
UNIVERSITI SAINS MALAYSIA

Second Semester Examination
Academic Session 2004/2005

March 2005

KAA 504 - Electrochemical Methods

Time : 3 hours

Please make sure this paper consists of SEVEN printed pages before answering the questions.

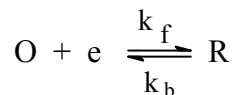
Answer FIVE questions. This paper contains SIX questions.

Only the first five questions answered by the candidate will be marked.

List of symbols attached.

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1. Consider the simplest possible electrode process, wherein species O and R engage in a one-electron transfer at the interface without being involved in any other chemical step,



- (a) Use the activated complex theory for explaining clearly how the applied potential affects the rate constant of an electron-transfer reaction. Draw free energy curves and use proper equations for your explanation.

(7 marks)

- (b) Derive the current-overpotential equation

$$i = i_o \left[\frac{C_O(0, t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0, t)}{C_R^*} e^{(1-\alpha) f \eta} \right]$$

where i = the anodic or cathodic current.

i_o = exchange current

C_O^* , C_R^* = bulk concentration of species O or R.

$C_O(0, t)$, $C_R(0, t)$ = concentration of species O or R at the electrode surface at time t ,

α = transfer coefficient

η = overpotential, $E - E_{eq}$

f = F/RT

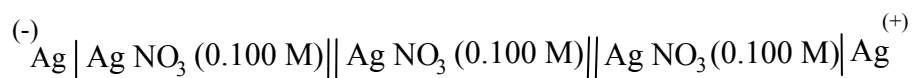
(8 marks)

- (c) Draw a polarization curve that shows the dependence of the relative current densities j_a/j_o , j_c/j_o and j/j_o on the overpotential. How does the variation of the transfer coefficient affect the polarization curve ?

(5 marks)

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2. (a) Consider the three-compartment cell:



where the symbol \parallel signifies sintered glass disks that divide the compartments and prevent mixing, but not ionic movement. The volume of AgNO_3 solution in each compartment is 25.00 mL. An external power supply is connected to the cell with the polarity shown. Current is supplied until 96.5 C have passed, causing Ag to deposit on the cathode and Ag to dissolve from the anode.

- (i) How many grams of Ag have deposited on the cathode?
- (ii) If the transference number of Ag^+ were 1.00 (i.e. $t_{\text{Ag}^+} = 1.00$, $t_{\text{NO}_3^-} = 0.00$), what would the concentrations of Ag^+ be in the three compartments after electrolysis?
- (iii) Suppose the transference number for Ag^+ were 0.00 (i.e. $t_{\text{Ag}^+} = 0.00$, $t_{\text{NO}_3^-} = 1.00$), what would the concentrations of Ag^+ be in the three compartments after electrolysis?
- (iv) In an actual experiment like this, it is found experimentally that the concentration of Ag^+ in the anode compartment has increased to 0.121 M. Calculate t_{Ag^+} and $t_{\text{NO}_3^-}$.

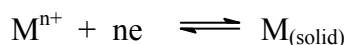
(12 marks)

- (b) In an experiment on the $\text{Pt}/\text{H}_2/\text{H}^+$ electrode in dilute H_2SO_4 the following current densities were observed at 25 °C. Evaluate the transfer coefficient, α and the exchange current density, j_0 for the electrode.

η/mV	50	100	150	200	250
$j/\text{mA cm}^{-2}$	2.66	8.91	29.9	100	355

(8 marks)

3. (a) Derive the sampled-current voltammogram for the reduction of a simple metal ion to a metal that plates out on the electrode. The electrode reaction is



Assume that the reaction is reversible and that the activity of solid M is constant and equal to 1. How does $E_{1/2}$ vary with I_d and the concentration of M^{n+} , respectively?

(10 marks)

- (b) The following measurements were made at 25 °C on the reversible sampled-current voltammogram for the reduction of a metallic complex ion to metal amalgam ($n=2$):

Concentration of ligand salt, NaX (M)	$E_{1/2}$ (V vs SCE)
0.10	-0.448
0.50	-0.531
1.00	-0.566

- (i) Calculate the number of ligands X^- associated with the metal ion M^{2+} in the complex.
- (ii) Calculate the stability constant of the complex if $E_{1/2}$ for the reversible reduction of the simple metal ion is +0.081 V vs SCE. Assume that D values for the complex ion and the metal atom are equal, and that all activity coefficients are unity.

(10 marks)

4. (a) It has been suggested that by measurement of $\frac{I_p}{\nu^{1/2}}$ for a Nernstian linear potential sweep voltammetric curve, and by carrying out a potential step experiment in the same solution at the same electrode to obtain the limiting current of $I_t^{1/2}$, the n value of an electrode reaction can be determined without the need to know A, C_o^* , or D_o . Demonstrate that this is the case. Why would this method be unsuitable for irreversible reactions?

(10 marks)

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- (b) The following measurements were made on a reversible polarographic wave at 25°C. The process could be written as



E(V vs SCE)	\bar{i} (μA)
-0.395	0.48
-0.406	0.97
-0.415	1.46
-0.422	1.94
-0.431	2.43
-0.445	2.92

If $\bar{i}_d = 3.24 \mu\text{A}$ calculate,

- (i) The number of electrons involved in the electrode reaction, and
- (ii) The formal potential (vs NHE) of the couple involved in the electrode reaction, assuming $D_O = D_R$.

(10 marks)

5. Plot schematically the polarization curve for the corrosion of a divalent metal M that has the following electrochemical parameters:

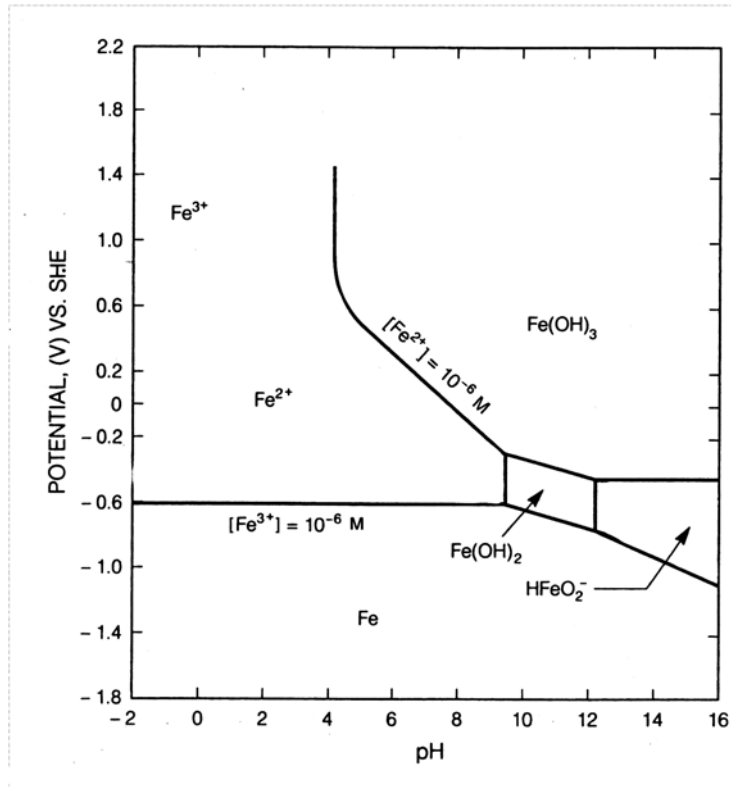
Corrosion potential (E_{corr})	= -0.500 V vs SCE
Passivity potential (E_{pass})	= -0.150 V vs SCE
Pitting potential (E_{pit})	= -0.950 V vs SCE
Protection potential (E_{pro})	= -0.410 V vs SCE
Corrosion current density (i_{corr})	= $2.50 \times 10^{-3} \text{ A cm}^{-2}$

Assuming that the value of Tafel constant, β_a and β_c , for the polarization curve are $0.130 \text{ V decade}^{-1}$ and $0.145 \text{ V decade}^{-1}$, respectively, calculate the polarization resistance (R_p) and the corrosion rate (in mils per year) for the metal M. The equivalent weight and density of the metal M are 27.95 g eq.^{-1} and 7.60 g cm^{-3} , respectively.

(20 marks)

6. (a) Explain clearly the meaning of the following terms when used in the context of Pourbaix diagrams as shown below: immunity; active corrosion and passivation.

(4 marks)



- (b) Use the Pourbaix diagram to obtain the corrosion potential of iron in water at pH 6.
- (2 marks)
- (c) Calculate the corrosion potential at pH 6 by means of the Nernst equation and hence briefly explain the effect of pH on the corrosion of iron at the horizontal line of Pourbaix diagram.
- (5 marks)
- (d) What are the applications and limitations of Pourbaix diagram to the real situation?
- (5 marks)
- (e) Based on Pourbaix diagram, suggest two possible methods for controlling the corrosion of iron in water.
- (4 marks)

LIST OF SYMBOLS:

Symbol	Meaning
i	the anodic or cathodic current
i_0	exchange current
C_O^*, C_R^*	bulk concentration of species O or R
$C_O(0,t), C_R(0,t)$	concentration of species O or R at the electrode surface at time t .
α	transfer coefficient
η	Overpotential, $E-E_{eq}$
f	F/RT
j	Current density
j_0	Exchange current density
$E_{1/2}$	Half potential
I_d	Diffusion current
n	Number of electron involve in redox reaction
D	Diffusion coefficient
I_p	Peak current
\bar{I}	Average current
\bar{I}_d	Average diffusion current
v	Scan rate
t	Time
A	Geometrical surface area of electrode
D_O	Diffusion coefficient of oxidized species
D_R	Diffusion coefficient of reduced species
NHE	Normal hydrogen electrode