RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. Honours in Chemistry
Fourth Year – Semester II Examination – July 2020

CHE 4307 – ADVANCED PHYSICAL CHEMISTRY II

Time: Three (03) hours

Answer all questions.
Use of a non-programmable calculator is permitted.

$h = 6.626 \times 10^{-34}$ J S	$R = 8.314$ J $K^{-1} mol^{-1}$
Charge of the electron = 1.602×10^{-19} Coulombs	$k_b = 1.381 \times 10^{-23}$ J K^{-1}
Mass of the electron = 9.11×10^{-31} kg	$c = 3 \times 10^8$ m s^{-1}

1.

a) Molecular partition function and average energy of a molecule are given by

$q = \sum_j e^{-\beta E_j}$ and $\overline{E} = \sum_j E_j \frac{e^{-\beta E_j}}{q}$ respectively.

Derive a relationship between the molecular partition function and average energy.

(30 marks)

b) Starting from $q = \sum_j e^{-\beta E_j}$, show that the average pressure, $\bar{p}$, can be given as

$\bar{p} = k_b T \left(\frac{\partial \ln q}{\partial V}\right)_{N,T}$ (30 marks)

c) If the average energy, $\overline{E} = k_b T^2 \left(\frac{\partial \ln q}{\partial T}\right)_{N,V}$

Derive an expression for enthalpy Δ H, in terms of molecular partition function.

(40 marks)

2. Rotational contribution for the total molecular partition function, q_r , of a linear molecule can be given as

$$q_r = \frac{T}{\theta_r} \text{ where } \theta_r = \frac{h^2}{8\pi^2 I k_b}.$$

Answer the following questions regarding the $^1H^{35}Cl$ at 25°C, given that the $B = 10.591$ cm^{-1} and $r = 1.275$ Å.

(Cont'd)

a) Define all the terms involve in the above equations. (20 marks)
b) Calculate the reduced mass of $^{1}H^{35}Cl$. (20 marks)
c) Estimate the moment of inertia. (20 marks)
d) Calculate the rotational temperature. (20 marks)
e) Calculate the rotational partition function. (20 marks)

3. Answer the following questions, assuming the reaction obeys the transition state theory.

$$A + B \rightleftharpoons AB^{\#} \xrightarrow{k^{\#}} P$$

where equilibrium constant and product formation rate constant are $K_C^{\#}$ and $k^{\#}$ respectively.

a) Write down the expression for the equilibrium constant $K_C^{\#}$ (20 marks)
b) Give the expression for the rate constant $k^{\#}$ (20 marks)
c) Show that $k_{overall} = K_C^{\#} \times k^{\#}$ (20 marks)
d) If the energy of the activated complex, $E = h\nu^{\#}$, show that the

$k_{overall} = K_c^{\#} \times \frac{k_b T}{h}$ (40 marks)

4.

a) Lindemann proposed the following mechanism for a unimolecular gas phase reaction;

$$A + M \xrightarrow{k_1} A^* + M$$

$$A^* + M \xrightarrow{k_2} A + M$$

$$A^* \xrightarrow{k_3} \text{Products}$$

Where A is the reactant molecule, A* is the energized molecule and M is an inert gas molecule.

k_1, k_2 and k_3 are the rate constants of the three elementary steps.

i. State the assumptions made in the above proposed mechanism. (10 marks)
ii. Show that at low pressures of M, the rate of reaction increases with increase in pressure of M. (20 marks)
iii. Show that the unimolecular rate constant reaches to a maximum value of

$\frac{k_1 k_3}{k_2}$ at infinite pressure.

(20 marks)

(Cont'd)

b) Use the collision theory of gas-phase reactions to calculate the theoretical value of the second-order rate constant for the reaction H_2 (g) +I_2 (g) $\longrightarrow$ 2HI (g) at 650 K, assuming that it is elementary bimolecular and the probability factor is 1. The collision cross-section is 0.36 nm^2, the reduced mass is 3.32×10^{-27} kg, and the activation energy is 171 kJ mol^{-1}. (50 marks)

5.

a) Briefly explain

i. Slater Determinant

ii. Born-Oppenheimer approximation

iii. The independent particle approximation

(15×3 marks)

a) b) The speed of an electron is found to be 1 km s^{-1} within an accuracy of 0.02%. Calculate the uncertainty in its position. (15 marks)

c) What do you mean by eigenfunction and eigenvalue? Explain your answer with suitable examples. (10 marks)

d) Write the Full Hamiltonian for the He atom. (30 marks)

6. A quantum mechanical particle confined to move in one dimension between x = 0 and x = L is found to have a state described by the wave function.

$$\Psi(x) = A\sin\left(\frac{2\pi}{L}x\right)$$

a) Determine the constant A such that the wave function is normalized. (20 marks)

b) Using the result of part (a), find probability that the particle will be found between x = 0 and x – L/3 (20 marks)

c) What is the difference between the time-dependent Schrodinger equation and the time independent Schrodinger equation? Explain your answer.

(20 marks)

(Cont'd)

03

d) Consider a quantum particle of mass m that is completely free to travel in one-dimension, $V(x) = 0$.

i. Write out the full expression for the time independent Schrödinger equation.

ii. Show that $\Psi(x) = Ae^{ikx} + Be^{ikx}$ is a general solution where k = 2mE $k = \sqrt{\frac{2mE}{\hbar}}$

iii. Consider the two cases where $A = 0$ and then where $B = 0$. Determine if these wavefunctions are (separately) eigenfunctions of the momentum operator and, if so, what the eigenvalues are.

iv. Are there any restrictions on the total energy for this particle?

(10×4 marks)

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