NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF APPLIED CHEMISTRY
END OF FIRST SEMESTER EXAMINATIONS – DECEMBER 2004
ANALYTICAL CHEMISTRY II – SCH 2106
TIME: 3 HOURS

INSTRUCTIONS TO CANDIDATES

Answer **All** questions from Section A and **Any Three** from Section B.
Section A carries 40 marks and Section B carries 60 marks.
Total Marks - 100

SECTION A

1. Draw a clearly labelled diagram of a gas-sensing probe for the determination of carbon dioxide. Explain how it operates. [10 marks]

2. (a) A 2.00 mL urine specimen was treated with a reagent to generate a colored adduct with phosphate, and the sample was then diluted to 100 mL. Exactly 5.00 mL of a phosphate solution containing 0.0300 mg phosphate/mL were added to the second 2.00 mL sample, which was treated in the same way as the original sample. The absorbance of the first solution was 0.428; that of the second was 0.538. Calculate the milligrams of phosphate per millimeter of the specimen. [6 marks]

   (b) Calculate the thermodynamic potential of the following cell and indicate whether it is galvanic or electrolytic.

   $Pt|UO_2^{2+}(0.0150\ M), U^{4+}(0.200\ M), H^{+}(0.0300\ M||Fe^{2+}(0.0100\ M), Fe^{3+}(0.0250\ M)|Pt$ [6 marks]

3. Draw a typical polarographic wave and show clearly all the points on the curve, which give information of significance in either qualitative or quantitative work. Explain [8 marks]

4. (a) The quantum efficiency, Φ, of fluorene is approximately 1.0 while that of biphenyl is about 0.2. With the aid of the structural formulae of these compounds explain this statement. [6 marks]

   (b) Define: (i) releasing agent

   (ii) Doppler broadening [4 marks]

SECTION B

5. (a) Calculate E^0 for the process:

$$AgIO_3(s) + e^- \Leftrightarrow Ag(s) + IO_3^-$$

For $AgIO_3$, $Ksp = 3.1 \times 10^{-8}$ [5 marks]

(b) Use the shorthand notation to describe a cell consisting of a saturated calomel electrode as an anode and a silver cathode that could be used to measure pIO_3 [2 marks]

(c) Derive an equation that relates the potential of the cell in (b) to pIO_3. [4 marks]

(d) Calculate pIO_3 if the cell in (b) has a potential of 0.294. [3 marks]

(e) Calculate the formation constant K_f for $Ag(CN)_2^-$ if the cell develop a potential of –0.625 V. $[Ag(CN)_2^-] = 7.50 \times 10^{-3}$ M and $[CN^-] = 0.0250$ M [6 marks]

6. (a) Nickel and iron are examples of nonabsorbing species, which require chemical treatment prior to UV/VIS determination. Explain how you would determine the concentrations of such analytes in a sample using UV/VIS spectrometry, taking into account the reagents required and the reactions involved to convert the analytes to absorbers. [8 marks]

(b) Write short notes on the following:

(i) Concentration polarization

(ii) Kinetic polarisation

(iii) Charge transfer absorption [12 marks]

7. (a) Give a detailed account of chemical interferences encountered in atomic absorption spectroscopy. Give examples where possible. [12 marks]

(b) Draw a diagram of a ISFET for measuring pH. Explain how this device responds to changes in the hydronium ion concentration. [8 marks]

8. (a) A 40 mL aliquot of 0.0500 M HNO_2 is diluted to 75.0 mL and titrated with 0.0800 M Ce^{4+}. Assume that the hydrogen concentration is at 1.00 M throughout the titration. (Use 1.44 V for the formal potential of the cerium system.)

(i) Calculate the potential of the indicator electrode with respect to a saturated calomel reference electrode after the addition of 10.0, 25.00, 40.00, 49.00, 49.9, 50.1, 51.00, 55.00, and 60.00 mL of cerium(IV).

(ii) Plot the titration curve for these data

[20 marks]

End of question Paper!!!

Appendix

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Some Standard and Formal Electrode Potentials

Half-Reaction	E^0, V[a]	Formal Potential, V[b]
Aluminum		
$Al^{3+} + 3e^- \rightleftharpoons Al(s)$	−1.662	
Antimony		
$Sb_2O_5(s) + 6H^+ + 4e^- \rightleftharpoons 2SbO^+ + 3H_2O$	+0.581	
Arsenic		
$H_3AsO_4 + 2H^+ + 2e^- \rightleftharpoons H_3AsO_3 + H_2O$	+0.559	0.577 in 1 M HCl, $HClO_4$
Barium		
$Ba^{2+} + 2e^- \rightleftharpoons Ba(s)$	−2.906	
Bismuth		
$BiO^+ + 2H^+ + 3e^- \rightleftharpoons Bi(s) + H_2O$	+0.320	
$BiCl_4^- + 3e^- \rightleftharpoons Bi(s) + 4Cl^-$	+0.16	
Bromine		
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1.065	1.05 in 4 M HCl
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.087[c]	
$BrO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}Br_2(l) + 3H_2O$	+1.52	
$BrO_3^- + 6H^+ + 6e^- \rightleftharpoons Br^- + 3H_2O$	+1.44	
Cadmium		
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	−0.403	
Calcium		
$Ca^{2+} + 2e^- \rightleftharpoons Ca(s)$	−2.866	

Half-Reaction	E^0, V[a]	Formal Potential, V[b]
Lead		
$Pb^{2+} + 2e^- \rightleftharpoons Pb(s)$	−0.126	−0.14 in 1 M $HClO_4$; −0.29 in 1 M H_2SO_4
$PbO_2(s) + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$	+1.455	
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	−0.350	
Lithium		
$Li^+ + e^- \rightleftharpoons Li(s)$	−3.045	
Magnesium		
$Mg^{2+} + 2e^- \rightleftharpoons Mg(s)$	−2.363	
Manganese		
$Mn^{2+} + 2e^- \rightleftharpoons Mn(s)$	−1.180	
$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$		1.51 in 7.5 M H_2SO_4
$MnO_2(s) + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	+1.23	
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.51	
$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2(s) + 2H_2O$	+1.695	
$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$	+0.564	
Mercury		
$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(l)$	+0.788	0.274 in 1 M HCl; 0.776 in 1 M $HClO_4$; 0.674 in 1 M H_2SO_4
$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$	+0.920	0.907 in 1 M $HClO_4$
$Hg^{2+} + 2e^- \rightleftharpoons Hg(l)$	+0.854	
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	+0.268	0.244 in sat'd KCl; 0.282 in 1 M KCl; 0.334 in 0.1 M KCl
$Hg_2SO_4(s) + 2e^- \rightleftharpoons 2Hg(l) + SO_4^{2-}$	+0.615	
Nickel		
$Ni^{2+} + 2e^- \rightleftharpoons Ni(s)$	−0.250	
Nitrogen		
$N_2(g) + 5H^+ + 4e^- \rightleftharpoons N_2H_5^+$	−0.23	
$HNO_2 + H^+ + e^- \rightleftharpoons NO(g) + H_2O$	+1.00	
$NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O$	+0.94	0.92 in 1 M HNO_3
Oxygen		
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.776	
$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^-$	+0.88	
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229	
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.682	
$O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O$	+2.07	
Palladium		
$Pd^{2+} + 2e^- \rightleftharpoons Pd(s)$	+0.987	
Platinum		
$PtCl_4^{2-} + 2e^- \rightleftharpoons Pt(s) + 4Cl^-$	+0.73	
$PtCl_6^{2-} + 2e^- \rightleftharpoons PtCl_4^{2-} + 2Cl^-$	+0.68	
Potassium		
$K^+ + e^- \rightleftharpoons K(s)$	−2.925	