BINDURA UNIVERSITY OF SCIENCE EDUCATION

CHEMISTRY DEPARTMENT

BSc Chemical technology and BSc Education

COURSE: **CH 301: PHYSICAL CHEMISTRY III**

2 HOURS OCT 2024

Answer any five (5) questions. Each question carries **20 MARKS**.

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1. (a) In a reaction mechanism, (i) what is the difference between an *activated complex* and an *intermediate*? (ii) What is meant by the rate-determining step? Which elementary reaction in a reaction mechanism is often the rate-determining step? **[4 marks]**

   (b) The following are two statements pertaining to the reaction $2A + B \rightarrow 2C$, for which the rate law is $rate = k[A][B]$. Identify which statement is true and which is false, and explain your reasoning.

   (i) The value of k is *independent* of the initial concentrations $[A]_0$ and $[B]_0$.

   (ii) The unit of the rate constant for this reaction can be expressed either as s^{-1} or min^{-1}. **[4 marks]**

   (c) Which allotropic form of carbon is used for making electrodes? **[2 marks]**

   (d) A zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential. **[4 marks]**

   (e) What is the difference between molecular mechanics methods and density functional theory **[6 marks]**

2. (a) (i) Derive the Michaelis-Menten equation. **[7 marks]**

   (ii) Under what conditions does the Michaelis –Menten equation reduce to $v = k_b[E_0]$? **[2 marks]**

(b) The effective rate constant for a gaseous reaction which has a Lindemann-Hinshelwood mechanism is 2.12×10^{-4} s^{-1} at 1.13 kPa and 2.15×10^{-5} s^{-1} at 11 Pa. Calculate the rate constant for the activation step in the mechanism. **[5 marks]**

(ii) Using the following data for the reaction A +B $\rightarrow$C , determine the order of the reaction with respect to A and B, and the rate constant for the reaction:

[A](M)	**[B](M)**	**Initial rate (Ms^{-1})**
2.30×10^{-4}	3.10×10^{-5}	5.25×10^{-4}
4.60×10^{-4}	6.20×10^{-5}	4.20×10^{-3}
9.20×10^{-4}	6.20×10^{-5}	1.68×10^{-2}

[6 marks]

3. (a) Describe the two models used to explain the binding of a substrate to the active site of an enzyme. **[6 marks]**

(b) You are performing an experiment using ^{3}H (half-life $=1.6 \times 10^{4}$ days) labeled phenylalanine in which the five aromatic hydrogens are labeled. To perform the experiment, the initial activity cannot be lower than 10% of the initial activity when the sample was received. How long after receiving the sample can you wait before performing the experiment? **[5 marks]**

(c) Consider the following sequential reaction:

$$A \xrightarrow{k} P$$

(i) If the reaction is one-half order with respect to $[A]$, what is the integrated rate law expression for this reaction? **[6 marks]**

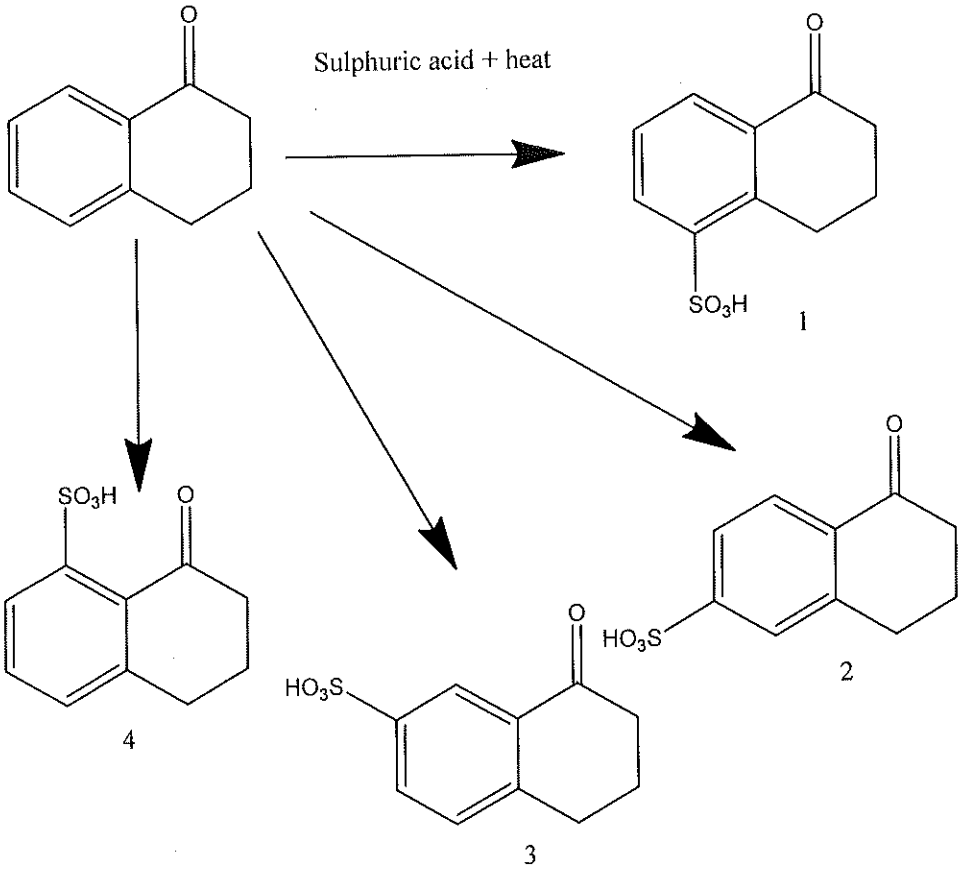
(ii) What plot would you construct to determine the rate constant k for the reaction? **[3 marks]**

4. (a) Why do deviations from ideal behavior occur at lower concentrations for electrolyte solutions than for solutions in which the solute species are uncharged? **[6 marks]**

(b) Calculate $\gamma_{\pm}$ for a 0.0080 m solution of K_2SO_4 at 298K. Assume complete dissociation. **[6 marks]**

(c) Calculate the ionic strength in a solution that is 0.0750 m in K_2SO_4, 0.0085 m in Na_3PO_4, and 0.0150 m in $MgCl_2$. **[8 marks]**

5. (a) Design a computational chemistry experiment you would perform for you to be able to deduce which isomer will have the greatest yield, thus the most stable. **[12 marks]**



(b) For which of the following problems would Hartree-Fock theory provide a good estimate? *Justify your reasoning.*

(i) Homolytic bond dissociation of the C-F bond in H_3C-F molecule.

(ii) Enthalpy of reaction for cis-trans isomerization of 1,2-dichloroethylene

(iii) Singlet-triplet energy splitting of methylene (CH_2)

(iv) Enthalpy of reaction for reduction of benzene:

$(C_6H_6 + 6CH_4 \rightarrow 3C_2H_4 + 3C_2H_6)$ **[8 marks]**

6. (a) Consider the half-cell reaction $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$. By what factor are n, Q, E, and E° changed if all the stoichiometric coefficients are multiplied by the factor two? Justify your answers. **[8 marks]**

(b) Why can batteries only be recharged a limited number of times?

[2 marks]

(c) Determine the half-cell reactions and the overall cell reaction, calculate the cell potential, and determine the equilibrium constant at 298.15 K for the cell

$$\mathrm{Pt}(s)\left|\mathrm{Mn}^{2+}\left(aq, a_{\pm}=0.0150\right), \mathrm{Mn}^{3+}\left(aq, a_{\pm}=0.200\right)\right\|\mathrm{Zn}^{2+}\left(aq, a_{\pm}=0.100\right)\left|\mathrm{Zn}(s)\right.$$

Is the cell reaction spontaneous as written? **[10 marks]**

END OF QUESTION PAPER