RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Special) Degree in Chemistry
Fourth Year - Semester II Examination – June / July 2018

CHE 4307 – ADVANCED PHYSICAL CHEMISTRY II

Time: Three (03) hours

Answer all questions.

Use of a non-programmable calculator is permitted.

$h = 6.626 \times 10^{-34}$ JS $\qquad N_A = 6.023 \times 10^{-23}\ \text{mol}^{-1} \qquad R = 8.314\ \text{J K}^{-1}\text{mol}^{-1}$

$k_b = 1.381 \times 10^{-23}\ \text{J K}^{-1} \qquad c = 3 \times 10^{8}\ \text{m s}^{-1}$

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

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1. 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.

(Cont'd)

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i. Show that at low pressures of M, the unimolecular rate constant (k_{uni}) increases with increase in pressure of M. **(30 marks)**

ii. Show that the unimolecular rate constant reaches to a maximum value of $\frac{k_1 k_3}{k_2}$ at infinite pressure.

(20 marks)

iii. State the assumptions made in the above mechanism. **(10 marks)**

b) At a temperature of 250 K, the pre-exponential factor (A) for the reaction

$$H_{2(g)} + Cl_{(g)} \rightarrow HCl_{(g)} + H_{(g)}$$

is found to be 8×10^{10} $dm^3\ mol^{-1}\ s^{-1}$. Determine the steric parameter (ρ) for this reaction.

($M_{Cl} = 35.45\ g\ mol^{-1}$; $M_{H_2} = 2.00\ g\ mol^{-1}$; $r_{Cl} = 200$ pm ; $r_{H_2} = 150$ pm)

(40 marks)

2. a) For a gas phase reaction $E_a = \Delta H^\circ_{\#} + RT(1 - \Delta n)$

where $\Delta H^\circ_{\#}$ is the enthalpy of activation and Δn = products – reactants

Using activated complex theory, show that for a trimolecular gas phase reaction the pre-exponential factor (A) is

$$A = e^3 \frac{k_b T}{h} e^{\Delta S^\circ_{\#}/R}$$

Where $\Delta S^\circ_{\#}$ = entropy change in passing from initial state to the activated state.

(40 marks)

b) The E_a and pre-exponential factor for a reaction,

$$A_2 + B_2 \rightleftharpoons 2AB$$

are 15.5 kJ mol^{-1} and 10.9×10^{10} $dm^3\ mol^{-1}\ sec^{-1}$, respectively. Calculate the values of $\Delta H^{\#}$ and $\Delta S^{\#}$ at 1000K. **(40 marks)**

c) Discuss the limitations of activated complex theory. **(20 marks)**

3. a) Derive the relationship between molecular partition function and the enthalpy from first principles. **(40 marks)**

b) The rotational partition function of a rigid diatomic molecule is given by

$$q_{rot} = \frac{8\pi^2 k_b T I}{\sigma h^2}$$

and the rotational energy levels of a diatomic molecule are given by

$$E_j = \frac{J(J+1)h^2}{8\pi I}$$

Where σ is the symmetry number.

i. Derive the above relation

ii. Calculate the rotational contribution to the molar energy of one mole of HCl gas at 300K. **(60 marks)**

(H= 1.00, Cl=35.45)

4. a) Prove that translational partition function for a molecule is given by

$$q_t = \frac{V}{\Lambda^3}$$

Where

$$\Lambda = (\frac{h^2}{2\pi mkT})^{1/2}$$

The energy of a particle in a cubic box is

$$E_n = \frac{n^2 h^2}{8ma^2}$$

(40 marks)

b) Calculate

i. the thermal wavelength

ii. the translational partition function of an Ar atom in a cubic box of side 1.00 cm at 300 K and 3000K. **(40 marks)**

c) At what temperature does the thermal wavelength of an argon atom become comparable to its diameter? **(20 marks)**

5. a) Briefly explain

i. The Ultraviolet Catastrophe

ii. The Photoelectric Effect

iii. Wave-Particle Duality

iv. Heisenberg uncertainty principle

(40 marks)

b) What should be the range values of the work function of a metal in order to be useful in a photo cell for detecting visible light? **(10 marks)**

c)

i. Find the eigenfunctions and eigenvalues of the operator $\frac{d}{dx}$

ii. If we impose the boundary condition that the eigenfunctions remain finite as $X \rightarrow \pm\infty$ find the eigenvalues **(40 marks)**

d) Briefly state that goal of the Self-consistent Field (SCF) Theory and main downside of this theory. **(10 marks)**

6. a) Full Hamiltonian for the Schrodinger equation $\hat{H}\Psi=E\Psi$ is given by;

$$H = -\sum_{i}^{\text{electronic}} \frac{\hbar}{2m_e}\nabla_i^2 - \sum_{k}^{\text{nuclei}} \frac{\hbar}{2m_k}\nabla_k^2 - \sum_{i}^{\text{electronic}} \sum_{k}^{\text{nuclei}} \frac{Z_k e}{r_{ik}}\nabla_i^2 + \sum_{k<l}^{\text{nuclei}} \frac{e^2 Z_l Z_k}{r_{kl}}\nabla_k^2 + \sum_{i<j}^{\text{electronic}} \frac{e^2}{r_{ij}}$$

Typically the approximation is made that the 2nd term can be ignored and that the 4th term becomes a constant. What is the name for this approximation? Briefly explain your answer and account for the advantage of its in computational calculations.

(20 marks)

(Cont'd)

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a) Name three post-HF methods available and briefly explain them with examples.

(30 marks)

b) Explain the following terms using a potential energy surface.

i. Saddle points

ii. Global minima.

(20 marks)

c) Using an appropriate example explains what a Slater Determinant (SD) is and how it is satisfies the antisymmetry requirement.

(30 marks)

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