

UNIVERSITY OF RUHUNA
BACHELOR OF SCIENCE SPECIAL DEGREE –LEVEL I
EXAMINATION JULY - 2016

SUBJECT: Chemistry
COURSE UNIT: CHE 4132

TIME: Two (2) hours

Answer All questions

Speed of light (c)	= $2.997 \times 10^8 \text{ m s}^{-1}$
Universal gas constant (R)	= $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant (F)	= $9.648 \text{ } 530 \times 10^4 \text{ C mol}^{-1}$
Planck constant (h)	= $6.626 \times 10^{-34} \text{ J s}$
Boltzmann constant (k)	= $1.38 \times 10^{-23} \text{ J K}^{-1}$
Charge of the electron (e)	= $1.602 \times 10^{-19} \text{ C}$
Vacuum permittivity (ϵ_0)	= $8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$

I. Answer all parts

- (a) Briefly explain the photoelectric effect and discuss how Einstein explained this using Planck's quantization hypothesis. Briefly explain how this observation contributed to the development of quantum mechanics. (25 marks)
- (b) (i) State the second postulate of quantum mechanics and explain what you understand by linear operators and Hermitian operators.
(ii) Show that the momentum operator along the x - direction, $(-ih/2\pi)d/dx$, is a Hermitian operator. (30 marks)
- (c) (i) Briefly explain the harmonic oscillator model used for representing vibrating diatomic molecules.
(ii) The Schrodinger equation for a harmonic oscillator is

$$-\frac{h^2}{8\pi^2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2 \psi = E\psi$$

- (A) Write the energy levels of a vibrating diatomic molecule according to the solution of this equation.

- (B) Show that the $\psi_0(x) = N_0 e^{-\frac{1}{2}\alpha x^2}$ is a satisfactory solution to the Schrodinger equation of the simple harmonic oscillator,

$$\text{where } \alpha = \frac{2\pi}{h} \sqrt{k\mu}.$$

- (C) Show that

$$N_0 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}$$

$$\left[\int_{-\infty}^{+\infty} e^{-ax^2} = \left(\frac{\pi}{a}\right)^{\frac{1}{2}} \right]$$

(45 marks)

2. Answer **all** parts

- (a) Bond rotations in a molecule lead to stretching of bonds and hence the centrifugal distortion reduces the separation between adjacent rotational spectral lines. With the rigid rotator approximation, the pure rotational energy levels are given by

$$E_j = BJ(J + 1) \text{ cm}^{-1},$$

where B is the rotational constant and J is number of the particular level.

- (i) Give the value of the J of the highest intense spectral line that originates the transition. (10 marks)
- (ii) Account the change in the energy due to the bond stretching caused by rotation. (10 marks)
- (iii) Derive the relationship between rotational constant (B), and the centrifugal distortion constant (D) through vibrational frequency of the bond ($\bar{\nu}$)

$$\text{Here, } D = \frac{h^3}{32\pi^4 I^2 r^2 k c} \text{ cm}^{-1} \quad (15 \text{ marks})$$

- (b) The fundamental absorption and first overtone of carbon monoxide molecule are given by the following two expressions (1) and (2), respectively.

$$\bar{\nu}_{\text{fundam}} = 2143 + 3.83 m \text{ cm}^{-1} \text{-----(1)}$$

$$\bar{\nu}_{\text{overtone}} = 4260 + 3.83 m \text{ cm}^{-1} \text{-----(2)}$$

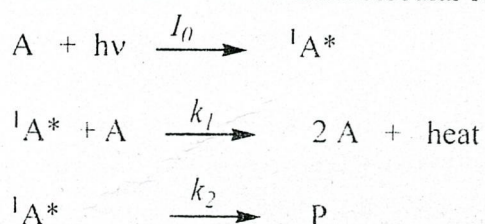
- (i) Calculate the first two spectral lines in each of P and R branch of the fundamental absorption. (10 marks)
- (ii) Calculate the equilibrium vibrational frequency and the anharmonicity constant (10 marks)

- (iii) Calculate the centrifugal distortion constant and the force constant of the carbon monoxide bond. (20 marks)
- (iv) Show that the separation between two maxima corresponding to P and R branches of fundamental absorption is given by

$$\Delta\bar{\nu} = \sqrt{8kTB/hc} + 3.83 \text{ cm}^{-1} \quad (25 \text{ marks})$$

03. Answer **all** parts

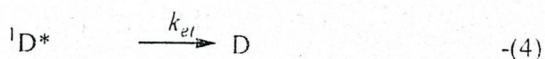
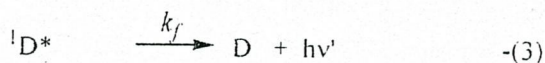
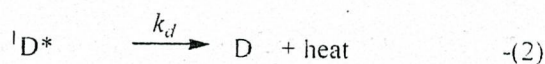
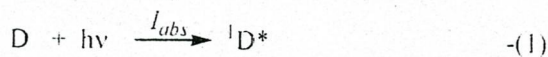
- (a) Simple photochemical reaction can be described by the following elementary kinetic steps which are nearly identical to the Lindemann unimolecular reaction scheme.



- (i) Write a differential rate equation for the rate of change of the intermediate species ${}^1A^*$ using this kinetic scheme.
- (ii) Making appropriate approximations solve the equation in part a(i) above for $[{}^1A^*]$.
- (iii) Under what conditions would the result of part (ii) above lead to a rate equation for the appearance of product, dP/dt , which is independent of the concentration of A?
- (iv) Find an expression for quantum yield Φ in terms of rate constants and $[A]$
- (v) Under what conditions does $\Phi \rightarrow 1$?

(55 marks)

- (b) In the most general sense, the formation of ${}^1D^*$ and its subsequent decay, when unperturbed, *via* nonradiative, radiative, and oxidative intramolecular electron transfer can be described by reactions (1)-(4). Here I_a is the rate at which the light is absorbed by D and k 's represent rate constants for internal conversion (k_d), fluorescent emission (k_f) and intramolecular electron transfer (k_{et}).



Write expressions for the fluorescence life time (τ) and quantum yield (Φ) (derivation is not necessary) when:

(i) $^1D^*$ has essentially the same photophysics, but which lacks the electron transfer step.

(ii) $^1D^*$ undergoes all three decay processes, and hence show that the intramolecular electron transfer rate constant can be given by either $k_{et} = \frac{1}{\tau} - \frac{1}{\tau^0}$ or

$k_{et} = k_f \left(\frac{1}{\Phi} - \frac{1}{\Phi^0} \right)$ where τ, τ^0 are fluorescence life times and Φ, Φ^0 are fluorescence quantum yields with and without the electron transfer decay respectively.

(30 marks)

(c) Porphyrins (P) and quinones (Q) undergo light initiated electron transfer reactions. The natural radiative decay rate constant of the porphyrin is $5 \times 10^8 \text{ s}^{-1}$. Without the quinone the porphyrin is found to have a fluorescence quantum yield of 0.25. However, when a quinone molecule is linked to the porphyrin, the fluorescence quantum yield drops to 0.05. Assuming that the only difference between the porphyrin by itself and the porphyrin-quinone combination is that electron transfer can occur from the excited state of the porphyrin to the quinone (forming P^+Q^-), what is the rate constant for light initiated electron transfer in the porphyrin/quinone molecular complex?

(15 marks)

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