UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE SPECIAL DEGREE (LEVEL I) SEMESTER II EXAMINATIONS DECEMBER 2017

SUBJECT: Chemistry

COURSE UNIT: Time: CHE 4223

Three (03) hours

Answer **all** questions

Speed of light (c)	$= 2.997 \times 10^8$ m s^{-1}
Universal gas constant (R)	$= 8.31510$ J K^{-1} mol^{-1}
Faraday constant (F)	$= 9.64853 \times 10^4$ C mol^{-1}
Plank constant (h)	$= 6.626 \times 10^{-34}$ J s
Boltzmann constant (k_B)	$= 1.386 \times 10^{-23}$ J K^{-1}
Electron charge (e)	$= -1.602 \times 10^{-19}$ C
Vacuum permittivity (ε_0)	$= 8.854 \times 10^{-12}$ J^{-1} C^2 mol^{-1}
1 eV	$= 1.602 \times 10^{-19}$ J

01. Answer all parts

(a) Considering a single phase open system containing a mixture of n different non-reacting species, write down an expression for total differential of the Gibbs energy of this system. Identify all the symbols in the equation.

(15 marks)

(b) (i) Write a short account on colligative properties.

(10 marks)

(ii) The freezing point depression of a 0.005 mol kg^{-1} solution of sodium sulphate in water was found to be 0.0265 °C. Calculate the degree of dissociation of the salt at this concentration. Assume that the density of solution is 1.0 g cm^{-3}.

Note: K_f for water is 1.86 K kg mol^{-1} and the relative molar mass of sodium sulphate is 142.

(25 marks)

(c) (i) Distinguish between partial molar volume and apparent molar volume of a component in a mixture. Write down the equation for apparent molar volume, ϕ_V, of a binary system and name all the symbols in it.

(15 marks)

(ii) Sketch the variation of total volume of a binary solution vs solute molal concentration (m) to illustrate the difference between partial and apparent molar volumes.

(15 marks)

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(iii) The partial molar volume can be measured by fitting the observed volume (as a function of composition) using a curve fitting programme. In an experiment performed using a two component (D and E) system, it was found that the total volume of the mixture has the following functional form.·

$$V = A + Bn_D + C(n_D^2 - 1),$$

A, B and C are constants. Consider that n_D and n_E are the number of moles of components, D and E in the mixture.

I. For the above given system, write down the expression for the partial molar volume of the component D at any composition.

II. Hence obtain the expression for partial molar volume of component E.

(20 marks)

02. Answer **all** parts

(a) "The important aspect about an **ensemble** is that it is a collection **of imaginary replications** of the system, so that we are free to let the number of members be as large as we like; when necessary, we let it reach infinity". Comment on this statement and explain what you understand by time average and ensemble average.

(20 marks)

(b)

(i) Boltzmann proposed, what is now known as the 2nd postulate of statistical thermodynamics, the definition of S as $S = k_B \ln W$. Explain the meaning of all the terms in this equation paying special attention to W.

(ii) It has been experimentally estimated that absolute entropy of solid carbon dioxide at temperatures closer to absolute zero is $5.7 \ J \ K^{-1}$, does not approach zero as expected. Give your reasons for this discrepancy.

(30 marks)

(c) The rotational partition function of a heteronuclear diatomic molecule is given by

$$q^R = \frac{T}{\theta_r} = \frac{8\pi^2 I k_B T}{h^2}$$

(i) Identify all the symbols in this equation.

(ii) Explain the significance θ_r and hence describe the conditions under which this equation has been derived.

(iii) Calculate the rotational partition function for the molecule CO at 350.0 K. The moment of inertia for CO = $1.46 \times 10^{-46} \ kg \ m^2$. Justify your reasoning for (ii) by using the value you calculated for θ_r.

(iv) Calculate the molar internal energy of CO at 350.0 K. Does your result agree with the classical result from the equipartition theorem?

[Hint: $U^R = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V$]

03. Answer all parts   (50 marks)

Kinetics studies of the reaction between NO and Cl_2 was carried out in a laboratory by both experimentally and theoretically.

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

(a) Initial rates of the reaction with respect to the initial concentration of each reactant are given below.

Expt. number	Rate /10^{-4} mol dm^{-3} s^{-1}	NO / mol dm^{-3}	Cl_2 / mol dm^{-3}
1	3.31	0.50	0.50
2	13.31	1.00	0.50
3	26.64	1.00	1.00

(i) Find the rate law of the reaction.

(10 marks)

(ii) The following reaction mechanism is proposed for the reaction and show that the proposed mechanism obeys the rate law found in part (i) above.

(20 marks)

$$NO + Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOCl_2 \qquad Fast$$

$$NOCl_2 + NO \xrightarrow{k_2} 2NOCl \qquad Slow$$
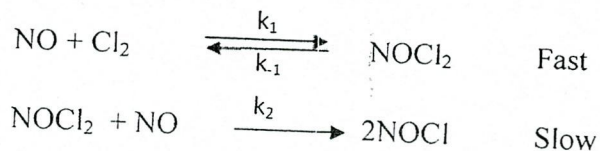
(b) Collision theory with the kinetic theory of gases gives the expression for the average of the reaction rate constant as $k(T) = p\pi b_{max}^2 v_r \exp\left(-\frac{\varepsilon^*}{kT} \right)$. All terms have their usual meanings and $v_r = \left(\frac{8kT}{\pi\mu} \right)^{1/2}$

(i) Account on the contributions from each term in the expression to the rate constant.

(20 marks)

(ii) Compare this expression with the empirical formula developed by Arrhenius, $k = A\exp\left(-\frac{E_A}{kT} \right)$, where E_a is the molar value of the activation energy.

(10 marks)

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(iii) The experimental value of the pre-exponential factor (Arrhenius constant, A) for the above reaction was found to be $A = 4.0 \times 10^9$ dm^3 mol^{-1} s^{-1} at 298 K and the cross sectional areas of NO and Cl$_2$, [σ(NO), σ(Cl$_2$)], are 0.42 nm^2 and 0.93 nm^2, respectively. Estimate the P factor for the reaction. Relative molecular masses of NO and Cl$_2$ are 30 and 71, respectively.

(40 marks)

04. Answer **all** parts

(a) An anion is more likely to shed some solvent molecules from its **solvation sphere** and get **specifically** adsorbed to form the **inner Helmholtz plane (IHP)** where as a solvated cation is likely to get **non – specifically** adsorbed to form the **outer Helmholtz plane (OHP)**." Discuss this sentence, within the context of modeling of the electric double layer paying special attention to bold phrases / words.

(20 marks)

(b) "The Helmholtz model overemphasizes and the Gouy – Chapman model underemphasizes the rigidity of local solution." Explain this sentence briefly and point out how these short comings of the two models mentioned above were improved in the Stern model.

(25 marks)

(c) The main problem of the Stern model, which is a hybridized version of the Helmholtz and Gouy – Chapman model, is that it ignored the variation of the dielectric constant across the electrical double layer. Explain how this anomaly was overcome in the water – dipole model by J. O'M. Bockris et.al.

(15 marks)

(d) The Butler – Volmer equation is

$$j = j_0\{\exp[(1 - \alpha)\eta F/RT] - \exp(-\alpha\eta F/RT)\}$$

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

(20 marks)

(ii) The transfer coefficient of a certain electrode in contact with M^{2+} and M^{3+} in aqueous solution at 25 °C is 0.41. The current density is found to be 62.0 mA cm^{-2} when the overvoltage is 130 mV. What is the overvoltage required for a current density of 78 mA cm^{-2}?

(20 marks)

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