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RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

BSc Honours in Chemistry
Fourth Year - Semester II Examination – January / February 2023

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	$N_A = 6.023 \times 10^{-23}\ \mathrm{mol^{-1}}$	$R = 8.314\ \mathrm{J\ K^{-1} mol^{-1}}$
$k_b = 1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}$	$c = 3 \times 10^{8}\ \mathrm{m\ s^{-1}}$	$M_{Cl} = 35.45\ \mathrm{g\ mol^{-1}}$

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

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1. a) Explain the term ensemble in statistical thermodynamics using a suitable example. How does the canonical ensemble, microcanonical ensemble and grand canonical ensemble differ from each other.

(40 marks)

b) Answer following questions using Lindemann theory with respect to a unimolecular gas phase reaction. Define all the terms. State assumptions clearly.

i. Show that at low pressures of M, the unimolecular rate constant increases with increase in pressure of M.

(40 marks)

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

(20 marks)

2.

a) Derive the following relationship from <u>first principles.</u>

$$\bar{E} = -\frac{\partial lnq}{\partial \beta}$$

Where,

$\bar{E}$ =average energy
q = molecular partition function
$\beta = \frac{1}{kT}$, k = Boltzmann constant, and T = temperature

(60 marks)

b) Derive the relationship between molecular partition function and enthalpy.

(20 marks)

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

3.

a) Discuss the requirements for an effective collision.

(20 marks)

b) From first principles, derive an expression for collision frequency.

(30 marks)

c) Use the collision theory of gas-phase reactions to calculate the theoretical value of the second-order rate constant for the reaction $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ at 500 K, assuming that it is an elementary bimolecular reaction and the probability factor is 1. The collision cross-section is 0.56 nm^2, and the activation energy is 180 kJ mol^{-1}.

(50 marks)

4.

a) From first principles, prove that translational partition function for a molecule is given by:

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

(30 marks)

b) Calculate the thermal wavelength and the translational partition function of an He atom in a cubic box of side 1.00 cm at 500 K.

(40 marks)

c) At what temperature does the thermal wavelength of an He atom become comparable to its radius?

(30 marks)

5. a) Explain the essence of the Mach-Zehnder experiment. Discuss the quantum and classical superposition based on this experiment.

(25 marks)

b) State the meaning of quantum entanglement. Comment on the electron-electron correlation in multi-electron atoms.

(25 marks)

c) State the meaning of self-superposition. How this concept leads to wavefunction normalization.

(25 marks)

d) A hydrogenic wave function is shown below. Name its state. Show all your arguments.

$$\Psi_B(r,\theta,\phi) = \sqrt{\frac{8}{729\pi a_0^3}}\left(\frac{r}{a_0} - \frac{r^2}{6a_0^2}\right)e^{-r/3a_0}\cos(\theta)$$

(25 marks)

6 Part I

a) Give two examples of quantum perturbation systems highlighting unperturbed states. State the meaning of non-degenerate perturbation of a quantum system.

(25 marks)

b) Write down the Schrodinger equation with perturbation. Identify all terms therein.

(25 marks)

c) Prove that $E_n^{(1)} =< n_0 \mid \delta H \mid n_0 >$.

(25 marks)

d) Consider a particle in a box experiment with $\mu_i = x(x-a)$ trial wave function and $\psi_n(0) = \psi_n(a) = 0$ boundary conditions. Use the variation method to calculate the trial energy of the system. Deduce the error of the energy estimates.

(25 marks)

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