UNIVERSITY OF ESWATINI

SUPPLIMENTARY EXAMINATION 2019/2020

TITLE OF PAPER: ANALYTICAL CHEMISTRY II

COURSE NUMBER: CHE 411

TIME ALLOWED: THREE (3) HOURS

INSTRUCTIONS: ANSWER ANY FOUR (4) QUESTIONS

Special Requirements

1. Data sheet.

YOU ARE NOT SUPPOSED TO OPEN THIS PAPER UNTIL PERMISSION TO DO SO HAS BEEN GIVEN BY THE CHIEF INVIGILATOR.

QUESTION 1 [25]

a) In Polarography, what is meant by:

i) The over potential [2]

ii) The charging current (use a diagram to illustrate) [3]

b) Describe migration as one of the main mass transfer processes in polarography, state whether the process is desired, and what means are put in place to eliminate it if undesired. [3]

c) Use Fick's Law and the Cottrell equation to derive the Ilkovic equation for quantitative polarography. [5]

d) With the aid of a large, labeled diagram, explain how the dropping mercury electrode (DME) works. [4]

e) Discuss three (3) properties of mercury that makes it suitable for polarographic work. [3]

f) The standard addition method in Polarography is most useful when the sample matrix is complex. A 50ml waste water sample from a Nickel mine dump gave a wave height of 5.38μA in a polarographic analysis. When 0.500 ml of solution containing 25 mM Ni^{2+} was added, th wave height measured 8.25 μA. Calculate the concentration of nickel in the unknown (in ppm), given that supporting electrolyte alone gave a residual current of 0.05 μA. [5]

QUESTION 2 [25]

a) Apart from migration, how else do electroactive ions in solution move towards the mercury electrode in polarography? [2]

b) In polarography, the current is sometimes observed to "overshoot" the diffusion current before settling back down at the plateau. What causes these current maxima, and how are they eliminated? [2]

c) In polarography, analyses are conducted within an electrochemical window governed by the anodic and cathode limits. Discuss the origins of these limits with the aid of chemical equations. [4]

d) Oxygen waves are a nuisance in the polarographic determinations of heavy metals. However, levels of dissolved oxygen in water samples can be measured polarographically.

(i) Explain the origins of oxygen waves in polarography using supporting chemical equations. [4]

(ii) How is oxygen experimentally removed in polarography? [1]

(iii) Suppose tap water is scanned in a polarograph without deaeration, and the following is observed: E ½ = 0.05 V; $i_{d,\,ave}$ = 1.81μA, when the rate of flow of mercury is 2.00 mg/sec and the drop interval is 5 sec. Calculate the concentration of oxygen in the tap water in ppm units (diffusion coefficient =2.12 x 10^{-5} cm^2/sec). [5]

e) Sometimes useful information can be derived from the rising portion of the polarographic wave, for example, the number of electrons involved in the reduction. For benzoquinone, the following data were obtained in the rising portion of a polarographic wave:

E vs SCE (V)	I μA
+0.210	0.591
+0.190	0.146
+0.170	4.646
+0.150	6.299

Calculate the value of n if $I_{d,max}$ = 7.008 μA. [7]

QUESTION 3 **[25]**

b) Describe the three (3) main requirements that enable an electrode to be considered a "reference electrode" [3]

c) A reference electrode encountered frequently in analytical measurements is abbreviated "SCE".

(i) What does the acronym SCE stand for? [1]

(ii) Use a diagram to describe the components of the SCE. [3]

(iii) Write down the electrode reaction of the SCE and state its potential. [2]

(iv) State one disadvantage of the SCE [1]

d) Unless it is to be measured, the liquid junction potential is undesirable in direct potentiometry. Explain the origin of a liquid junction potential in potentiometry, and indicate how it is eliminated. [3]

e) With regards to the Orion fluoride ion selective electrode,

i) Describe the structure of the electrode with the aid of a diagram. [4]

ii) Calculate electromotive force of the electrode. [2]

iii) Explain the role of each of three (3) components of TISAB used in conjunction with the fluoride electrode [6]

QUESTION 4 **[25]**

a) Consider an amperometric titration of Pb^{2+} with titrant $Titr^{2-}$ to form PbTitr using one polarized electrode.

i) On one plot, sketch the current/volatage curves ($E_{½,\,Pb}$ = -0.4V vs SCE) at the points at which the titration is 0%, 50%, 100%, 110% complete. [4]

ii) If the dropping mercury electrode is held constant at -1.0V vs SCE, plot the resultant titration curve, assuming that the titrant is not electroreducible. [3]

iii) Sketch the current/voltage curve that you would expect if Titr $^{2-}$, being non-electrodeducible, were to be titrated with Pb^{2+} instead, at the points indicated in a (i) above. [4]

iv) Sketch the shape of the titration curve that would result if Titr $^{2-}$ were to be electroreducible as well. [3]

b) Consider a biamperometric titration in which Fe^{2+} is titrated with Ce^{4+} according to the reaction: $Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$. Given that the Fe^{3+} / Fe^{2+} couple gets reduced at more negative potentials than the Ce^{3+}/Ce^{4+} couple,

i) Sketch the current-potential curves for points at which the fraction titrated is 0.1, 0.5, 1.0 and 1.2, assuming an impressed voltage of 100 mV across the electrodes [4]

ii) Sketch the biamperometric titration curve for this system. [2]

c) Explain how the pH glass electrode works using equations to support your answer. [5]

QUESTION 5 **[25]**

(a) Write down the Nernst equation, and explain all the terms appearing in it. [3]

(b) In potetiometry, potentials are measured relative to the standard hydrogen electrode (SHE) potential.

i) Draw the SHE, and label all its components [4]

ii) Write down the electrochemical equation taking place within the SHE and state its standard electrode potential [2]

(c) For the electrochemical cell:

Cd (s) / Cd Cl_2 (aq, 0.0538 M) // Ag NO_3 (aq, 0.0320M) / Ag (s)

i) What component is represented by the symbol "//"? [1]

ii) How is it constructed? [2]

iii) How does it work? [2]

iv) Would the cell be galvanic as written? [4]

(d) With regards to the pH glass membrane electrode, describe

i) The terms k_{as} and β in the equation: $E = k_{as} - \beta\,(0.05916)\log \frac{A_{H+,\,inner}}{A_{H+,\,outer}}$ [4]

ii) The "alkaline error" [1]

iii) How the glass membrane can be modified to produce a sodium ion electrode [1]

iv) The "acid error" [1]

QUESTION 6 [25]

a) Modern methods in polarography seek to reduce capacitive current. Use a diagram to explain the origins of capacitive currents in polarography [3]

b) Use diagrams to explain the difference in time behavior between capacitive current and Faradaic current, and their resulting superposition at the dropping mercury electrode. [3]

c) Use diagrams to show the dependence of Faradaic and charging current on concentration. [3]

d) Explain how the current is sampled in Tast Polarography, and compare the:

i) Resolution [1]

ii) Detection limits [1]

iii) Appearance of the polarogram [1]

between Tast Polarography and Classical Polarography.

e) Explain how the current is sampled in Differential Pulse Polarography (DPP), and compare the:

i) Resolution [1]

ii) Detection limits [1]

iii) Appearance of polarogram [1]

between DPP and DC Polarography.

f) Anodic Stripping Voltammetry (ASV) surpasses flame atomic absorption spectroscopy in the determination of ultra trace levels of lead in drinking water in terms of detection limits.

i) With the aid of a diagram, explain the instrumentation used in ASV. [4]

ii) Use a diagram and equations to describe the deposition step in ASV. [2]

iii) Use a diagram and equation to describe the stripping step in ASV. [2]

iv) Explain why it is more sensitive than FAAS in terms of detection limits. [2]

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1.008 H 1																	4.003 He 2
2	6.941 Li 3	9.012 Be 4											10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	14.998 F 9	20.180 Ne 10
3	22.990 Na 11	24.305 Mg 12											26.982 Al 13	28.086 Si 14	30.974 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
4	39.098 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.942 V 23	51.996 Cr 24	54.938 Mn 25	55.847 Fe 26	58.933 Co 27	58.69 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.922 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36
5	85.468 Rb 37	87.62 Sr 38	88.906 Y 39	91.224 Zr 40	92.906 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.91 Rh 45	106.42 Pd 46	107.87 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.90 I 53	131.29 Xe 54
6	132.91 Cs 55	137.33 Ba 56	138.91 *La 57	178.49 Hf 72	180.95 Ta 73	183.85 W 74	186.21 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.97 Au 79	200.59 Hg 80	204.38 Tl 81	207.2 Pb 82	208.98 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	223 Fr 87	226.03 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109	(267) Uun 110								

TRANSITION ELEMENTS

Atomic mass → 10.811
Symbol → B
Atomic No. → 5

*Lanthanide Series	140.12 Ce 58	140.91 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.96 Eu 63	157.25 Gd 64	158.93 Tb 65	162.50 Dy 66	164.93 Ho 67	167.26 Er 68	168.93 Tm 69	173.04 Yb 70	174.97 Lu 71
**Actinide Series	232.04 Th 90	231.04 Pa 91	238.03 U 92	237.05 Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103

() indicates the mass number of the isotope with the longest half-life.

General data and fundamental constants

Quantity	Symbol	Value
Speed of light	c	$2.997\,924\,58 \times 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\,177 \times 10^{-19}$ C
Faraday constant	$F = eN_A$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = kN_A$	$8.314\,51$ J K^{-1} mol^{-1}
		$8.205\,78 \times 10^{-2}$ dm^3 atm K^{-1} mol^{-1}
		62.364 L Torr K^{-1} mol^{-1}
Planck constant	h	$6.626\,08 \times 10^{-34}$ J s
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34}$ J s
Avogadro constant	N_A	$6.022\,14 \times 10^{23}$ mol^{-1}
Atomic mass unit	u	$1.660\,54 \times 10^{-27}$ kg
Mass of electron	m_e	$9.109\,29 \times 10^{-31}$ kg
proton	m_p	$1.672\,62 \times 10^{-27}$ kg
neutron	m_n	$1.674\,93 \times 10^{-27}$ kg
Vacuum permeability	μ_0	$4\pi \times 10^{-7}$ J s^2 C^{-2} m^{-1}
		$4\pi \times 10^{-7}$ T^2 J^{-1} m^3
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12}$ J^{-1} C^2 m^{-1}
	$4\pi\varepsilon_0$	$1.112\,65 \times 10^{-10}$ J^{-1} C^2 m^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}$ J T^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}$ J T^{-1}
Electron g value	g_e	$-2.002\,32$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Rydberg constant	$R_\infty = m_e e^4/8h^3 c$	$1.097\,37 \times 10^{5}$ cm^{-1}
Fine structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ N m^2 kg^{-2}
Standard acceleration of free fall	g	$9.806\,65$ m s^{-2}

† Exact (defined) values

f	p	n	μ	m	c	d	k	M	G
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

Prefixes