UNIVERSITY OF ESWATINI

Final Examination– 2020/2021

TITLE OF PAPER: Electroanalytical Chemistry

COURSE NUMBER: CHE614

TIME ALLOWED: Three Hours

INSTRUCTIONS:

Answer any four (4) questions of the six (6) questions and every question holds 25 marks.

NB: All questions are to be answered in a separate answer sheet.

This Examination Paper Contains **SIX** Printed Pages Including This Page

You are not supposed to open the paper until permission to do so has been granted by the Chief Invigilator.

Question 1 [25]

a) What are the oxidation state of vanadium in the ions respectively? (6)
   i. VO_4^{3-}
   ii. VO^{2+}

b) Which type of a metal can be used in cathodic protection of iron against rusting? (4)

c) The following chemical reaction is occurring in an electrochemical cell.

$$Mg(s) + 2Ag^{+}(0.0001\ M) \longrightarrow Mg^{2+}(0.10\ M) + 2Ag(s)$$

The E° electrode values are:

$Mg^{2+}/Mg = -2.36\ V$

$Ag^{+}/Ag = 0.81\ V$

For this cell calculate/write

   i. Standard cell potential E^{o}_{cell} (4)
   ii. Cell potential $(E)_{cell}$ (5)
   iii. The symbolic representation/notation of the above cell. (4)
   iv. Is the above cell reaction be spontaneous? (2)

Question 2 [25]

a) Explain using examples why electrochemistry is well suited for chemical and biochemical sensing applications. What types of sensors have been developed? What are their advantages and special features? [10]

b) Briefly discuss the working principles of differential pulse polarography. Account for its enhanced sensitivity over the conventional (d.c) polarography. [10]

c) Compare and contrast the working principles of a constant voltage electrolysis and controlled potential (constant cathode/anode potential) electrolysis. Which of the two is more selective? [5]

Question 3 [25]

a) Briefly discuss the following electrochemical techniques and give examples of their uses:

i. Electrogravimetry [5]

ii. Coulometry [5]

iii. Potentiometry [5]

iv. Voltammetry [5]

v. Cyclic voltammetry [5]

QUESTION 4 [25]

a) Describe how a student can use anodic stripping voltammetry for the detection of Cd^{2+} in a water sample. Use diagrams to illustrate your answer.

$Cd^{2+}(aq) + 2e^{-} \rightarrow Cd(s)$ $E = -0.40V$ [15]

b) Describe and discuss electrode modification, its importance and applications [10]

QUESTION 5 [25]

a) Define E°. [3]

b) What is an electrochemically reversible redox system? [3]

c) What is the role of salt bridge in galvanic cells? [5]

d) What are reference electrodes? Give two examples. [5]

e) How will you predict the spontaneity of any redox system using emf? [5]

f) What is an ion selective electrode? [4]

QUESTION 6 [25]

a. What are the conditions for an electrochemical cell to act as a standard cell? [5]

b. What is a secondary reference electrode? Give one example with its electrode potential value. [10]

c. Design an experimental setup from which you could obtain electrical work from the following redox reaction. [10]

$$Cd(s) + 2AgCl(s) \rightleftharpoons Cd^{2+}(aq) + 2\,Ag(s) + 2Cl^{-}(aq)$$

Make sure that you label the following items in your diagram:

i. The anode and the cathode

ii. The direction of electron flow

iii. The positive and the negative electrode

iv. Give the half reaction at each electrode.

THE END **/100/**

TABLE 20.1 • Standard Reduction Potentials in Water at 25 °C

E°_{red} (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
+1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
+1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
+1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
+1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
+0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
+0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0 [defined]	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
−0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

Table 1A.2 The gas constant ($R = N_A k$)

R	
8.314 47	$J\ K^{-1}\ mol^{-1}$
$8.205\ 74 \times 10^{-2}$	$dm^3\ atm\ K^{-1}\ mol^{-1}$
$8.314\ 47 \times 10^{-2}$	$dm^3\ bar\ K^{-1}\ mol^{-1}$
8.314 47	$Pa\ m^3\ K^{-1}\ mol^{-1}$
62.364	$dm^3\ Torr\ K^{-1}\ mol^{-1}$
1.987 21	$cal\ K^{-1}\ mol^{-1}$

The Faraday Constant, F	**96485C/mol**
The Avogadro's Constant, L	**6.02×10^{23}**
Electronic charge,e	**1.6023×10^{-19}C**

TABLE 18.1 Standard Reduction Potentials at 25 °C

Reduction half-reaction		$E°$(V)
$F_2(g) + 2e^-$	$\rightarrow 2F^-(aq)$	2.87
$Ce^{4+}(aq) + e^-$	$\rightarrow Ce^{3+}(aq)$	1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\rightarrow Mn^{2+}(aq) + 4H_2O(\ell)$	1.51
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-(aq)$	1.36
$O_2(g) + 4H^+(aq) + 4e^-$	$\rightarrow 2H_2O(\ell)$	1.23
$Br_2(\ell) + 2e^-$	$\rightarrow 2Br^-(aq)$	1.06
$NO_3^-(aq) + 4H^+(aq) + 3e^-$	$\rightarrow NO(g) + 2H_2O(\ell)$	0.96
$Ag^+(aq) + e^-$	$\rightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\rightarrow Fe^{2+}(aq)$	0.77
$I_2(s) + 2e^-$	$\rightarrow 2I^-(aq)$	0.54
$Cu^{2+}(aq) + 2e^-$	$\rightarrow Cu(s)$	0.34
$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-(aq)$	0.222
$Sn^{4+}(aq) + 2e^-$	$\rightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\rightarrow H_2(g)$	0.000
$Pb^{2+}(aq) + 2e^-$	$\rightarrow Pb(s)$	−0.126
$Ni^{2+}(aq) + 2e^-$	$\rightarrow Ni(s)$	−0.25
$Cr^{3+}(aq) + e^-$	$\rightarrow Cr^{2+}(aq)$	−0.41
$Fe^{2+}(aq) + 2e^-$	$\rightarrow Fe(s)$	−0.44
$Zn^{2+}(aq) + 2e^-$	$\rightarrow Zn(s)$	−0.76
$Ba^{2+}(aq) + 2e^-$	$\rightarrow Ba(s)$	−1.57
$Al^{3+}(aq) + 3e^-$	$\rightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\rightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\rightarrow Na(s)$	−2.714
$Li^+(aq) + e^-$	$\rightarrow Li(s)$	−3.045