CHEM 842: ADVANCED ELECTROANALYTICAL METHODS

Instruction: Answer ALL the questions

Useful data are provided

General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.997 925 58*	10^8	$m\,s^{-1}$
Elementary charge	e	1.602 176	10^{-19}	C
Faraday's constant	$F = N_A e$	9.648 53	10^4	$C\,mol^{-1}$
Boltzmann's constant	k	1.380 65	10^{-23}	$J\,K^{-1}$
Gas constant	$R = N_A k$	8.314 47		$J\,K^{-1}\,mol^{-1}$
		8.314 47	10^{-2}	$dm^3\,bar\,K^{-1}\,mol^{-1}$
		8.205 74	10^{-2}	$dm^3\,atm\,K^{-1}\,mol^{-1}$
		6.236 37	10	$dm^3\,Torr\,K^{-1}\,mol^{-1}$
Planck's constant	h	6.626 08	10^{-34}	J s
	$\hbar = h/2\pi$	1.054 57	10^{-34}	J s
Avogadro's constant	N_A	6.022 14	10^{23}	mol^{-1}
Atomic mass constant	m_u	1.660 54	10^{-27}	kg
Mass				
electron	m_e	9.109 38	10^{-31}	kg
proton	m_p	1.672 62	10^{-27}	kg
neutron	m_n	1.674 93	10^{-27}	kg
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	8.854 19	10^{-12}	$J^{-1}\,C^2\,m^{-1}$
	$4\pi\varepsilon_0$	1.112 65	10^{-10}	$J^{-1}\,C^2\,m^{-1}$
Vacuum permeability	μ_0	4π	10^{-7}	$J\,s^2\,C^{-2}\,m^{-1}\,(=T^2\,J^{-1}\,m^3)$
Magneton				
Bohr	$\mu_B = e\hbar/2m_e$	9.274 01	10^{-24}	$J\,T^{-1}$
nuclear	$\mu_N = e\hbar/2m_p$	5.050 78	10^{-27}	$J\,T^{-1}$
g value	g_e	2.002 32		
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	5.291 77	10^{-11}	m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 35	10^{-3}	
	α^{-1}	1.370 36	10^2	
Second radiation constant	$c_2 = hc/k$	1.438 78	10^{-2}	m K
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3 c^2$	5.670 51	10^{-8}	$W\,m^{-2}\,K^{-4}$
Rydberg constant	$R = m_e e^4/8h^3 c\varepsilon_0^2$	1.097 37	10^5	cm^{-1}
Standard acceleration of free fall	g	9.806 65*		$m\,s^{-2}$
Gravitational constant	G	6.673	10^{-11}	$N\,m^2\,kg^{-2}$

*Exact value

QUESTION ONE (20 MARKS)

(a)

Ceresa, Pretsch, and Bakker[41] investigated three ISEs for determining calcium concentrations. All three electrodes used the same membrane, but differed in the composition of the inner solution. Electrode 1 was a conventional ISE with an inner solution of 1.00×10^{-3} M $CaCl_2$ and 0.10 M NaCl. Electrode 2 (low activity of Ca^{2+}) had an inner solution containing the same analytical concentration of $CaCl_2$, but with 5.0×10^{-2} M EDTA adjusted to a pH of 9.0 with 6.0×10^{-2} M NaOH. Electrode 3 (high Ca^{2+} activity) had an inner solution of 1.00 M $Ca(NO_3)_2$.

(a) Determine the Ca^{2+} concentration in the inner solution of Electrode 2.

(b) Determine the ionic strength of the solution in Electrode 2.

(c) Use the Debye-Hückel equation and determine the activity of Ca^{2+} in Electrode 2. Use 0.6 nm for the α_X value for Ca^{2+} (see Appendix 2).

(d) Electrode 1 was used in a cell with a calomel reference electrode to measure standard calcium solutions with activities ranging from 0.001 M to 1.00×10^{-9} M. The following data were obtained.

Activity of Ca^{2+}, M	Cell Potential, mV
1.0×10^{-3}	93
1.0×10^{-4}	73
1.0×10^{-5}	37
1.0×10^{-6}	2
1.0×10^{-7}	-23
1.0×10^{-8}	-51
1.0×10^{-9}	-55

Plot the cell potential versus the pCa and determine the pCa value where the plot deviates more than 5% from linearity (the limit of linearity; see Section 1E-2). For the linear portion, determine the slope and intercept of the plot. Does the plot obey Equation 23-29 as expected?

(e) For Electrode 2, the following results were obtained.

Activity of Ca^{2+}, M	Cell Potential, mV
1.0×10^{-3}	228
1.0×10^{-4}	190
1.0×10^{-5}	165
1.0×10^{-6}	139
5.6×10^{-7}	105
3.2×10^{-7}	63
1.8×10^{-7}	36
1.0×10^{-7}	23
1.0×10^{-8}	18
1.0×10^{-9}	17

Again plot cell potential versus pCa and determine the range of linearity for Electrode 2. Determine the slope and intercept for the linear portion. Does this electrode obey Equation 21-24 for the higher Ca^{2+} activities?

(f) Electrode 2 is said to be super-nernstian for concentrations from 10^{-7} M to 10^{-6} M. Why is this term used? If you have access to a library that subscribes to *Analytical Chemistry* or has web access to the journal, read the article. This electrode is said to have Ca^{2+} uptake. What does this mean and how might it explain the response?

(g) Electrode 3 gave the following results.

Activity of Ca^{2+}, M	Cell Potential, mV
1.0×10^{-3}	175
1.0×10^{-4}	150
1.0×10^{-5}	123
1.0×10^{-6}	88
1.0×10^{-7}	75
1.0×10^{-8}	72
1.0×10^{-9}	71

Plot the cell potential versus pCa and determine the range of linearity. Again determine the slope and intercept. Does this electrode obey Equation 23-29?

(h) Electrode 3 is said to have Ca^{2+} release. Explain this term from the article and describe how it might explain the response.

(i) Does the article give any alternative explanations for the experimental results? If so, describe these alternatives.
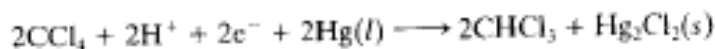
(10 marks)

(b)

Calculate the time required for a constant current of 0.905 A to deposit 0.300 g of (a) Tl(III) as the element on a cathode, (b) Tl(I) as the Tl_2O_3 on an anode, and (c) Tl(I) as the element on a cathode.

(2 marks)
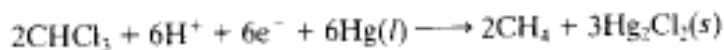
(b)

At a potential of -1.0 V (versus SCE), carbon tetrachloride in methanol is reduced to chloroform at a Hg cathode:

$$2CCl_4 + 2H^+ + 2e^- + 2Hg(l) \longrightarrow 2CHCl_3 + Hg_2Cl_2(s)$$

At -1.80 V, the chloroform further reacts to give methane:

$$2CHCl_3 + 6H^+ + 6e^- + 6Hg(l) \longrightarrow 2CH_4 + 3Hg_2Cl_2(s)$$

Several 0.750-g samples containing CCl_4, $CHCl_3$, and inert organic species were dissolved in methanol and electrolyzed at -1.0 V until the current approached zero. A coulometer indicated the charge required to complete the reaction, as given in the second column of the following table. The potential of the cathode was then adjusted to -1.80 V. The additional charge required to complete the reaction at this potential is given in the third column of the table. Calculate the percent CCl_4 and $CHCl_3$ in each mixture.

Sample No.	Charge Required at -1.0 V, C	Charge Required at -1.8 V, C
1	11.63	68.60
2	21.52	85.33
3	6.22	45.98
4	12.92	55.31

(6 marks)

(d)

1. Polarography is considered, so far as the sample is concerned, as a non-destructive method of analysis. Is this true?

2. Why is stirring of the solution avoided in polarography?

3. The method of standard additions is considered as yielding more reliable results than that of standard solutions. Why?

4. Why, for the dropping mercury electrode, does the height of the column of Hg have an influence upon the value of the current of diffusion? Upon what is this effect based?

QUESTION TWO (20 MARKS)

(a)

A sample of 25 mL prepared for an electrolysis experiment has a zinc concentration of approximately 2×10^{-8} M which leads to the passage of a current of 1.5 nA. Calculate the time necessary to deposit 3% of the Zn present.

Show that the technique of stripping is more sensitive.

(2 marks)

(b)

For a fully electrochemically irreversible one-electron system, show how analysis of the voltammetry may yield information about the transition state for the process.

(4 marks)

(c)

For a fully reversible one-electron reduction, what gradient will be obtained for a plot of $\ln|I|$ vs E? Assume that the redox species is confined to a thin layer such that

$$[A]_0 + [B]_0 = [A]_{bulk} \qquad (2.2)$$

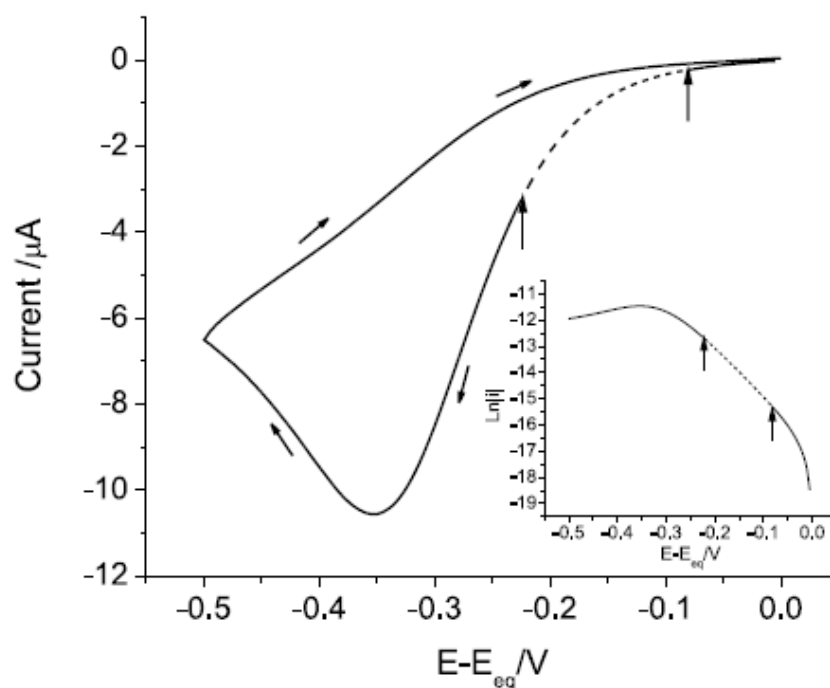and that the diffusive flux may be treated as proportional to the concentration difference $([A]_0 - [A]_{bulk})$.

Fig. 2.3 The cyclic voltammetric response for an irreversible one-electron reduction process, with the region required for Tafel analysis highlighted. The inset shows the Tafel plot for the forward scan highlighted is the required linear region. The voltage scan starts at 0.0 V and sweeps negatively to −0.5 V before returning to 0.0 V (small arrows indicate scan direction).

(4 marks)

(d)

(i) Discuss the necessity of supporting electrolyte for conventional voltammetry, with reference to: a) the double layer; b) electric fields in bulk solution; c) the non-ideality of an electrolytic solution.

(ii) Under what conditions might the addition of excess supporting electrolyte be inappropriate or impossible?

(10 marks)

QUESTION THREE (20 MARKS)

(a)

A potential step experiment was carried out in a solution containing 0.05 M ferrocyanide ($[Fe(CN)_6]^{4-}$) dissolved in a solution containing a large excess of inert electrolyte. Care was taken to ensure that there was no stirring of the solution during the experiment. The potential was stepped from a value where there was no reaction to a potential at which the $[Fe(CN)_6]^{4-}$ was oxidised to $[Fe(CN)_6]^{3-}$ at a mass transport controlled rate, and the following currents were recorded:

t/s	0.1	0.2	0.4	0.8	1.2
I/mA	6.9	4.9	3.4	2.4	2.0

(i) Explain why it is necessary to have a large excess of inert electrolyte present for the experiment.

(ii) Why is it important to make sure that there is no stirring of the solution during the experiment?

(iii) Make a sketch of the concentration of $[Fe(CN)_6]^{4-}$ as a function of distance away from the electrode immediately before the potential step and at two different times after the potential step.

(iv) Given that the area of the electrode was 0.3 cm², calculate the diffusion coefficient for $[Fe(CN)_6]^{4-}$ in the solution.

(v) Why is the time scale of the experiment limited to around a second?

(8 marks)

(b)

Figure 4.2 depicts a cyclic voltammogram for the one-electron irreversible reduction of species A to B, where the electrochemical rate constant (k^0) equals 10^{-6} cm s^{-1} and the transfer coefficient (α) is 0.5. Problem 4.1 discussed the salient features of a reversible cyclic voltammogram; with reference to this, explain the major differences between the two cases. Specifically refer to reasons:

- why the peak-to-peak separation is greater for the irreversible case.
- why the reverse peak current for the irreversible case is substantially less than the forward peak current.
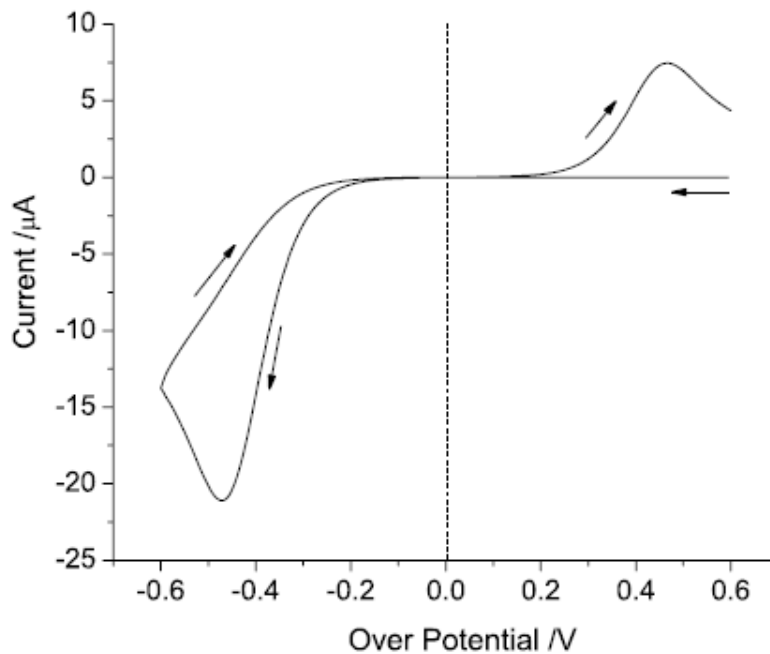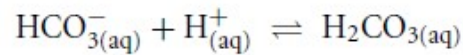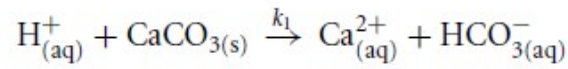

Fig. 4.2 Cyclic voltammogram for the irreversible reduction of A to B. Arrows indicate the scan direction. The current has been plotted against overpotential $\left(E - E^{\ominus}_{\mathrm{f},A/B}\right)$.

(4 marks)

(c)

Small particles of calcite (calcium carbonate, $CaCO_3$) dissolve in acidic solution by means of the following mechanism:

$$H^+_{(aq)} + CaCO_{3(s)} \xrightarrow{k_1} Ca^{2+}_{(aq)} + HCO^-_{3(aq)}$$

$$HCO^-_{3(aq)} + H^+_{(aq)} \rightleftharpoons H_2CO_{3(aq)}$$

$$H_2CO_{3(aq)} \rightarrow H_2O_{(l)} + CO_{2(g)}$$
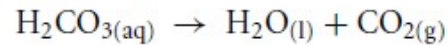
The following rate law has been measured [R.G. Compton *et al.*, *Freshwater Biology* 22 (1989) 285] for the reaction of protons at the calcite surface:

$$J_{Ca^{2+}}/\text{mol cm}^{-2}\,\text{s}^{-1} = k_1[H^+]_0 \qquad (5.3)$$

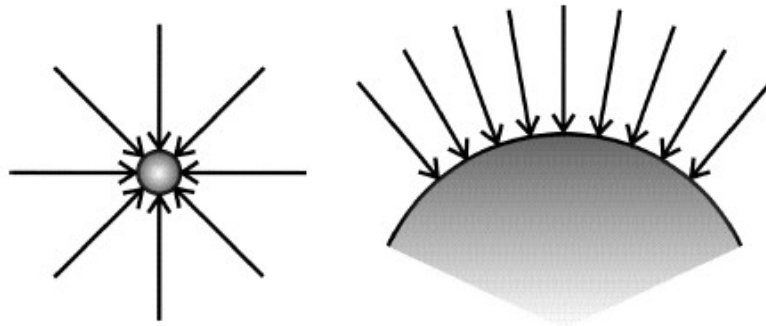where $k_1 = 0.043$ cm s^{-1} at 25°C.

Fig. 5.2 Schematic of convergent and linear types of diffusion towards spherical electrodes of different sizes.

Explain the form of the rate equation and suggest an explanation for the observation that while large ($>100\,\mu$m) particles of calcite dissolve with a rate controlled by the diffusion of protons to the calcite surface, for much smaller particles the surface controlled reaction quantifed by Eq. 5.3 is found to apply. Assume a value of 7.5×10^{-5} cm^2 s^{-1} for the diffusion coefficient of H$^+$ in aqueous solution.

(4 marks)

(d)

Through the use of *highly ordered pyrolytic graphite* (HOPG) it is possible to produce an electrode which is predominantly 'basal' in character, but even with such a surface, edge plane defects will be present in the form of 'steps' (as indicated in Fig. 6.1). Careful preparation can lead to a surface where these edge plane defects are up to 1–10 μM apart.

(i) From your knowledge of the electrochemistry of carbon surfaces, explain how these edge plane steps can dominate the observed voltammetry.

(ii) Suggest why, when modelling such systems, the use of a one-dimensional diffusion model is inappropriate.

(3 marks)

PERIODIC TABLE OF THE ELEMENTS

Metals
Nonmetals
Metalloids

IA 1																		0 18
1 **H** 1.008	IIA 2											IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17		2 **He** 4.0026
3 **Li** 6.941	4 **Be** 9.0122											5 **B** 10.81	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.9984		10 **Ne** 20.1797
11 **Na** 22.9898	12 **Mg** 24.3050	IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	8	VIIIB 9	10	IB 11	IIB 12	13 **Al** 26.9815	14 **Si** 28.085	15 **P** 30.9738	16 **S** 32.06	17 **Cl** 35.453		18 **Ar** 39.948
19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.9559	22 **Ti** 47.867	23 **V** 50.9415	24 **Cr** 51.9961	25 **Mn** 54.9380	26 **Fe** 55.845	27 **Co** 58.9332	28 **Ni** 58.6934	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.723	32 **Ge** 72.63	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.904		36 **Kr** 83.798
37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.9058	40 **Zr** 91.224	41 **Nb** 92.9064	42 **Mo** 95.96	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.9055	46 **Pd** 106.42	47 **Ag** 107.8682	48 **Cd** 112.411	49 **In** 114.818	50 **Sn** 118.710	51 **Sb** 121.760	52 **Te** 127.60	53 **I** 126.9045		54 **Xe** 131.293
55 **Cs** 132.9055	56 **Ba** 137.327	57 **La*** 138.9055	72 **Hf** 178.49	73 **Ta** 180.9479	74 **W** 183.84	75 **Re** 186.207	76 **Os** 190.23	77 **Ir** 192.217	78 **Pt** 195.084	79 **Au** 196.9666	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.9804	84 **Po** (209)	85 **At** (210)		86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **Ac**** (227)	104 **Rf** (265)	105 **Db** (268)	106 **Sg** (271)	107 **Bh** (270)	108 **Hs** (277)	109 **Mt** (276)	110 **Ds** (281)	111 **Rg** (280)	112 **Cn** (285)	113 **Uut** (284)	114 **Fl** (289)	115 **Uup** (288)	116 **Lv** (293)	117 **Uus** (294)		118 **Uuo** (294)

*Lanthanide Series

58 **Ce** 140.116	59 **Pr** 140.9076	60 **Nd** 144.242	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.964	64 **Gd** 157.25	65 **Tb** 158.9254	66 **Dy** 162.500	67 **Ho** 164.9303	68 **Er** 167.259	69 **Tm** 168.9342	70 **Yb** 173.054	71 **Lu** 174.9668

** Actinide Series

90 **Th** 232.0381	91 **Pa** 231.0359	92 **U** 238.0289	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

Note: Atomic masses are 2009 IUPAC values (up to four decimal places). More accurate values for some elements are given in the table inside the back cover.