# EASTERN UNIVERSITY, SRI LANKA

## SPECIAL DEGREE EXAMINATION IN CHEMISTRY

## FOURTH YEAR FIRST SEMESTER-2009/2010

## (FEB/MARCH' 2014)

## CHS07 Physical Chemistry II

**Answer all questions** **Time: 02 hours**

You may find the following information useful

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| Velocity of light (c) =2.99 x$10^8$ m $s^{-1}$ |
| Plank's constant (h) = 6.626 x $10^{-34}$J s |
| Boltzmann constant (k) = 1.38 x $10^{-23}$ J $K^{-1}$ |
| Gas constant (R =$N_A$k) = 8.314 J $K^{-1}$ $mol^{-1}$ |
| Avogadro constant ($N_A$) = 6.02x$10^{23}$ $mol^{-1}$ |
| *Electron mass (me) = 9.1 x $10^{-31}$kg* |

1) a) The reaction $H_3AsO_3 + I_3^- + H_2O \rightarrow H_3AsO_4 + 3I^- + 2H^+$ takes place in aqueous solution through the following step.

$$H_3AsO_3 \rightleftharpoons H_2AsO_3^- + H^+ \quad \text{..... (i)}$$

$$H_2O + I_3^- \rightleftharpoons H_2OI^+ + 2I^- \quad \text{...... (ii)}$$

$$H_2AsO_3^- + H_2OI^+ \rightleftharpoons H_2AsO_3I + H_2O \quad \text{.....(iii)}$$

$$H_2AsO_3I + H_2O \rightarrow H_3AsO_4 + H^+ + I^- \quad \text{..... (iv)}$$

The rate constants for the reactions (i), (ii), and (iii) are $k_1, k_2,$ and $k_3$ respectively and $k_4$ is the rate constant for the rate determining step (iv). Show that the rate of the reaction is given by $\frac{K'[H_3AsO_3][I_3^-]}{[I^-]^2[H^+]}$ and find the constant $K'$.

[40 marks]

b) i) Starting with Arrhenius equation show that the activation energy, E, of a reaction is given by the equation,

$$E = \frac{RT^2}{K}\frac{dK}{dT}$$

[10 marks]

ii) By integrating, show that $\ln\frac{K_2}{K_1} = \frac{E}{R}\left(\frac{T_2-T_1}{T_1T_2}\right)$ [use $\frac{d(\ln K)}{dK} = \frac{1}{k}$] [15 mar

c) i) Explain the term 'Quantum efficiency' with reference to photochemical reactions: [05 mar

ii) The reaction $X \rightarrow 2Y + Z$ takes place with absorption of light of wavelength 430 nm. W a certain amount of X was exposed to this light, 1.602 mmol of Z was formed. If 4.8 x1 photons were absorbed in this process, calculate the quantum efficiency. [20 mar

iii) In another experiment 139 kJ of photon energy was absorbed. Calculate the number moles of Y formed? [10 mark

Answer **two** of the following parts (a), (b) and (c).

**Part (a)**

i) Assuming that the arrangement of ions around a central ion obeys Boltzmann distribution law, show that the charge density $\rho_r$ at a distance $r$ from the central ion where the potential is $\psi_r$ is given by the equation,

$$\rho_r = -\frac{1}{kT}\sum N_i^0 z_i^2 e^2 \psi_r$$

ii) In a spherically symmetric field, the Poisson equation can be written as,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right) = -\frac{\rho_r}{\varepsilon_0\varepsilon_r}$$

Show that the solution to $\psi_r$ takes the form,

$$\psi_r = A\frac{e^{-kr}}{r}$$

iii) Assuming,

$$A = \frac{z_i e}{4\pi\varepsilon_0\varepsilon_r}\frac{e^{\kappa a}}{1+\kappa a}$$

Derive an expression for the potential on the central ion due to its ionic atmosphere.

[50 mar

**Part (b)**

The reaction $Ox + ne \rightleftharpoons Red$ takes place at an electrode through the simplest mechanism. The forward rate constant is $k_f$ and the reverse rate constant is $k_r$.

i) Using the reaction profile and Arrhenius equation derive equations giving the relationships between $k_f$ and the electrode potential and $k_r$ and the electrode potential.

ii) Hence, derive an equation relating the current ($i$), electrode potential ($E$) and the surface concentrations of the electroactive species.

iii) Show that the exchange current ($i_0$) which flows in both directions under equilibrium conditions is given by the equation,

$$i_0 = nFAk^0[Ox]_0^{(1-\alpha)}[Red]_0^{\alpha}$$

where the symbols have their usual meanings.

iv) Hence derive the current over potential equation,

$$i = i_0\left\{\frac{[Ox]}{[Ox]_0}e^{-\alpha nF\eta/RT} - \frac{[Red]}{[Red]_0}e^{(1-\alpha)nF\eta/RT}\right\}$$

[50 marks]

**Part (c)**

Consider the cell Pt'/$Ag_{(s)}$/ $AgCl_{(s)}$/ KCl, $H_2O$/ Hg/Pt". Starting with the equation $-d\gamma = \sum \Gamma_i d\bar{\mu}_i$ derive the electrocapillary equation,

$$-d\gamma = \Gamma_{H_2O} d\mu^s_{H_2O} + \Gamma_{K^+} d\mu^s_{KCl} + q_M dV$$

(The symbols have their usual meanings.)

Using the Gibbs-Duhem equation, $\sum x_i d\mu_i = 0$ derive the equation

$$q_M = -\left(\frac{\partial \gamma}{\partial V}\right)_{T,p,\mu}$$

[50 marks]

3) Answer all parts (a) and (b).

**Part (a)**

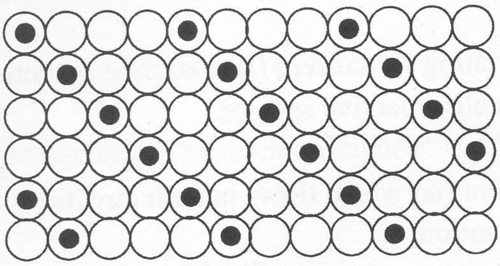
i) Explain how short-range lateral repulsive interactions between adsorbate atoms can lead to well-ordered structures in the adsorbate layer.

ii) What is the effect of attractive lateral interactions at low values of adsorbate coverage?

iii) In the limit of very strong nearest-neighbour repulsive lateral interactions, determine the closet distance between adsorbate atoms on the Ni{100} surface of saturation coverage. Give a sketch of this monolayer adsorbate structure relative to the underlying unreconstructed metal surface, and give the Wood's notation for the structure.

[50 marks]

**Part (b)**



The above figure shows adsorption geometry of O on Pt{100}. Write down the Wood' notation and the matrix notation.

[50 mar

) Derive an expression for the number of collisions taking place between two ideal molecule A and B in unit volume in unit time in terms of concentrations A, B and m relative speed of an ideal gas molecule.

[20 mar

ii) Calculate the frequency factor, A, for the elementary reaction $NO + O_2 \rightarrow NO_2 +$ assuming that the molecular radii of $NO$ and $O_2$ are 140 pm and 200 pm respectively.

[20 mar

iii) If the experimental value of A for this reaction is 8 x $10^{11}$ $cm^3$ $mol^{-1}$ $s^{-1}$. Calculate the ste factor and comment on this value.

[20 mar

Explain the following terms in catalysis

i) Promoters

ii) Poisons

[40 mar

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