



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.

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

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

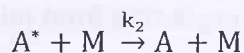
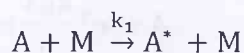
$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

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

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

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



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)

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

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

(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



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

$$(M_{\text{Cl}} = 35.45 \text{ g mol}^{-1} ; M_{\text{H}_2} = 2.00 \text{ g mol}^{-1} ; r_{\text{Cl}} = 200 \text{ pm} ; r_{\text{H}_2} = 150 \text{ pm})$$

(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 $\Delta n = \text{products} - \text{reactants}$

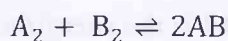
Using activated complex theory, show that for a trimolecular gas phase reaction the pre-exponential factor (A) is

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

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,



are 15.5 kJ mol^{-1} and $10.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$, respectively. Calculate the values of $\Delta H^\circ_{\#}$ and $\Delta S^\circ_{\#}$ 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

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

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.

- Derive the above relation
- 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

$$\Lambda = \left(\frac{h^2}{2\pi m k T} \right)^{1/2}$$

The energy of a particle in a cubic box is

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

(40 marks)

- b) Calculate

- the thermal wavelength
- 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;

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

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 explain what a Slater Determinant (SD) is and how it satisfies the antisymmetry requirement.

(30 marks)

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