University of Canterbury

Mid Year Examination and Test Period 2009

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

Time Allowed: 80 minutes

Number of pages: SIX

Answer **BOTH** questions.

Both questions are of equal value.

TURN OVER

1. Answer **THREE** of (a) – (d):

(a) Answer **all** parts (i) – (iv).

(i) What is the essential characteristic of a reference electrode?

(ii) List the components of any commonly used reference electrode and write an equation showing the redox reaction for the electrode.

(iii) Explain why the electrode chosen in (b) meets the essential requirements of a reference electrode.

(iv) Electrochemists sometimes use a bare silver wire as a ‘pseudo’ reference electrode for non-aqueous electrolyte solutions. Suggest why a silver wire may be ‘good enough’ as a reference electrode for short-timescale measurements but is unreliable for long-timescale measurements.

(b) Answer **all** parts (i) – (iii).

(i) For a potential-step experiment, use concentration profiles to explain, in detail, why the current is highest immediately after the step and decreases with time.

(ii) Suggest how to test for mass-transport control in a potential-step experiment.

(iii) If the system is shown to be under mass-transport control, what can you deduce about the rate of electron transfer at the electrode?

Question 1 continued on following page

Question 1 continued

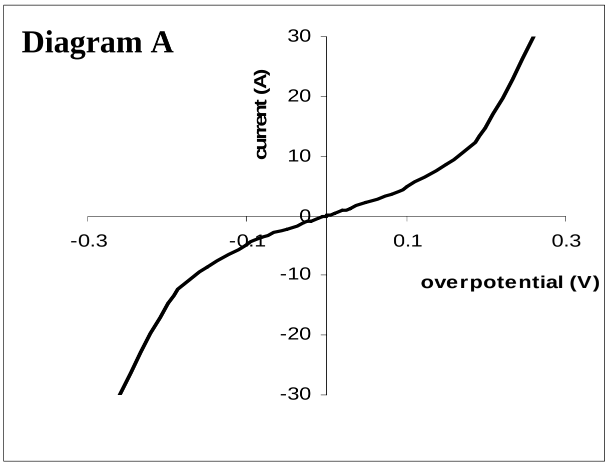
(c) Answer **all** parts (i) – (ii).

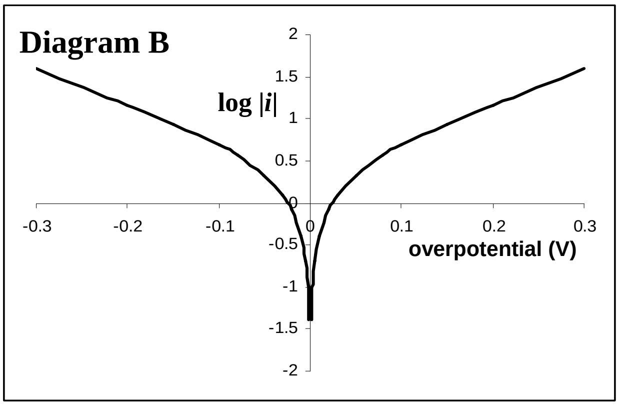
(i) Diagram A below shows a current-overpotential curve, and diagram B the corresponding Tafel plot for the following redox couple:

$$O + e^- \leftrightarrow R$$

(A) Explain how the exchange current can be determined from a Tafel plot.

(B) Account for the deviation from linearity of the Tafel plot, when the overpotential is close to zero.





(ii) 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:

$2Cl^- \rightarrow Cl_2 + 2e^-$	$E_e = 1.3$ V	(1)
$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$	$E_e = 1.0$ V	(2)

Explain briefly how and why exchange-current data could be used to identify suitable electrode materials for the anode reaction in the chlor-alkali process.

Question 1 continued on following page

Question 1 continued

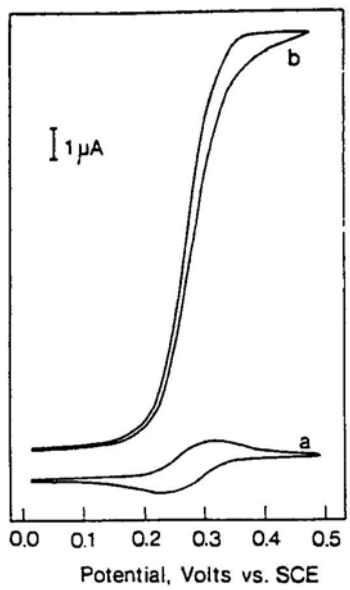
(d) Answer **all** parts (i) – (iii).

The figure below shows proof-of-concept for the electrochemical detection of glucose using the enzyme glucose oxidase (GOx) and the mediator ferrocene monocarboxylic acid (FCA). For cyclic voltammogram a), the solution contains FCA and D-glucose; for cyclic voltammogram b) the solution contains FCA, D-glucose and GOx.

(i) Considering only the forward scan (i.e. from 0 to 0.5 V), explain, using concentration profiles, why voltammogram a) has a peaked shape.

(ii) Explain why voltammogram b) reaches a much higher current than voltammogram a) and explain why the current increases to a plateau in b) and not to a peak.

(iii) Briefly explain the significance of the voltammograms with respect to the development of devices for the mediated electrochemical detection of glucose.



2. All parts are worth equal marks.

Write notes on **ALL** of the following:

(a) Step-growth polymerization

(b) Types of polyethylene

(c) The most-probable distribution of polymer sizes, $n_i = U^i(1-U)$

(d) Size exclusion chromatography

(e) The Mayo equation, $\dfrac{1}{DP_\text{n}} = \dfrac{k_\text{tr}[\text{CTA}]}{k_\text{p}[\text{M}]} + \dfrac{[\text{R}^\bullet](2k_\text{td} + k_\text{tc})}{k_\text{p}[\text{M}]}$

(f) The rate law for radical polymerization, $\dfrac{\text{d}x}{\text{d}t} = \left(\dfrac{k_\text{p}^2 f k_\text{d}}{k_\text{t}}\right)^{0.5} (1-x)[\text{I}]^{0.5}$

(g) Copolymer microstructure

END OF PAPER