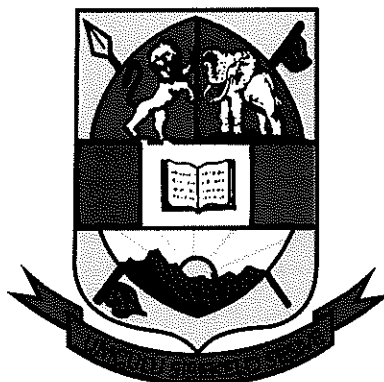


UNIVERSITY OF ESWATINI



**Final Examination– 2020/2021**

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<b>TITLE OF PAPER:</b>	<b>Electroanalytical Chemistry</b>
<b>COURSE NUMBER:</b>	<b>CHE614</b>
<b>TIME ALLOWED:</b>	<b>Three Hours</b>

**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.**

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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)
- $\text{VO}_4^{3-}$
  - $\text{VO}^{2+}$
- 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.



The  $E^\circ$  electrode values are:

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

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

For this cell calculate/write

- Standard cell potential  $E^\circ_{\text{cell}}$  (4)
- Cell potential  $(E)_{\text{cell}}$  (5)
- The symbolic representation/notation of the above cell. (4)
- 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<sup>2+</sup> in a water sample. Use diagrams to illustrate your answer.



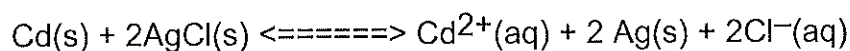
- b) Describe and discuss electrode modification, its importance and applications [10]

**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]



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/**

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

$E_{\text{red}}^{\circ}$ (V)	Reduction Half-Reaction
+2.87	$\text{F}_2(\text{g}) + 2 \text{e}^{-} \longrightarrow 2 \text{F}^{-}(\text{aq})$
+1.51	$\text{MnO}_4^{-}(\text{aq}) + 8 \text{H}^{+}(\text{aq}) + 5 \text{e}^{-} \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$
+1.36	$\text{Cl}_2(\text{g}) + 2 \text{e}^{-} \longrightarrow 2 \text{Cl}^{-}(\text{aq})$
+1.33	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^{+}(\text{aq}) + 6 \text{e}^{-} \longrightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$
+1.23	$\text{O}_2(\text{g}) + 4 \text{H}^{+}(\text{aq}) + 4 \text{e}^{-} \longrightarrow 2 \text{H}_2\text{O}(\text{l})$
+1.06	$\text{Br}_2(\text{l}) + 2 \text{e}^{-} \longrightarrow 2 \text{Br}^{-}(\text{aq})$
+0.96	$\text{NO}_3^{-}(\text{aq}) + 4 \text{H}^{+}(\text{aq}) + 3 \text{e}^{-} \longrightarrow \text{NO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$
+0.80	$\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \longrightarrow \text{Ag}(\text{s})$
+0.77	$\text{Fe}^{3+}(\text{aq}) + \text{e}^{-} \longrightarrow \text{Fe}^{2+}(\text{aq})$
+0.68	$\text{O}_2(\text{g}) + 2 \text{H}^{+}(\text{aq}) + 2 \text{e}^{-} \longrightarrow \text{H}_2\text{O}_2(\text{aq})$
+0.59	$\text{MnO}_4^{-}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) + 3 \text{e}^{-} \longrightarrow \text{MnO}_2(\text{s}) + 4 \text{OH}^{-}(\text{aq})$
+0.54	$\text{I}_2(\text{s}) + 2 \text{e}^{-} \longrightarrow 2 \text{I}^{-}(\text{aq})$
+0.40	$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^{-} \longrightarrow 4 \text{OH}^{-}(\text{aq})$
+0.34	$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^{-} \longrightarrow \text{Cu}(\text{s})$
0 [defined]	$2 \text{H}^{+}(\text{aq}) + 2 \text{e}^{-} \longrightarrow \text{H}_2(\text{g})$
-0.28	$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^{-} \longrightarrow \text{Ni}(\text{s})$
-0.44	$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^{-} \longrightarrow \text{Fe}(\text{s})$
-0.76	$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^{-} \longrightarrow \text{Zn}(\text{s})$
-0.83	$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^{-} \longrightarrow \text{H}_2(\text{g}) + 2 \text{OH}^{-}(\text{aq})$
-1.66	$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^{-} \longrightarrow \text{Al}(\text{s})$
-2.71	$\text{Na}^{+}(\text{aq}) + \text{e}^{-} \longrightarrow \text{Na}(\text{s})$
-3.05	$\text{Li}^{+}(\text{aq}) + \text{e}^{-} \longrightarrow \text{Li}(\text{s})$

**Table 1A.2 The gas constant ( $R=N_Ak$ )**

<b><i>R</i></b>	
8.314 47	J K <sup>-1</sup> mol <sup>-1</sup>
8.205 74×10 <sup>-2</sup>	dm <sup>3</sup> atm K <sup>-1</sup> mol <sup>-1</sup>
8.314 47×10 <sup>-2</sup>	dm <sup>3</sup> bar K <sup>-1</sup> mol <sup>-1</sup>
8.314 47	Pa m <sup>3</sup> K <sup>-1</sup> mol <sup>-1</sup>
62.364	dm <sup>3</sup> Torr K <sup>-1</sup> mol <sup>-1</sup>
1.987 21	cal K <sup>-1</sup> mol <sup>-1</sup>

<b>The Faraday Constant, F</b>	<b>96485C/mol</b>
<b>The Avogadro's Constant, L</b>	<b>6.02 x 10<sup>23</sup></b>
<b>Electronic charge, e</b>	<b>1.6023 x 10<sup>-19</sup>C</b>

**TABLE 18.1** Standard Reduction Potentials at 25 °C

Reduction half-reaction	$E^\circ(\text{V})$
$\text{F}_2(\text{g}) + 2\text{e}^-$	2.87
$\text{Ce}^{4+}(\text{aq}) + \text{e}^-$	1.61
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^-$	1.51
$\text{Cl}_2(\text{g}) + 2\text{e}^-$	1.36
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$	1.23
$\text{Br}_2(\ell) + 2\text{e}^-$	1.06
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^-$	0.96
$\text{Ag}^+(\text{aq}) + \text{e}^-$	0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^-$	0.77
$\text{I}_2(\text{s}) + 2\text{e}^-$	0.54
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$	0.34
$\text{AgCl}(\text{s}) + \text{e}^-$	0.222
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^-$	0.15
$2\text{H}^+(\text{aq}) + 2\text{e}^-$	0.000
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^-$	-0.126
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^-$	-0.25
$\text{Cr}^{3+}(\text{aq}) + \text{e}^-$	-0.41
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$	-0.44
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$	-0.76
$\text{Ba}^{2+}(\text{aq}) + 2\text{e}^-$	-1.57
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^-$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^-$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^-$	-2.714
$\text{Li}^+(\text{aq}) + \text{e}^-$	-3.045