_B$)	$=1.386 \times 10^{-23}$ J K^{-1}
Charge of the electron (e)	$= -1.602 \times 10^{-19}$ C
Vacuum permittivity (ε_0)	$=8.854 \times 10^{-12}$ J^{-1} C^2 m^{-1}
1 eV	$=1.602 \times 10^{-19}$ J

01. Answer **all** parts.

(a) Partition function in statistical thermodynamics is also called thermal wave function.

(i) Discuss the validity of the above statement briefly.

(15 marks)

(ii) Identifying the terms, write down the general expression for partition function.

(10 marks)

(iii) Assume that non-interacting molecule has only three equally spaced nondegenerate energy levels ($\Delta E = \epsilon\ J\ and\ ground\ state = 0\ J$).

(I) 5550 of such molecules were distributed among those energy levels to obtain the most probable configuration. Assume that there are 50 molecules in the highest energy state of the most probable configuration. Find how many molecules are in the ground state and how many molecules are in the first excited state

(20 marks)

(II) Give any other configuration for the above molecules

(05 marks)

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(III) Confirm that the configuration given in (I) is more probable than (II)
(Note: Sterling approximation: $\ln x! = x \ln x - x$)

(10 marks)

(IV) Calculate thé entropy, S and $G - G(0)$ at 298 K, for the configuration in (I) above.

(Note: $G - G(0) = -nRT \ln\left(\frac{q}{N}\right)$

(10 marks)

(b) A flexible polymer chain can be modeled as a set of rigid links (length λ). It can be shown that for N links, the number of configurations is

$$W = AL^2 exp\left(-\frac{L^2}{NA^2}\right)$$

where L is the end-to-end distance and A is a constant.

(i) Prove that S is a maximum when $L = \sqrt{N} A$

(15 marks)

(ii) Calculate ΔS for stretching the chain by 10%. Assume N=100 and a mole of chains.

(15 marks)

02. Answer all parts.

(a) Define the chemical potential, μ of a constituent in a mixture.

(10 marks)

(b) Giving brief descriptions, write down the expressions for:
   (i)   Partial molar volume of a mixture,
   (ii)   Total thermodynamic volume of a binary mixture
   (iii) Excess molar volume of a binary solution.

(18 marks)

(c) Derive the Gibbs Duhem equation to show that variation in chemical potential of one component affects the same of the other component in a binary mixture.

(20 marks)

(d) If the total volume of a methanol solution at 25 ^{0}C containing 1 kg of water is given by the expression, V/mL= 1000 + 32.280b+12.144 $b^{3/2}$ where b is the numerical value of the molality of methanol (with no units).

(i) Write down the expression for the partial molar volume of methanol.

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(ii) Using the Gibbs Duhem equation, derive an expression for the partial molar volume of water in this solution.

[Note: The molar volume of pure water and methanol are 18.079 and 40.5 cm^3 mol^{-1} respectively.]

(iii) Find the excess molar volume of the solution.

(52 marks)

03. Answer **all** parts.

Kinetics theories of chemical reactions provide molecular level interpretation for reaction rate. Transition state theory is based on the ratio of transition state partition function to the products of partition functions of the reactants. Therefore, structure of the transition state plays a vital role in this theory.

(a) Gas phase reaction between Br_2 and H_2 which forms HBr molecule may be carried out by two experimental techniques. The first method is direct reaction between two molecules under suitable experimental conditions. The second method is the photochemical method which is proposed to follow a radical chain mechanism. Consider the direct reaction between two molecules

$$H_2\,(g) + Br_2\,(g) \longrightarrow 2HBr(g)$$

(i) Draw the structure of transition state due to the most effective collision of two molecules

(10 marks)

(ii) Account the contributions from translational, rotational, vibrational degrees of freedom to the total number of degrees of freedom for each reactant and activated complex.

(20 marks)

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(iii) Show that the product of partition functions due to Br_2 molecule is given by

$$q_{reactants} = \frac{64(\pi k T)^{7/2}}{h^6} \frac{(m_{Br})^{3/2} I_{Br}}{v_{Br}}$$

NOTE: Partition function for each mode of motion

Translational motion $z_t = (2\pi m k T)^{3/2}/h^3$,

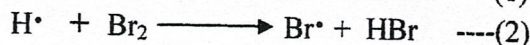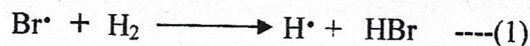Rotational linear molecule $z_r = 8\pi^2 I k T/h^2 \sigma$,

Rotational nonlinear molecule $z_r = \left[\pi^{\frac{1}{2}}(8\pi^2 k T)^{3/2}/h^3 \sigma \right] \times (I_A I_B I_C)^{1/2}$

and

each vibrational degree of freedom $z_v = [1 - \exp\left(-\frac{hv}{kT}\right)]^{-1}$

(20 marks)

(b) Propagation step of in the phothochemical reaction consists of two reactions

$$Br^{\bullet} + H_2 \longrightarrow H^{\bullet} + HBr \quad ----(1)$$
$$H^{\bullet} + Br_2 \longrightarrow Br^{\bullet} + HBr \quad ----(2)$$

Experimental data for the reaction (1) is given below and computational calculations show that it passes through nonlinear transition state. Calculate the ratio of the partition function of transition state to those of reactants.

(50 marks)

Moment of Inertia of H_2 = 0.277 amu Å^2
Vibrational frequency of H_2 is 4161 cm^{-1}
Two equal bending frequencies of transition state is 379.9 cm^{-1}
Three moments of Inertia of transition state are = 7.33, 5.42 and 8.33 amu Å^2
Atomic masses of H and Br are 1 and 80 amu, respectively

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04. Answer **all** parts.

(a) A clear description of the structure of electrode – solution interface is imperative to understanding the heterogeneous electron transfer mechanisms.

(i) The earliest model of the electrode – solution interface was proposed by the German scientist Hermann von Helmholtz in 1853. Discuss this model paying special attention to solvated and non solvated species.

(12 marks)

(ii) It is understood that the Helmholtz model overemphasizes rigidity of the interface whereas the Gouy – Chapman model proposed a more diffused and less rigid interfacial solution. Discuss this statement by comparing the two electrode – electrolyte models referred here.

(12 marks)

(iii) Explain how the Stern model overcame the two opposite extremities adopted by the above two models by combining the main features of both models.

(13 marks)

(iv) All three models mentioned so far have totally ignored the important role played by the solvent i.e. water. Water – dipole model of electrode – electrolyte interface was proposed by J. O'M. Bockris and his team in 1963. Explain how this model incorporated the role of water into the electrode – electrolyte interface.

(13 marks)

(b) The Butler – Volmer equation is

$$j = j_o\{\exp(1 - \alpha)\eta F/RT - \exp(-\alpha\eta F/RT)\}$$

(i) Identify all the terms in this equation and comment on the significance of η and j_o.

(12 marks)

(ii) Obtain the limiting forms of this equation when η possess large positive (> 120 mV) and large and negative (< -120 mV) values. Hence explain what you understand by a Tafel plot.

(13 marks)

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(iii) When η is small (< 10 mV), obtain the limiting form of the above equation.

(10 marks)

The j_0 value of a $Pt(s)/H_2(g)/H^+(aq)$ electrode in an appropriate electrochemical set up at 298 K is 0.78 mA cm^{-2}. If the area of the Pt electrode is 5.85 cm^2 and the pH of the solution is 2.75, calculate the current flowing through this Pt electrode.
(Note: $e^x = 1 + x + x^2/2! + \cdots\cdots$ and RT/F = 25.69 mV at 298 K)

(15 marks)

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