



NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

FACULTY OF APPLIED SCIENCES

DEPARTMENT OF APPLIED CHEMISTRY

ELECTROCHEMICAL METHODS

SCH 5114

FIRST SEMESTER EXAMINATION QUESTION PAPER

2024

This examination paper consists of 3 pages

Time Allowed:	3 hours
Total Marks:	100
Special Requirements:	Periodic Table
Internal Examiner:	Dr. A. Maringa
External Examiner:	Prof. G. Mehlana

INSTRUCTIONS

1. Answer all questions from Section A and **ANY THREE** questions from Section B.
2. Section A carries **40 marks** and each question in Section B carries **20 marks**.
3. Use of calculators is permissible

Mark Allocation

Questions	Marks
1	40
2	20
3	20
4	20
5	20
Total Possible Marks	100

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SECTION A

1. (a) Define
- (i) Voltammograms [2 marks]
 - (ii) Hydrodynamic voltammetry [2 marks]
 - (iii) Nernst equation [2 marks]
 - (iv) Formal potential. [2 marks]
 - (v) liquid-junction potential. [2 marks]
- (b) State the 5 uses of a supporting electrolyte. [5 marks]
- (c) List factors that are considered when choosing electrode materials. [5 marks]
- (d) Calculate the potential of a copper electrode immersed in
- (i) 0.0380 M $\text{Cu}(\text{NO}_3)_2$. [5 marks]
 - (ii) 0.0650 M in NaCl and saturated with CuCl. [5 marks]
- (e) The Nernst equation is often used to predict how a system will respond when the concentrations of redox species in solution change or when the electrode potential is changed. Given the Nernst equation in the following form,

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_r}{a_o}$$

Explain what the symbols mean and how the equation relates to the concentrations of redox species. [10 marks]

SECTION B

2. An electrochemical cell consists of zinc and copper electrodes, each dipped in separate beakers of electrolyte solutions zinc sulphate and copper(II) sulphate respectively. A voltmeter is placed between the two electrodes and connected to them via conducting wires, and a NaCl(aq) salt bridge straddles across the two half-cell beakers. Given that the standard reduction potentials for the Zn^{2+}/Zn and Cu^{2+}/Cu redox couples are - 0.76 V and + 0.34 V respectively,
- (a) Show that the overall cell potential measured by the voltmeter is 1.1 V. [5 marks]
- (b) Using an appropriate diagram, illustrate the electrochemical cell described above and indicate the direction of electron flow. Explain the roles of the voltmeter and salt bridge in this cell. [15 marks]
3. (a) Explain what voltammetry is and describe key features of this experimental technique. [10 marks]
- (b) Using the example of an applied step potential, explain why a current is produced at the cathode and describe the changes in current response with time. [10 marks]
4. Discuss the advantages that hydrodynamic voltammetry offers compared to voltammetry done using stagnant electrolyte solutions. [20 marks]
5. (a) The interfacial electrochemical techniques are divided into static techniques and dynamic techniques. Describe each technique, giving examples. [10 marks]
- (b) List the advantages and disadvantages of the dropping mercury electrode compared with platinum or carbon microelectrodes. [10 marks]

END OF QUESTION PAPER

Standard and Formal Electrode Potentials

Half-Reaction	E°, V^*	Formal Potential, V^\dagger
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 [†]	
$BrO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}Br_2(l) + 3H_2O$	+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	
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 ₂ SO 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 ₂ SO 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	

Standard and Formal Electrode Potentials

Half-Reaction	E°, V^*	Formal Potential, V^\dagger
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 [†]	
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+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 [†]	
$IO_3^- + 2Cl^- + 6H^+ + 4e^- \rightleftharpoons ICl_2^- + 3H_2O$	+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 ₂ SO 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 ₂ SO ₄
Lead		
$Pb^{2+} + 2e^- \rightleftharpoons Pb(s)$	-0.126	
$PbO_2(s) + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$	+1.455	-0.14 in 1 M HClO ₄ ; -0.29 in 1 M H ₂ SO ₄
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	-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 ₂ SO 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 ₂ SO 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	

Standard and Formal Electrode Potentials

Half-Reaction	E°, V^*	Formal Potential, V^\dagger
Platinum		
$\text{PtCl}_4^{2-} + 2e^- \rightleftharpoons \text{Pt}(s) + 4\text{Cl}^-$	+0.755	
$\text{PtCl}_6^{2-} + 2e^- \rightleftharpoons \text{PtCl}_4^{2-} + 2\text{Cl}^-$	+0.68	
Potassium		
$\text{K}^+ + e^- \rightleftharpoons \text{K}(s)$	-2.925	
Selenium		
$\text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4e^- \rightleftharpoons \text{Se}(s) + 3\text{H}_2\text{O}$	+0.740	
$\text{SeO}_4^{2-} + 4\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2\text{SeO}_3 + \text{H}_2\text{O}$	+1.15	
Silver		
$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}(s)$	+0.799	0.228 in 1 M HCl; 0.792 in 1 M HClO ₄ ; 0.77 in 1 M H ₂ SO ₄
$\text{AgBr}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{Br}^-$	+0.073	
$\text{AgCl}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{Cl}^-$	+0.222	0.228 in 1 M KCl
$\text{Ag}(\text{CN})_2^- + e^- \rightleftharpoons \text{Ag}(s) + 2\text{CN}^-$	-0.31	
$\text{Ag}_2\text{CrO}_4(s) + 2e^- \rightleftharpoons 2\text{Ag}(s) + \text{CrO}_4^{2-}$	+0.446	
$\text{AgI}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{I}^-$	-0.151	
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} + e^- \rightleftharpoons \text{Ag}(s) + 2\text{S}_2\text{O}_3^{2-}$	+0.017	
Sodium		
$\text{Na}^+ + e^- \rightleftharpoons \text{Na}(s)$	-2.714	
Sulfur		
$\text{S}(s) + 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2\text{S}(g)$	+0.141	
$\text{H}_2\text{SO}_3 + 4\text{H}^+ + 4e^- \rightleftharpoons \text{S}(s) + 3\text{H}_2\text{O}$	+0.450	
$\text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	+0.172	
$\text{S}_4\text{O}_6^{2-} + 2e^- \rightleftharpoons 2\text{S}_2\text{O}_3^{2-}$	+0.08	
$\text{S}_2\text{O}_8^{2-} + 2e^- \rightleftharpoons 2\text{SO}_4^{2-}$	+2.01	
Thallium		
$\text{Tl}^+ + e^- \rightleftharpoons \text{Tl}(s)$	-0.336	-0.551 in 1 M HCl; -0.33 in 1 M HClO ₄ , H ₂ SO ₄
$\text{Tl}^{3+} + 2e^- \rightleftharpoons \text{Tl}^+$	+1.25	0.77 in 1 M HCl
Tin		
$\text{Sn}^{2+} + 2e^- \rightleftharpoons \text{Sn}(s)$	-0.136	-0.16 in 1 M HClO ₄
$\text{Sn}^{4+} + 2e^- \rightleftharpoons \text{Sn}^{2+}$	+0.154	0.14 in 1 M HCl
Titanium		
$\text{Ti}^{3+} + e^- \rightleftharpoons \text{Ti}^{2+}$	-0.369	
$\text{TiO}^{2+} + 2\text{H}^+ + e^- \rightleftharpoons \text{Ti}^{3+} + \text{H}_2\text{O}$	+0.099	0.04 in 1 M H ₂ SO ₄
Uranium		
$\text{UO}_2^{2+} + 4\text{H}^+ + 2e^- \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O}$	+0.334	
Vanadium		
$\text{V}^{3+} + e^- \rightleftharpoons \text{V}^{2+}$	-0.255	
$\text{VO}^{2+} + 2\text{H}^+ + e^- \rightleftharpoons \text{V}^{3+} + \text{H}_2\text{O}$	+0.337	
$\text{V}(\text{OH})_4^+ + 2\text{H}^+ + e^- \rightleftharpoons \text{VO}^{2+} + 3\text{H}_2\text{O}$	+1.00	1.02 in 1 M HCl, HClO ₄
Zinc		
$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}(s)$	-0.763	