EASTERN UNIVERSITY, SRI LANKA

FOURTH EXAMINATION IN SCIENCE-2010/2011

SPECIAL DEGREE IN CHEMISTRY

CHS 07 Physical Chemistry II

wer all questions **Time Allowed: Two hours**

ocity of Light (c) = 2.99×10^8 m s^{-1}	Planck's constant (h) = 6.626×10^{-34} J s
Boltzmann's constant (k) = 1.38×10^{-23} J K^{-1}	Mass of electron (m_e) = 9.1×10^{-31} kg
Gas constant (R) = 8.314 J K^{-1} mol^{-1}	Charge of an electron (e)= 1.602×10^{-19} C

a) Consider the following mechanism for the thermal decomposition of D_2.

$$D_2 \rightarrow 2D$$
$$D + D_2 \rightarrow P_B + D^1$$
$$D^1 \rightarrow P_A + D$$
$$2D \rightarrow P_A + P_B$$

Where D_2, P_A, P_B are stable hydrocarbons and D and D^1 are radicals. Determine the rate of decomposition of D_2 and show that the rate of the reaction depends only on the concentration of D_2.

(40 marks)

b) Define the quantum yield of a photochemical reaction.
In an experiment to measure the quantum yield of a photochemical reaction, the absorbing substance was exposed to 490 nm light from a 100 W source for 45 minutes. The intensity of the transmitted light was 40% of the intensity of the incident light. As a result of irradiation, 0.344 mol of the absorbing substance was decomposed. Calculate the quantum yield.

(25 marks)

Contd....

c) Consider the following acid-catalysed reaction.

$$HA + H^+ \rightleftharpoons HAH^+ \text{ (fast)}$$
$$HAH^+ + B \rightarrow BH^+ + AH \text{ (slow)}$$

Prove that the rate of this reaction is independent of the concentration of H^+ (acid constant (K_a) of the conjugate acid of B is $[B][H^+]/[BH^+]$).

(35 marks)

2.

a) A bimolecular elementary reaction in gas phase having a second-order rate constant k_2 i shown below:

$$A(g) + B(g) \rightarrow P(g)$$

Using collision theory

I) derive an expression for collision frequency of the gas molecule A (Z_{AA}).

Ii) derive an expression for collision frequency of both gas molecules A and B (Z_{AB}).

Iii) show that $k_2 = Ae^{-E_a/RT}$ where A is the pre-exponential factor.

(30 marks)

b) Experimental and theoretical values of A found to be different for many reactions hence the above expression in a(iii) could be corrected by introducing a steric facto

i) Write the corrected expression for k_2.

ii) Calculate the steric factor for the reaction: $H_2 + C_2H_4 \rightarrow C_2H_6$ at 628 K given the pre-exponential factor is 1.24×10^6 L mol^{-1} s^{-1}.

(30 marks)

c) α) Define the following terms:

i. Chemisorption
ii. Physisorption

(10 marks)

β) Draw the chemisorption potential energy curves for the following case of adsorption of a homonuclear diatomic molecule B_2 where there is:

i. no dissociation
ii. energy barrier E_a for dissociation.
iii. no activation barrier for dissociative adsorption.

(30 marks)

Contd...

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) Which saturation coverage and structure would you expect for an adsorbate on a hexagonal fcc {111} surface with:

I. strongly repulsive 1st neighbour and attractive 2nd neighbour interactions.

II. strongly repulsive 1st and 2nd neighbour interactions?

Draw the saturation structures and find the right notation (Matrix and Wood).

(50 marks)

b) i) Explain what is meant by the term "work function" making reference to a diagram showing the electrostatic potential of a solid in the vicinity of free surface.

ii) Explain the influence of adsorbates on the work function Φ and provide a qualitative explanation for the sign and magnitude of the following adsorbate-induced work function $\Delta\Phi$ at fractional coverage Θ.

System	Θ	$\Delta\Phi$/eV
O on Ni	0.5	+0.30
Cs on W	0.3	-2.9
Ne on W	1.0	-0.15
Xe on W	0.4	-1.13

(50 Marks)

The reaction $O_X + ne \rightleftharpoons Red$ takes place at an electrode through the electron transfer and mass transfer mechanism. The forward reaction rate constant is k_c and the backward reaction rate constant is k_a.

Using the reaction profile and Arrhenius equation, show that the current density (j) is given by the equation,

$$j = j_o\left\{ \frac{[Red]}{[Red]_o} e^{(1-\alpha)nF\eta/RT} - \frac{[O_x]}{[O_x]_o} e^{-\alpha nF\eta/RT} \right\}$$

where the symbols have their usual meanings.

(25 marks)

Contd...

ii) **Hence, derive the Butler – Volmer equation (current over potential equation)**

$$j = j_o\{\ e^{(1-\alpha)nF\eta/RT} - e^{-\alpha nF\eta/RT}\}$$

(10 marks)

iii) **Show that the following relations,**

I) $\left|\frac{\eta}{j}\right| = RT/J_O nF$, **when η << 1 (low over potential limit).**

II) $|j| = j_o\ e^{(1-\alpha)nF\eta/RT}$, **when η is large and positive value.**

(20marks)

iv) **Obtain the Tafel plot for the relation of** $|j| = j_o\ e^{(1-\alpha)nF\eta/RT}$.

(10 marks)

v) **The transfer coefficient (α) of a certain electrode in contact with M^+ and M^{2+} aqueous solution at 25 ˚C is 0.39. The current density is found to be 55.0 mA cm when the over potential (η) is 125 mV.**

I) **What is the over potential required for a current density of 75 mA cm^{-2}?**

II) **Determine the exchange of current density (j_O).**

(35 marks)

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