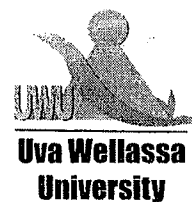


Uva Wellassa University of Sri Lanka  
 Faculty of Science and Technology  
 Science and Technology Degree Program  
 Third year First Semester Examination – July/August 2016  
 SCT 331-3 Material Chemistry I



**Instructions to candidates**

Duration: Three (03) hours

Number of questions: Six (06)

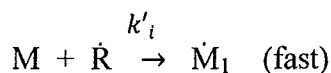
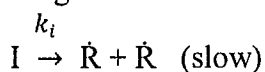
**Answer All Questions**

Mark allocation: 100 marks

1. a. State differences between stepwise polymerization and chain polymerization. Give an example for each kind. (3 marks)

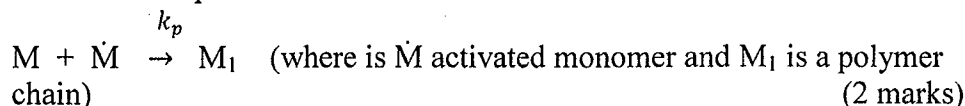
b. What are the three basic steps in chain polymerization? (3 marks)

c. i. Following is the mechanism for the first step in chain polymerization.



where, I is an initiator,  $\dot{R}$  is a radical species, M monomer and  $\dot{M}_1$  is an activated monomer. Write the rate expression for the above mechanism. (2 marks)

ii. Following is generalized reaction for the next step in chain polymerization. Write the rate expression for this reaction.



iii. The rate expressions for the formation and deletion of radical monomers are given by following expressions.

$$(d[\dot{M}]/dt)_{\text{formation}} = 2f k_i [I]$$

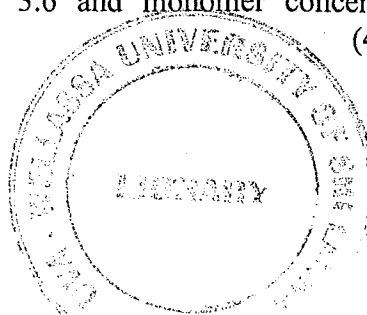
$$(d[\dot{M}]/dt)_{\text{depletion}} = -2 k_t [\dot{M}]^2$$

$f$  is the fraction of radicals formed. Obtain an expression for  $[\dot{M}]$ . State any assumptions or approximations used. (3 marks)

iv. Define the term kinetic chain length ( $\nu$ ) of a polymer. Derive following expression for  $\nu$  using rate expressions stated in above parts (ii – iii).

$$\nu = 2k_r [M][I]^{-1/2} \quad \text{where, } k_r = (k_p/2) \sqrt{\frac{1}{fk_i k_t}} \quad (3 \text{ marks})$$

v. Consider a polymer formed by a chain polymerization method. Calculate how much does the kinetic chain length change ( $\nu_2/\nu_1$ ) if the concentration of the initiator is increased by a factor of 3.6 and monomer concentration is decreased by a factor of 4.2? (4 marks)



2. a. Explain following terms describing absorption process, radiative and non-radiative processes and spin multiplicity of transitions using an appropriate energy level diagram.
- fluorescence
  - phosphorescence
- (5 marks)
- b. Write generalized photochemical reactions for decay of excited species ( $A^*$ ) through,
- ionization
  - electron transfer
  - dissociation
- (3 marks)
- c. Stern-Volmer equation for fluorescence process is given below. Quantum yield and life times in the presence and absence of a quenching species are denoted as  $\phi_{f0}$ ,  $\tau_{f0}$  and  $\phi_f$ ,  $\tau_f$  and concentration, rate constant and life time of quenching species is given as  $\tau_0$ ,  $k_Q$ , and  $[Q]$ .

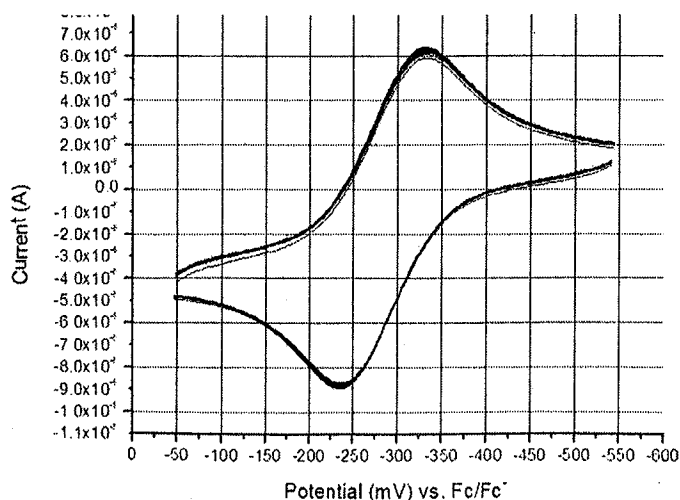
$$\left(\frac{\phi_{f,0}}{\phi_f}\right) = \left(\frac{\tau_{f,0}}{\tau_f}\right) = 1 + \tau_0 k_Q [Q]$$

- Rearrange the above equation in the form of  $y = mx + c$  format (3 marks)
- Following data are obtained for quenching of  $[\text{Ru}(\text{bpy})_3]^{2+}$  excited state in the presence of  $[\text{Fe}(\text{OH})_6]^{2+}$  in acidic medium. Determine rate constant for quenching reaction by plotting the linearized Stern-Volmer equation.

$[\text{Fe}(\text{OH})_6]^{2+}$ concentration $\times 10^{-4}$ M	$\tau \times 10^{-7}$ s
0	6
1.6	4.05
4.7	3.37
7	2.96
9.4	2.17

(4 marks)

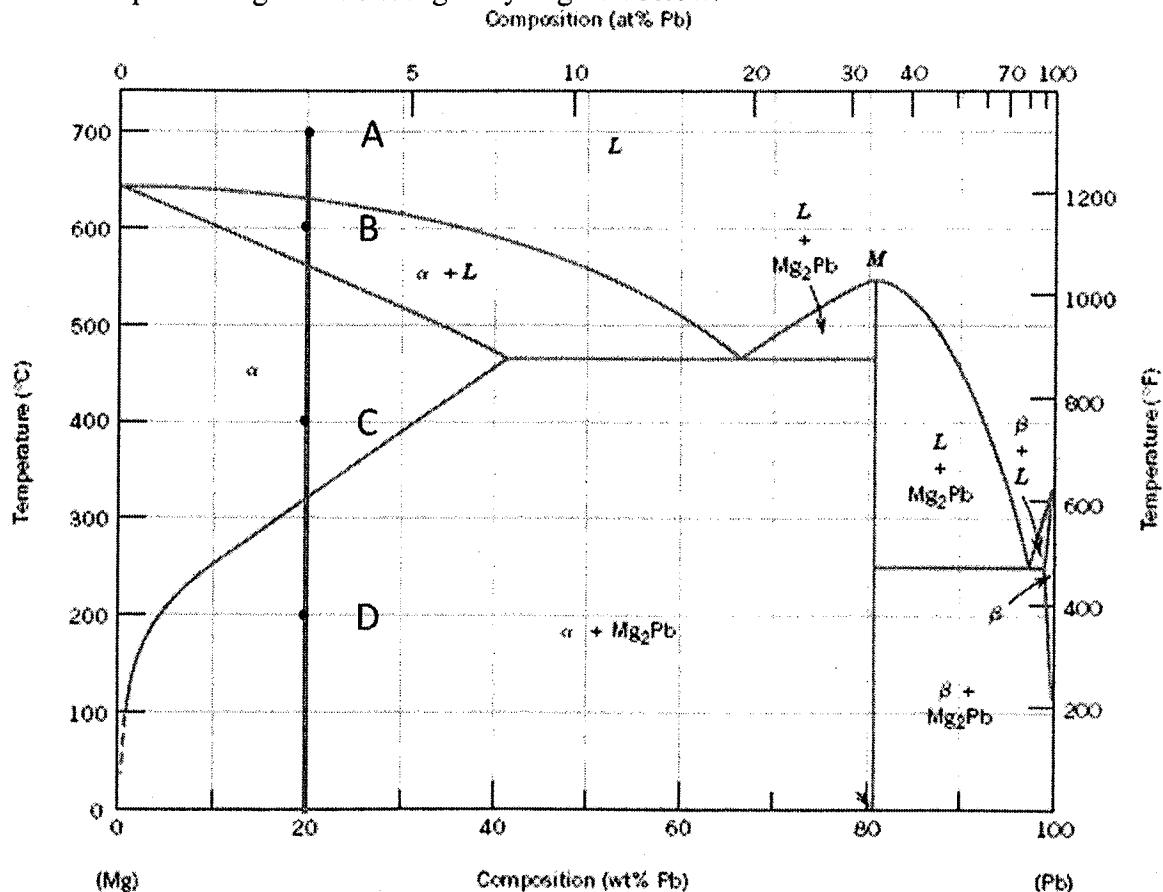
- 3.a. Draw the shape of the graph of i. potential variation with time ii. Current variation with applied potential as used in cyclic voltammetry. (4 marks)
- b. What is the purpose of using ferrocene in cyclic voltammetric experiments? (2 marks)
- c. Obtain values for the following parameters ( $E_{pa}$ ,  $E_{pc}$ ,  $I_{pa}$ ,  $I_{pc}$ ,  $E_{1/2}$ ,  $\Delta E$ ,  $I_{pc}/I_{pa}$ ) for the cyclic voltammogram given below. Giving comment on the reversibility of this redox process. (12 marks)



- d. State two applications where cyclic voltammetry can be used. (2 mark)

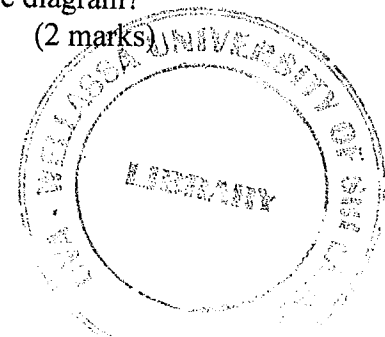
4. a. List three major differences between cyclic voltammetry and bulk electrolysis. (3 marks)
- b. A mixture contains  $\text{Cu}^{2+}$  ions ( $E_{1/2} = 120 \text{ mV vs. SCE}$ ) and  $\text{Fe}^{2+}$  ions ( $E_{1/2} = 440 \text{ mV vs. SCE}$ ).
- Draw the shape expected for linear sweep voltammogram (I vs. V) of the above mixture. (2 marks)
  - If you want to quantify the amount of  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  ions using bulk electrolysis, explain the steps in experimental process and calculations stating clearly the potentials at which bulk electrolysis will be carried out and giving equations for chemical reactions at each step. (4 marks)
- c. A constant current of  $0.900 \text{ A}$  is used to deposit copper at the cathode and evolve oxygen at the anode of an electrolytic cell.
- Write the balance reaction for the oxidation of water and reduction of copper. (2 marks)
  - Calculate the mass of copper deposited after passing current for 15 minutes. Assume no other redox reactions. ( $\text{Cu} = 63.55 \text{ g/mol}$ , Faraday constant =  $96500 \text{ C/mol}$ ) (4 marks)

5. The phase diagram of Pb/Mg alloy is given below.



- a. How would you identify the presence of a chemical compound in a phase diagram?

(2 marks)



b. Find temperature and corresponding composition if following are present in the above phase diagram.

- i. Eutectic point      ii. Compound      iii. Eutectoid point

(6 marks)

c. Draw changes in morphology when the liquid cooled from 700 °C to 200 °C along points A, B, C, and D. (6 marks)

d. Calculate the weight percentage of  $\alpha$  phase at points A, B, C, and D using the Lever rule. (6 marks)

6.a. What is the difference between homogeneous and heterogeneous nucleation? (5 marks)

(5 marks)

b. State how super cooling effect the size of crystals formed? (4 marks)

(4 marks)

c. Following is a phase transformation diagram of Fe – Fe<sub>3</sub>C system. If cooling was conducted below eutectoid point, draw morphological changes in the system when transformation was conducted using following different cooling pathways.

- i. A → B → C  
ii. D → E → F

(6 marks)

