NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF APPLIED CHEMISTRY
BACHELOR OF SCIENCE HONOURS DEGREE
END OF FIRST SEMESTER EXAMINATIONS – DECEMBER 2005
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. (a) Briefly describe the electrode of the first kind and derive the equation that relates the potential of the indicator electrode to the p-function. [4 marks]
   (b) Differentiate between concentration polarisation and kinetic polarisation. [4 marks]
   (c) Distinguish between diffusion current and faradaic current. [4 marks]

2. A simultaneous determination for cobalt and nickel can be based upon absorption by their their respective 8-hydroxyquiolinol complexes. Molar absorptivities corresponding to their absorption maxima are as follows:

	Molar Absorptivity, ε	
	365 nm	**700 nm**
Co	3529	428.9
Ni	3228	10.2

Calculate the molar concentrations of nickel and cobalt in each of the following solutions based upon the accompanying data:

Solution	**Absorbance, A (1.00-cm cells)**	
	365 nm	**700 nm**
(a)	0.598	0.039
(b)	0.902	0.072

[8 marks]

3. (i) List the errors that affect pH measurement with the glass electrode. [6 marks]

   (ii) Give a brief description of a phototube and a photomultiplier tube. Explain why the photomultiplier tube is more sensitive than the phototube detector. [5 marks]

   (iii) Draw a clearly labelled diagram of a Czerney-Turner grating monochromator. [4 marks]

In a hydrogen/oxygen flame, an atomic absorption peak for iron decreases in the presence of large concentrations of sulfate ion.

(a) Suggest an explanation for this observation [2 marks]

(b) Suggest three possible methods for overcoming the potential interference of sulfate in a quantitative determination of iron. [3 marks]

SECTION B

5. (a) With the aid of clearly labelled diagrams and appropriate equations, describe different types of ion-selective electrodes in terms of:

    (i) the construction of the electrodes [4 marks]

    (ii) differences in the response mechanisms [4 marks]

    (iii)applications [4 marks]

   (b) How does the gas-sensing probe differ from other membranes. Use the example of a CO_2 probe to support your answer. [4 marks]

   (c) Draw a diagram of a hollow cathode lamp. [4 marks]

6. (i) Calculate the standard potential for the reaction;

$$CuBr(s) + e^- \rightarrow Cu(s) + Br$$

For CuBr, $K_{sp} = 5.2 \times 10^{-9}$ [4 marks]

   (ii) Give a schematic representation of a cell with a copper indicator electrode as an anode and a saturated calomel electrode as a cathode that could be used for the determination of Br. [2 marks]

   (iii) Derive an equation that relates the measured potential of the cell in (ii) to pBr (assume that the junction potential is zero). [4 marks]

   (iv) Calculate the pBr of a bromide containing solution that is saturated with CuBr and contained in the cell described in (ii) if the resulting potential is -0.071V. [3 marks]

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

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

[7 marks]

7. (a) With the aid of a clearly labelled diagram describe in details the relaxation pathways that could be followed by an excited molecule when returning to its ground state, as a way of losing excess energy. [10 marks]

(b) Distinguish between Doppler broadening and pressure broadening. [4 marks]

(c) The quantum efficiency 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 the statement. [6 marks]

8. The chromium in an aqueous sample was determined by pipetting 10.00 mL of the unknown into each of five 50.00 mL volumetric flasks. Various volumes of a standard containing 12.2 ppm Cr were added to the flasks, and the solutions were diluted to volume.

Unknown, mL	Standard, mL	Absorbance
10.0	0.0	0.201
10.0	10.0	0.292
10.0	20.0	0.378
10.0	30.0	0.467
10.0	40.0	0.554

(i) Plot the absorbance as a function of volume of standard V_s. [3 marks]

(ii) Derive the expression relating absorbance to the concentrations of standard and unknown (c_s and c_x) and the volumes of the standard and unknown (V_s and V_x) as well as the volume to which the solutions were diluted. [3 marks]

(iii) Derive expressions for the slope and the intercept of the straight line obtained in (a) in terms of variables listed in (b). [3 marks]

(iv) Show that the concentration of the analyte is given by the relationship $c_x = bc_s/mV_x$, where m and b are the slope and the intercept of the straight line in (a). [3 marks]

(v) Determine values for m and b by the method of least squares. [3 marks]

(vi) Calculate the standard deviation for the slope and the intercept in (e). [2 marks]

(vii) Calculate the ppm Cr in the sample. [3 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]
Carbon		
$C_6H_4O_2$ (quinone) + $2H^+ + 2e^- \rightleftharpoons C_6H_4(OH)_2$	+0.699	0.696 in 1 M HCl, $HClO_4$, H_2SO_4
$2CO_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2C_2O_4$	−0.49	
Cerium		
$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$		+1.70 in 1 M $HClO_4$; +1.61 in 1 M HNO_3; +1.44 in 1 M H_2SO_4
Chlorine		
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.359	
$HClO + H^+ + e^- \rightleftharpoons \frac{1}{2}Cl_2(g) + H_2O$	+1.63	
$ClO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}Cl_2(g) + 3H_2O$	+1.47	
Chromium		
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	−0.408	
$Cr^{3+} + 3e^- \rightleftharpoons Cr(s)$	−0.744	
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33	
Cobalt		
$Co^{2+} + 2e^- \rightleftharpoons Co(s)$	−0.277	
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1.808	
Copper		
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+0.337	
$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0.153	
$Cu^+ + e^- \rightleftharpoons Cu(s)$	+0.521	
$Cu^{2+} + I^- + e^- \rightleftharpoons CuI(s)$	+0.86	
$CuI(s) + e^- \rightleftharpoons Cu(s) + I^-$	−0.185	
Fluorine		
$F_2(g) + 2H^+ + 2e^- \rightleftharpoons 2HF(aq)$	+3.06	
Hydrogen		
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.000	−0.005 in 1 M HCl, $HClO_4$
Iodine		
$I_2(s) + 2e^- \rightleftharpoons 2I^-$	+0.5355	
$I_2(aq) + 2e^- \rightleftharpoons 2I^-$	+0.615[c]	
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+0.536	
$ICl_2^- + e^- \rightleftharpoons \frac{1}{2}I_2(s) + 2Cl^-$	+1.056	
$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2(s) + 3H_2O$	+1.196	
$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2(aq) + 3H_2O$	+1.178[c]	
$IO_3^- + 2Cl^- + 6H^+ + 4e^- \rightleftharpoons ICl_2^- + 3H_2O$	+1.24	
$H_5IO_6 + H^+ + 2e^- \rightleftharpoons IO_3^- + 3H_2O$	+1.601	
Iron		
$Fe^{2+} + 2e^- \rightleftharpoons Fe(s)$	−0.440	
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771	0.700 in 1 M HCl; 0.732 in 1 M $HClO_4$; 0.68 in 1 M H_2SO_4
$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$	+0.36	0.71 in 1 M HCl; 0.72 in 1 M $HClO_4$, H_2SO_4

[redacted]

lf-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	

Half-Reaction	E^0, V[a]	Formal Potential, V[b]
Selenium		
$H_2SeO_3 + 4H^+ + 4e^- \rightleftharpoons Se(s) + 3H_2O$	+0.740	
$SeO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons H_2SeO_3 + H_2O$	+1.15	
Silver		
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.799	0.228 in 1 M HCl; 0.792 in 1 M $HClO_4$; 0.77 in 1 M H_2SO_4
$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-$	+0.073	
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+0.222	0.228 in 1 M KCl[c]
$Ag(CN)_2^- + e^- \rightleftharpoons Ag(s) + 2CN^-$	−0.31	
$Ag_2CrO_4(s) + 2e^- \rightleftharpoons 2Ag(s) + CrO_4^{2-}$	+0.446	
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	−0.151	
$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$	+0.017	
Sodium		
$Na^+ + e^- \rightleftharpoons Na(s)$	−2.714	
Sulfur		
$S(s) + 2H^+ + 2e^- \rightleftharpoons H_2S(g)$	+0.141	
$H_2SO_3 + 4H^+ + 4e^- \rightleftharpoons S(s) + 3H_2O$	+0.450	
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons H_2SO_3 + H_2O$	+0.172	
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	+0.08	
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01	
Thallium		
$Tl^+ + e^- \rightleftharpoons Tl(s)$	−0.336	−0.551 in 1 M HCl; −0.33 in 1 M $HClO_4$, H_2SO_4
$Tl^{3+} + 2e^- \rightleftharpoons Tl^+$	+1.25	0.77 in 1 M HCl
Tin		
$Sn^{2+} + 2e^- \rightleftharpoons Sn(s)$	−0.136	−0.16 in 1 M $HClO_4$
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0.154	0.14 in 1 M HCl
Titanium		
$Ti^{3+} + e^- \rightleftharpoons Ti^{2+}$	−0.369	
$TiO^{2+} + 2H^+ + e^- \rightleftharpoons Ti^{3+} + H_2O$	+0.099	0.04 in 1 M H_2SO_4
Uranium		
$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$	+0.334	
Vanadium		
$V^{3+} + e^- \rightleftharpoons V^{2+}$	−0.256	0.21 in 1 M $HClO_4$
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.359	
$V(OH)_4^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + 3H_2O$	+1.00	1.02 in 1 M HCl, $HClO_4$
Zinc		
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	−0.763	

[a] G. Milazzo, S. Caroli, and V. K. Sharma, *Tables of Standard Electrode Potentials*. London: Wiley, 1978.

[b] E. H. Swift and E. A. Butler, *Quantitative Measurements and Chemical Equilibria*. New York: Freeman, 1972.

[c] These potentials are hypothetical because they correspond to solutions that are 1.00 M in Br_2 or I_2. The solubilities of these two compounds at 25°C are 0.18 M and 0.0020 M, respectively. In saturated solutions containing an excess of $Br_2(l)$ or $I_2(s)$, the standard potentials for the half-reaction $Br_2(l) + 2e^- \rightleftharpoons 2Br^-$ or $I_2(s) + 2e^- \rightleftharpoons 2I^-$ should be used. In contrast, at Br_2 and I_2 concentrations less than saturation, these hypothetical electrode potentials should be employed.