63

RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc (General) Degree in Applied Sciences
Second Year – Semester II Examination–Oct / Nov 2017

CHE 2201 – PHYSICAL CHEMISTRY II

Answer FOUR questions only   Time: Two (2) hours

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eV$=1.602\times10^{-19}$ J, Planck's constant $= 6.626\times10^{-34}$ m^2 kg s^{-1}, electron charge $=1.602\times10^{-19}$ C

(1)

(a) What do you understand by the terms (i) rate of a reaction (ii) activated complex and (iii) activation energy?

(25 marks)

(b) Describe how the activation energy (E_A) could be measured experimentally and indicate how the data could be manipulated graphically to obtain a numerical estimate of E_A.

(25 marks)

(c) For a reaction, the energy of activation is zero. What is the value of rate constant at 300 K if $k = 1.6\times 106$ s^{-1} at 280 K?

(20 marks)

(d) Write a short note on the effect of temperature on the rate of a gas phase reaction.

(30 marks)

(2).

(a) The condensation reaction of acetone $(CH_3)_2CO$ in aqueous solution is catalysed by base B, which react reversibly with acetone to form the carbanion $C_3H_5O^-$. The carbanion then reacts with a molecule of acetone to give the product P. A simplified version of the reaction mechanism is as follows:

$$AH + B \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} BH^+ + A^-$$

$$A^- + HA \xrightarrow{K_2} P$$

where AH represents acetone and A^- is the carbanion. Use the steady state approximation to determine the concentration of the carbanion, and hence derive the rate equation for the formation of the product.

(40 marks)

(b) Show by suitable integration of the first order rate equation that the half life $t_{1/2}$ is independent of the initial reactant concentration C_0 and is given by $t_{\frac{1}{2}} = \frac{\ln 2}{2k}$ where k denotes the first order rate constant. What are the units of k?

(30 marks)

(c) A reaction is known to exhibit first order kinetics. At 300 K the concentration of reactant is reduced to one half of its initial value after 5000 s. At 310 K, the concentration is halved after 1000 s. Use this information to calculate:

(i) The rate constant for the reaction at 300 K

(ii) The time required for the reactant concentration to be reduced to one quarter of its initial value at 310 K

(iii) The activation energy of the reaction.

(30 marks)

(3) Electron diffraction makes use of 40 keV (40,000eV) electrons. Calculate their de Broglie wavelength.

(a) In the above calculation, you would determine the order of magnitude of nuclear energies. Assume that a nucleus can be represented as a cubic box of side 10^{-14} m. The particles in this box are the nucleons (protons and neutrons). Calculate the lowest allowed energy of a nucleon. Express your answer in MeV (1MeV = 10^6 eV)

(b) As a variant on the free-electron model applied to benzene, assume that the six π electrons are delocalized within a square plate of side 'a'. Calculate the value of 'a' that would account for the 268 nm ultraviolet absorption in benzene.

(c) Write down full Hamiltonian operator for He

(100 marks)

(4)

(a) Draw a completely labeled phase diagram for water and apply the Gibbs phase rule for the determination of number of degrees of freedom (F) at any point in the (i) liquid region, (ii) phase boundary between liquid and solid and (iii) triple point.

(30 marks)

(b) An ideal solution of toluene and benzene contains 6 moles of benzene and 4 moles of toluene at 25°C. The vapor pressure of pure benzene at 25^{O}C is 96 Torr, the vapor pressure of pure toluene is 29 Torr. Initially the mixture is at a pressure of 760 Torr and the mixture is only liquid. Then the pressure is slowly lowered until the total pressure is 60 Torr.

(i) What are the compositions of the liquid phase and vapor phase?

(ii) How many moles of liquid and vapor are there?

(iii) Draw the temperature composition phase diagram for the above solution

(40 marks)

(c) Ethanol and water mixture forms a minimum boiling point constant composition solution in the fractional distillation, Explain with a suitable diagram.

(30 marks)

(5) Answer both parts

Part A

(a) Consider a two-dimensional particle-in-a-box and the particle is free to move on a square plate of side 'a'. Explain the degeneracies of the lowest energy levels.

(b) Before quantum mechanics, many of the properties of matter could be accounted for by a model in which the electrons in an atom were treated as harmonic oscillators. Suppose the electron in hydrogen atom was bound with a force constant

$$k = \frac{9e^2}{64(4\pi\varepsilon_0)a_0^3}$$

where e is the electron charge, a_0 is the Bohr radius 0.529×10^{-10} m and $1/4\pi\varepsilon_0 = 8.99\times10^9$ in compatible units, such that k comes out in N m^{-1}

(i) Assuming that the electron behaves as a quantum-mechanical harmonic oscillator, derive a formula for the wavelength of the radiation which can be emitted or absorbed by a hydrogen atom.
(ii) Calculate this wavelength in nm

(50 marks)

Part B

(a) Explain how a catalyst serves to enhance the rate of a chemical reaction. What is the difference between heterogeneous and homogeneous catalysis?
(b) Consider the equilibrium between two phases A and B with chemical potentials μ^A and μ^B respectively.

$$A \rightleftharpoons B$$

Derive the following equation that shows the change in pressure with respect to temperature as given by

$$\frac{dp}{dT} = \frac{\Delta\bar{S}}{\Delta\bar{V}}$$

(50 marks)