BINDURA UNIVERSITY OF SCIENCE EDUCATION

CHEMISTRY DEPARTMENT

HBSc.Ed and CHEMICAL TECHNOLOGY

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

2 HOURS

Answer **ANY FIVE (5)** questions. Each question carries 20 marks.

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1. (a) Which of the following species would mostly likely be oxidized, if placed in a electrochemical cell with another species? Explain **[4 marks]**

   i. $Zn(s)$ *ii.* $Zn^{2+}(aq)$ *iii.* $Cu(s)$ *iv.* $Hg(l)$

   (b) The reaction below takes place in an electrochemical cell:

   $$Mg(s) + Ca^{2+}(aq) \rightarrow Mg^{2+}(aq) + Ca(s)$$

   Is the cell galvanic or voltaic? Explain **[4 marks]**

   (c) Suppose that an enzyme mixture contains an enzyme with a Michaelis constant of $5.0 \times 10^{-6} M$. If the substrate concentration in this mixture is $4.5 \times 10^{-6} M$, what is the fractional saturation of this enzyme mixture? **[5 marks]**

   (d) What is geometry optimisation? **[2 marks]**

   (e) What is the difference between molecular mechanics methods and density functional theory **[5 marks]**

2. (a) For a given enzyme catalyzed reaction, the Michaelis constant is 0.6 mM and the substrate concentration is 1.0 mM. What is the fractional saturation of the enzyme under these conditions? **[5 marks]**

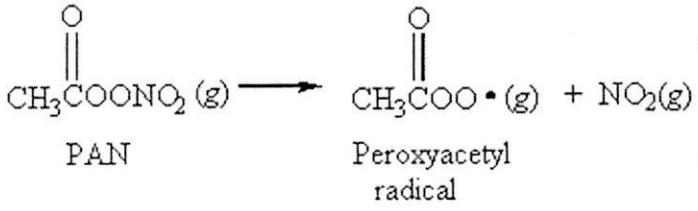
   (b) Rate constants for the first-order decomposition of acetone dicarboxylic acid
   $\mathbf{CO(CH_2COOH)_2(aq) \rightarrow CO(CH_3)_2(aq) + 2\ CO_2(g)}$
   are $k = 4.75 \times 10^{-4}\ s^{-1}$ at 293 K and $k = 1.63 \times 10^{-3}\ s^{-1}$ at 303 K. What is the activation energy, E_a, for this reaction? **[5 marks]**

(c) 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}. **[5 marks]**

(d) The smog constituent, peroxy acetyl nitrate (PAN) dissociates into peroxy acetyl radicals and $NO_2(g)$ in a first order reaction with a half-life of 32 min.



If the initial concentration of PAN in an air sample is 2.7×10^{15} molecules/L, what will be the concentration 2.24 h later? **[5 marks]**

3. Hydroxide ion is involved in the mechanism but not consumed in this reaction in aqueous solution.

$$OCl^-(aq) + I^-(aq) \rightarrow OH^- OI^-(aq) + Cl^-(aq)$$

(a) Using the data in the table below, determine the order of reaction with respect to

OCl^-, I^-, and OH^-, and the overall order. **[6 marks]**

$[OCl^-]$ (M)	$[I^-]$ (M)	$[OH^-]$ (M)	Rate of formation of OI^- ($molL^{-1}s^{-1}$)
0.0040	0.0020	1.00	4.8×10^{-4}
0.0020	0.0040	1.00	5.0×10^{-4}
0.0020	0.0020	1.00	2.4×10^{-4}
0.0020	0.0020	0.50	4.6×10^{-4}
0.0020	0.0020	0.25	9.4×10^{-4}

(b) Write the rate law, and determine the value of the rate constant, k. **[4 marks]**

(c) Show that the following mechanism is consistent with the net equation and with the rate law. Which is the rate–determining step?

$$OCl^-(aq) + H_2O(l) \rightarrow \leftarrow HOCl(aq) + OH^-(aq)$$

$$I^-(aq) + HOCl(aq) \rightarrow HOI(aq) + Cl^-(aq)$$

$$HOI(aq) + OH^-(aq) \rightarrow H_2O(l) + OI^-(aq)$$ **[6 marks]**

(d) Is it appropriate to refer to OH^- as a catalyst in this reaction? Explain.

[4 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) Force field energies are expressed as a sum of terms; arrange these terms in order of their relative importance by completing the table below.

Term	Scale ($kcalmol^{-1}$)
(i)	100
(ii)	10
(iii)	1
(iv)	2
(v) **Electrostatic**	0.5
(vi)	0.1

[5 marks]

(b) State the two primary limitations of the Hartree Fock method. **[4 marks]**

(c) Which of the following reactions are isodesmic?

(i) $H_2O \rightarrow H + OH$;

(ii) CH_3Cl + propane $\rightarrow$ *i*-propyl chloride + methane;

(iii) benzene + 3 H_2 → cyclohexane;
(iv) HOOH + CH_3OOF → HOOF + CH_3OOH. **[2 marks]**

(d) Which of the following is the exception? Give reasons
(i) AM1
(ii) BP86
(iii) MP2
(iv) B3LYP
(v) 6-311G **[3 marks]**

(e) What is the fundamental approximation that is made in Hartree-Fock theory?

[3 marks]

(f) Consider a molecule of oxygen (μ = 8 g mol^{-1}), which has a vibrational wavenumber ν/c = 1580 cm^{-1}. What is the force constant for this molecule, in N m^{-1}? **[3 marks]**

6. Consider the half-cell reaction

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

(a) 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.

[4+2+3+4 marks]

(b) Is the cell reaction spontaneous as written? **[3 marks]**

(c) Why can batteries only be recharged a limited number of times? **[2 marks]**

(d) For the above cell, state the anode and cathode. **[2 marks]**

END OF QUESTION PAPER