

University of Canterbury

Mid Year Examination and Test Period 2008

Prescription Number(s):	CHEM 333
Paper Title:	General Physical Chemistry

Time Allowed: 80 minutes

Number of pages: SEVEN

Answer **BOTH** questions.

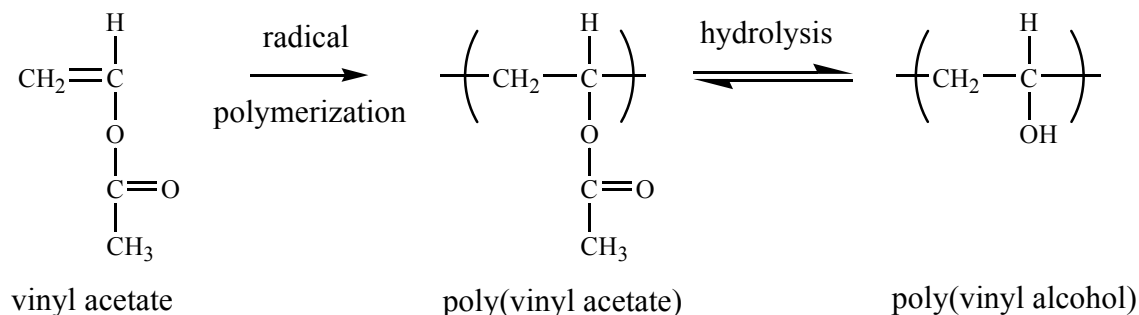
All questions are of equal value.

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1. (40 marks)

(a) (8 marks)

Poly(vinyl alcohol) is synthesized as follows:



- (i) Suggest an initiator for carrying out the polymerization step.
- (ii) Explain why poly(vinyl alcohol) cannot be synthesized directly from a monomer.
- (iii) As indicated, the ester hydrolysis step is an equilibrium process rather than a reaction that goes to completion. Hence what is called poly(vinyl alcohol) is more accurately described as a copolymer of vinyl alcohol and vinyl acetate. Would this copolymer best be classified as alternating, random or statistical? Explain your reasoning.

(b) (21 marks)

A chemist blended 100 g of monodisperse polyethylene of molar mass $140\,000 \text{ g mol}^{-1}$ and 200 g of monodisperse poly(1-butene) of molar mass $560\,000 \text{ g mol}^{-1}$.

- (i) Name and briefly describe a method for measuring the molar mass of a polymer.
- (ii) Calculate the weight-average molecular weight, M_w , of the blend.

Question 1 continued on the following page

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Question 1 continued

- (iii) Calculate the number-average molecular weight, M_n , of the blend.
- (iv) Calculate the polydispersity index of the blend.
- (v) Calculate the weight-average degree of polymerization, DP_w , of the blend.

[Useful information and hint: $M_r(\text{C}_2\text{H}_4) = 28$; $M_r(\text{C}_4\text{H}_8) = 56$.]

- (vi) As an alternative strategy to blending, a mixture of ethylene and 1-butene was polymerized using $\text{Al}(\text{C}_2\text{H}_5)_3/\text{TiCl}_4$ as catalyst. Draw the structure of the polymer thus produced, and explain whether it is linear or branched.

(c) (7 marks)

With reference to the equations below, briefly discuss how polymer size is controlled in each of radical polymerization and step-growth polymerization.

$$\frac{1}{DP_n} = \frac{k_{tr}[\text{CTA}]}{k_p[\text{M}]} \qquad \frac{1}{DP_n} = 1 - \frac{1}{2} f_{av} P$$

(d) (4 marks)

The rate law for radical polymerization is

$$\frac{dx}{dt} = \left(\frac{k_p^2 f k_d}{k_t} \right)^{0.5} (1-x)[\text{I}]^{0.5}$$

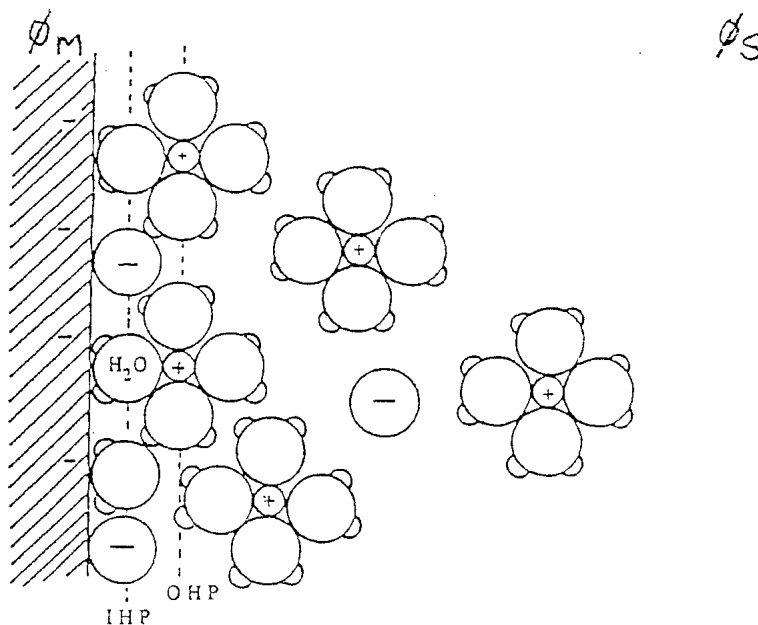
Name all the quantities in this equation.

2. (40 marks)

Answer **TWO** of (a) - (c).

(a) Answer **all** parts (i) – (iv).

The figure below will assist your answers to this question.



- (i) Explain the term **electrical double layer** and briefly describe a modern model of the electrical double layer.
- (ii) Describe, with explanation, how the electrical double layer may influence the driving force for electron transfer at an electrode.
- (iii) Explain why electrochemical experiments are usually undertaken in the presence of a high concentration of inert supporting electrolyte.
- (iv) From your general knowledge of electrode kinetics, suggest, with brief explanation, how a cyclic voltammogram would change if the concentration of inert supporting electrolyte was decreased to a low value.

Question 2 continued on following page

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Question 2 continued

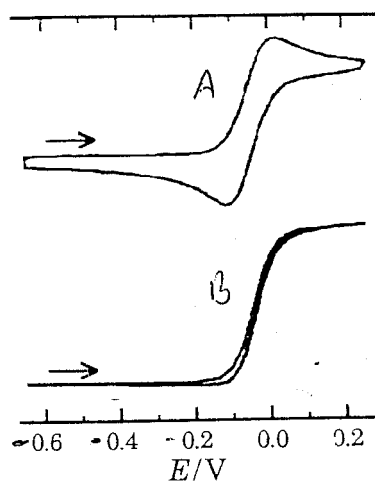
- (b) Answer **all** parts (i) – (iv).
- (i) In the context of electrode kinetics, what is the **exchange current**?
- (ii) Explain, in general terms (no equations required) how the exchange current can be determined. You should indicate what experimental data are required as a starting point.
- (iii) How can knowledge of the exchange current lead to kinetic information?
- (iv) During the chlor-alkali process for the production of Cl_2 and NaOH , two oxidation reactions can occur, with the relevant equilibrium potentials shown below:
- $$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \quad E_e = 1.3 \text{ V} \quad (1)$$
- $$2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^- \quad E_e = 1.0 \text{ V} \quad (2)$$
- (A) Explain why the equilibrium potentials for the two reactions indicate a possible problem for the chlor-alkali process.
- (B) Explain how the problem in (A) is circumvented in chlor-alkali plants.
- (C) Under the usual operating conditions, which of the reactions shown above will have the largest exchange current, and why?
- (D) In the context of electrode kinetics, define **overpotential**.
- (E) In industrial processes, why is it desirable to minimize the operating overpotential and how can this be achieved?

Question 2 continued on following page

Question 2 continued

(c) Answer **all** parts (i) – (v).

Non-steady state (A) and steady-state (B) voltammograms are shown below.



- (i) In the context of electrochemistry, define the term **steady-state**.
- (ii) Explain, in detail, with reference to concentration gradients, why cyclic voltammogram A has a peaked shape. Note it is necessary to account for the shape of the voltammogram on the **forward** scan only.
- (iii) What is the approximate $E_{1/2}$ of voltammogram A and what is the significance of the $E_{1/2}$ value?
- (iv) Voltammograms A and B were recorded under the same conditions except that for A, the electrode was stationary and for B it was rotated. Explain why rotating the electrode results in a steady-state voltammogram.
- (v) How would the limiting current (maximum current) in B change if the electrode rotation rate were increased? Briefly explain your answer.

END OF PAPER