



RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (General) Degree in Applied Sciences
Second Year Semester II Examination – February /March 2019

CHE 2201 –PHYSICAL CHEMISTRY II

Answer **All** questions.

Time: Two hours

Universal Gas Constant (R) = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Use of a non-programmable calculator is permitted.

1. (a) Define the following terms:

- (i) Elementary reaction. (ii) Overall order of a reaction.

10 marks

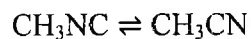
(b) A zero-order reaction is represented as:



- (i) Obtain an integrated rate law for the above reaction.
(ii) Show that its half life is a function of initial concentration of A.

25 marks

(c) The isomerization of methyl isonitrile to acetonitrile in the gas phase at 250°C



is first order with a rate constant of $3.00 \times 10^{-3} \text{ s}^{-1}$. If the initial concentration of CH_3NC is $0.107 \text{ mol dm}^{-3}$, how much time require for the concentration of CH_3NC to drop to $0.0142 \text{ mol dm}^{-3}$?

25 marks

(d) Use Boltzmann plots to explain the effect of temperature on rate of a reaction

20 marks

(e) Consider the reaction: $2\text{B} \rightarrow \text{C} + 3\text{D}$.

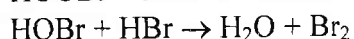
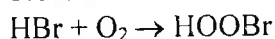
Calculate the activation energy for the above reaction if the rate constants at 300 K and 450 K are $0.134 \text{ L mol}^{-1} \text{ s}^{-1}$ and $0.569 \text{ L mol}^{-1} \text{ s}^{-1}$ respectively.

20 marks

2. (a) Give a brief account of catalysts used in chemical industry

30 marks

- (b) The following mechanism has been suggested for the gas phase oxidation of hydrogen bromide



No H_2O is found in the final products. Experimentally, the reaction is found to be first order with respect to HBr and O_2 .

- (i) Write a balanced equation for the oxidation of hydrogen bromide
- (ii) Why is the equation in part (i) unlikely to represent the reaction mechanism?
- (iii) Show that the above mechanism is consistent with the observed orders of reaction (obtain the rate expression by applying the steady state assumption)
- (iv) Which step is likely to be the rate determining step?

70 marks

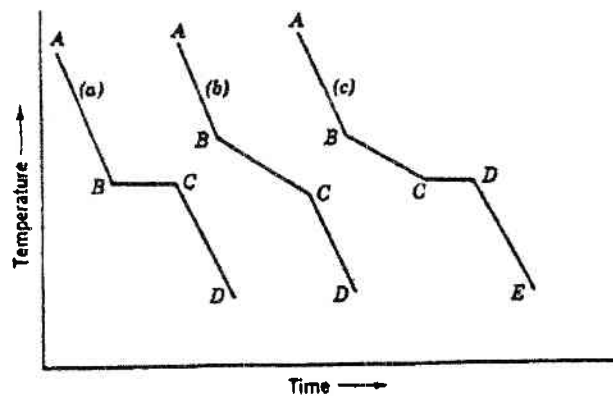
3. (a) Write down the Gibbs phase rule and define all the terms therein.

20 marks

- (b) Draw a fully labeled phase diagram for a one component system and apply the phase rule to show the number of phases, degrees of freedom and number of components in each phase region.

25 marks

- (c) In an experiment for the construction of a phase diagram for a binary system (solid X and solid Y), following cooling curves have been obtained. Explain the behavior of each curve referring to appropriate phase changes.



25 marks

- (d) With the help of labeled phase diagrams, differentiate between the distillation of azeotropic and zeotropic mixtures.

30 marks

4. (a) Briefly explain the particle-wave duality.

10 marks

- (b) (i) What is the energy of a particle in a 1D box of width a in its ground state? Explain your answer

20 marks

- (ii) Calculate $|\Psi|^2$ if $\Psi = a + ib$, where a and b are real numbers.

20 marks

- (c) The Hamiltonian for multi electron system composed of several nuclei consists of various parts. Write equations for the following terms in the Hamiltonian.

- (i) The kinetic energy of electrons
- (ii) The kinetic energy of nuclei
- (iii) The coulombic interactions between the nuclei and the electrons
- (iv) The coulombic interactions between the electrons

20 marks

- (d) Show that the operator $\frac{-\hbar}{2m} \frac{\partial^2}{\partial x^2} + V(x)$ represents the total energy of the system.

30 marks