



RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Honours) Degree in Chemistry
Fourth Year Semester II Examination – February /March 2019

CHE 4307 – ADVANCED PHYSICAL CHEMISTRY II

Time: Three (03) hours

Answer all questions.

Use of a non-programmable calculator is permitted.

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$k_b = 1.381 \times 10^{-23} \text{ J K}^{-1}$$

$$c = 3 \times 10^8 \text{ m s}^{-1}$$

$$1u = 1.6605 \times 10^{-27} \text{ kg}$$

$$1 \text{ Joule} = \frac{1}{1.602 \times 10^{-19}} \text{ eV}$$

1.

- a) Explain what is meant by canonical ensemble and how does it differ from microcanonical ensemble and grand canonical ensemble.

(20 marks)

- b) Show that the Helmholtz free energy, A is given by

$$A = -kT \ln Q$$

from first principles, where Q = canonical partition function.

(40 marks)

- c) Calculate the translational partition function of a H_2 molecule confined to a 100 cm^3 vessel at 25°C , where $m_{\text{H}_2} = 2.016 \text{ u}$.

(40 marks)

2.

- a) Discuss the significance of the symmetry number in determining the rotational partition function.

(20 marks)

- b) Show that the vibrational partition function for H_2O molecule is

$$q_v = \frac{e^{-\frac{\theta_v}{2T}}}{1 - e^{-\frac{\theta_v}{T}}}$$

Where θ_v = characteristic vibrational temperature

[Hint: Vibrational energy, $E_n = \left(n + \frac{1}{2}\right) h\nu$ where $n = 0, 1, 2, \dots$ and

Vibrational partition function, $q_v = \sum_n e^{-\beta E_n}$]

(40 marks)

- c) The wavenumbers of the three normal modes of H_2O molecule are 3656.7 cm^{-1} , 1594.8 cm^{-1} , and 3755.8 cm^{-1} . Evaluate the vibrational partition function of H_2O at 1226.85°C .

(40 marks)

3.

- a) Outline the salient features of the collision theory for a bimolecular, elementary reaction of the form $A + A \rightarrow \text{Products}$.

(20 marks)

- b) Derive an expression for collision frequency from first principles for the reaction in 3(a) above.

(40 marks)

- c) Arrhenius plot for a reaction was linear with a negative slope of $4.50 \times 10^4 \text{ K}$ and intercept of 10.50 for a reaction. Calculate E_a , ΔH° (at 25°C) and ΔS^\ddagger .

(40 marks)

4.

- a) Starting from the basic principles and using the activated complex theory, show that the overall rate constant (k_{ov}) of a bimolecular gas phase reaction is

$$k_{ov} = \frac{k_b T}{h} K_C^\ddagger$$

Where K_C^\ddagger is the equilibrium constant without the vibrational partition function along the reaction coordinate.

(30 marks)

- b) Discuss the drawbacks of collision theory.

(30 marks)

- c) The value of ΔS^\ddagger for a reaction has been obtained as $-80.5 \text{ J K}^{-1} \text{ mol}^{-1}$ at 400 K. Find the value of pre-exponential factor, A for the reaction using transition state theory.

(40 marks)

5.

- a) Briefly explain the following

i. Quantum reality

ii. Double slit experiment

(20 marks)

- b) In a hydrogen atom, the electron in the excited state $n=2$ remains there for 10^{-8} s on an average before making a transition to the ground state ($n=1$).

i. Calculate the uncertainty in energy of the excited state.

ii. What is the fraction of the transition energy?

iii. Compute the width of wave length corresponding to this.

(30 marks)

(Cont'd)

- c) Show that one of the solutions of the time - dependent Schrödinger equation in one dimension is

$$\Psi = Ae^{i(kx - \omega t)}$$

where A is a constant

$$k = \frac{p}{\hbar}$$

and

$$\omega = \frac{E}{\hbar}$$

(35 marks)

- d) What is the *Born–Oppenheimer* (BO) approximation? And write the electronic Hamiltonian operator according to the BO approximation.

(15 marks)

6.

a)

- i. What is the ground state energy of a particle of mass m trapped in a cubical box of dimension a .
- ii. How does it compare to the 1-D case?

(20 marks)

- b) The function $\psi = A \left(\frac{x}{L}\right)^2 \left[1 - \left(\frac{x}{L}\right)\right]$ is an acceptable wave function for the particle in a one dimensional infinitely deep box of length L . Calculate the normalization constant A .

(20 marks)

- c) The energy states for a particle in a 3-D box with lengths L_1 , L_2 , and L_3 are given by

$$E(n_1, n_2, n_3) = \frac{h^2}{8m} \left[\left(\frac{n_1}{L_1}\right)^2 + \left(\frac{n_2}{L_2}\right)^2 + \left(\frac{n_3}{L_3}\right)^2 \right]$$

These energy levels are sometimes used to model the motion of electrons in a central metal atom that is surrounded by six ligands.

(Cont'd)

- i. Show that the lowest energy level is non-degenerate and the 2nd level is triply degenerate if the box is cubical. Label the states by their quantum numbers n_1, n_2, n_3 .

(20 marks)

- ii. Consider a box of volume $V = L_1 \times L_2 \times L_3$ ($L_1 = L_2 = L_3$) with 3 electrons inside (2 in the lowest energy level, 1 in the next). Show that the total energy in this case is equal to

$$E = \frac{12h^2}{8mL_1^2}$$

(20 marks)

- d) Consider a particle in a state described by the ground state wave function and an excited state wave function found to be

$$\Psi_0 = \left(\frac{a}{\pi}\right)^{1/4} e^{-x^2/2}$$

$$\Psi_2 = \left(\frac{a}{\pi}\right)^{1/4} \frac{1}{\sqrt{2}} (2x^2 - 1) e^{-x^2/2}$$

Show that Ψ_0 and Ψ_2 are orthogonal to each other.

(20 marks)

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