

# NAMIBIA UNIVERSITY

OF SCIENCE AND TECHNOLOGY

### FACULTY OF HEALTH, NATURAL RESOURCES AND APPLIED SCIENCES

### **DEPARTMENT OF BIOLOGY, CHEMISTRY AND PHYSICS**

QUALIFICATION: BACHELOR OF SCIENCE									
QUALIFICATION CODE: 07BOSC	LEVEL: 6								
COURSE CODE: APP601S	COURSE NAME: ANALYTICAL PRINCIPLES AND PRACTICE								
SESSION: JULY 2023	PAPER: THEORY								
DURATION: 3 HOURS	MARKS: 100								

SUPPLEMENTARY/SECOND OPPORTUNITY EXAMINATION PAPER									
EXAMINER(S)	DR EUODIA HESS								
MODERATOR:	DR MARIUS MUTORWA								

#### **PERMISSIBLE MATERIALS**

Non-programmable Calculators

#### **ATTACHMENTS**

List of useful tables, formulas and constants

THIS EXAMINATION PAPER CONSISTS OF 10 PAGES (Including this front page and attachments)

1.6 What is the pH of a saturated solution of milk of magnesia, Mg(OH) <sub>2</sub> , if the Ksp of this compound is $1.2 \times 10^{-11}$ ?	(3)
(A) 3.5 (B) 9.2 (C) 10.5 (D) 10.9	
1.7 Bleaching powder reacts with iodide ion according to the following unbalanced equation: $OCl^- + l^- + H^+ \square  l_2 + Cl^- + H_2O$ A 0.6000 g sample of bleaching powder requires 35.24 mL of 0.1084 M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> to titrate the liberated iodine. The percentage of Cl in the sample is	(3)
(A) 22.58% CI (B) 5.15% CI (C) 11.29% CI (D) 45.16% CI	
1.8 Given the following half-reactions: $A^{2+} + e^- \rightarrow A^+ \qquad E^\circ = +1.70 \text{ V}$ $B^{4+} + 2e^- \rightarrow B^{2+} \qquad E^\circ = +0.60 \text{ V}$ $C^{3+} + e^- \rightarrow C^{2+} \qquad E^\circ = +0.90 \text{ V}$ The only reaction that could be used in a titration would be	(3)
(A) A+ with B4+ (B) A+ with C3+ (C) A <sup>2+</sup> with C <sup>2+</sup> (D) C <sup>2+</sup> with B <sup>4+</sup>	
1.9 During a potentiometric oxidation-reduction titration, the only place at which the $E_{\text{cell}}$ equals the E° of the substance being titrated is	(3)
<ul><li>(A) when the two half reactions are in equilibrium</li><li>(B) when twice the stoichiometric amount of titrant has been added</li><li>(C) at the equivalence point</li><li>(D) half way to the equivalence point</li></ul>	

- 1.10 A standard solution of 0.154 M HCl is used to determine the concentration of a NaOH solution whose concentration is unknown. If 33.5 mL of the acid solution are required to neutralize 25.0 mL of the base solution, the concentration of the NaOH in moles/liter is
- (3)

- (A) 25.0 / (0.154)(33.5)
- (B) (0.154)(25.0) / 33.5
- (C)(33.5 + 25.0) / 0.514
- (D) (0.514)(33.5) / 25.0

Question 2 [15]

2.1 To test a spectrophotometer's accuracy a solution of 60.06 ppm  $K_2Cr_2O_7$  in 5.0 mM  $H_2SO_4$  is prepared and analysed. This solution has an expected absorbance of 0.640 at 350.0 nm in a 1.0-cm cell when using 5.0 mM  $H_2SO_4$  as a reagent blank. Several aliquots of the solution produce the following absorbance values.

- (a) Calculate the mean and standard deviation of the measured absorbance values. (2)
- (b) Determine whether there is a significant difference between the experimental mean and the expected value at a = 0.01 (i.e. P= 99%). (6)
- 2.2 One way to check the accuracy of a spectrophotometer is to measure absorbencies for a series of standard dichromate solutions obtained from the National Institute of Standards and Technology. Absorbencies (A) are measured at 257 nm and compared to the accepted values. The results obtained when testing a newly purchased spectrophotometer are shown below.

Standard	Measured A	Expected A
1	0.2872	0.2871
2	0.5773	0.5760
3	0.8674	0.8677
4	1.1623	1.1608
5	1.4559	1.4565

Determine if the tested spectrophotometer is accurate at a = 0.05. (7)

Question 3 [15] 3.1 A solution containing 3.47 mM of analyte and 1.72 mM of standard gave peak areas of 3,473 and 10,222, respectively, in a chromatographic analysis. Then 1.00 mL of 8.47 mM standard was added to 5.00 mL of unknown solution, and the mixture was diluted to 10.0 mL. This solution gave peak areas of 5 428 and 4 431 for the analyte and standard, respectively. (a) Calculate the response factor for the analyte. (2)(b) Find the concentration of the standard in the 10.0 mL of mixed solution. (2)(c) Find the analyte concentration in the 10.0 mL of mixed solution. (2)(d) Find the analyte concentration in the original unknown. (2)3.2 The concentration of phenol in a water sample is determined by separating the phenol from non-volatile impurities by steam distillation, followed by reacting with 4-aminoantipyrine and  $K_3Fe(CN)_6$  at pH 7.9 to form a colored antipyrine dye. A phenol standard with a concentration of 4.00 ppm has an absorbance of 0.424. A water sample is steam distilled and a 50.00-mL aliquot of the distillate is placed in a 100-mL volumetric flask and diluted to volume with distilled water. The absorbance of this solution is found to be 0.394. (a) What is the concentration of phenol (in parts per million) in the water sample? (4) (b) What calibration method has been used here? (1)(c) Briefly explain your choice of the calibration method. (2)**Question 4** [15] 4.1 For the following unbalanced reaction at 25°C  $Fe^{2+} + MnO_4^- \square Fe^{3+} + Mn^{2+}$  (acidic medium)  $(E^{O}_{Fe3+/Fe2+} = 0.771 \text{ V}; E^{O}_{MnO4-/Mn2+} = 1.51 \text{ V})$ (a) Write the balanced oxidation and reduction half reactions as well as the overall reaction. (3)(b) Calculate the standard potential of the reaction. (1)(c) Calculate the equilibrium constant of the reaction. (2)(d) Calculate the potential under the following conditions:  $[Fe^{2+}] = 0.50 \text{ M}$ ,  $[Fe^{3+}] = 0.10 \text{ M}, [MnO_4^-] = 0.025 \text{ M}, [Mn^{2+}] = 0.015 \text{ M}, and a pH of 7.00.}$ (2)4.2 Calculate the pH of the solution that results from the addition of 0.040 moles of HNO<sub>3</sub> to a buffer made by combining 0.500 L of 0.380 M HC<sub>3</sub>H<sub>5</sub>O<sub>2</sub> ( $K_a = 1.30 \times 10^{-5}$ ) and 0.500 L of 0.380 M NaC<sub>3</sub>H<sub>5</sub>O<sub>2</sub>. Assume addition of the nitric acid has no effect on volume. (5)

(2)

4.3 Calculate the ionic strength of a 0.025 M solution of CuCl<sub>2</sub>

Question 5	[35]
5.1 50.0 mL of 0.0400 M formic acid (HCOOH, $K_a$ = 1.80 x 10 <sup>-4</sup> ) was titrated with 0.120 M NaOH.	
(a) Write the balanced reaction of the titration.	(2)
<ul><li>(b) calculate the volume of added titrant at the equivalence point.</li><li>(c) Calculate the pH after addition of the following volumes of the titrant</li></ul>	(1)
(i) 0.0 mL	(4)
(ii) 10.0 mL	(4)
(iii) 20.0 mL	(4)
5.2 25.0 mL of 0.01 M $V^{2+}$ is titrated using 0.01 M $Ce^{4+}$	
$(E^0_{V3+/V2+} = -0.255 \text{ V}; E^0_{Ce4+/Ce3+} = +1.72 \text{ V}).$	
(a) Write the two redox half-reactions, the overall reaction and the potential $(E)$	
expressions for both redox half-reactions.	(5)
(b) Calculate the potential of the titration after addition of	FIG. (1997)
(i) 15.0 mL Ce <sup>4+</sup>	(5)
(ii) 25.0 mL Ce <sup>4+</sup>	(5)
5.3 (a) Define gravimetry.	(1)
(b) List the different types of gravimetric methods.	(4)

**END** 

#### **Data Sheet**

Data Sheet 
$$t_{calculated} = \frac{\left| \overline{x} - \mu \right|}{s} \sqrt{N} \qquad t_{calculated} = \frac{\overline{d}}{s_d} \sqrt{n} \qquad t_{calculated} = \frac{\left| \overline{x}_a - \overline{x}_b \right|}{s_{pooled}} \times \sqrt{\frac{n_a \times n_b}{n_a + n_b}}$$
 
$$s_{pooled} = \sqrt{\frac{s_a^2(N_a - 1) + s_b^2(N_b - 1) + \dots}{N_a + N_b + \dots - N_{sets of data}}} \qquad \qquad \mu = \overline{x} \pm \frac{ts}{\sqrt{n}}$$
 Confidence

	V ''a'	1 · b · · · · · ·	. Tractaon	autu
Confidence	e			
degrees	50%	90%	95%	99%
Freedom	3070	5070	3370	
1	1.000	6.314	12.706	63.656
2	0.816	2.920	4.303	9.925
3	0.765	2.353	3.182	5.841
4	0.741	2.132	2.776	4.604
5	0.727	2.015	2.571	4.032
6	0.718	1.943	2.447	3.707
7	0.711	1.895	2.365	3.499
8	0.706	1.860	2.306	3.355
9	0.703	1.833	2.262	3.250
10	0.700	1.812	2.228	3.169
11	0.697	1.796	2.201	3.106
12	0.695	1.782	2.179	3.055
13	0.694	1.771	2.160	3.012
14	0.692	1.761	2.145	2.977
15	0.691	1.753	2.131	2.947
16	0.690	1.746	2.120	2.921
17	0.689	1.740	2.110	2.898
18	0.688	1.734	2.101	2.878
19	0.688	1.729	2.093	2.861
20	0.687	1.725	2.086	2.845
21	0.686	1.721	2.080	2.831
22	0.686	1.717	2.074	2.819
23	0.685	1.714	2.069	2.807
24	0.685	1.711	2.064	2.797
25	0.684	1.708	2.060	2.787
26	0.684	1.706	2.056	2.779
27	0.684	1.703	2.052	2.771
28	0.683	1.701	2.048	2.763
29	0.683	1.699	2.045	2.756
30	0.683	1.697	2.042	2.750
31	0.682	1.696	2.040	2.744
32	0.682	1.694	2.037	2.738
33	0.682	1.692	2.035	2.733
34	0.682	1.691	2.032	2.728
35	0.682	1.690	2.030	2.724
				+

#### Critical Values for the Rejection Quotient

	Q <sub>crit</sub> (	Reject if Q <sub>exp</sub> >	Q <sub>crit</sub> )
N	90% Confidence	95% Confidence	99% Confidence
3	0.941	0.970	0.994
4	0.765	0.829	0.926
5	0.642	0.710	0.821
6	0.560	0.625	0.740
7	0.507	0.568	0.680
8	0.468	0.526	0.634
9	0.437	0.493	0.598
10	0.412	0.466	0.568

N = number of observations

F(0.05, σ	num, σde	enom) fo	r a Two-1	Tailed F-T	est								
σnum⇒ σden∜	1	2	3	4	5	6	7	8	9	10	15	20	∞
1	647.8	799.5	864.2	899.6	921.8	937.1	948.2	956.7	963.3	968.6	984.9	993.1	1018
2	38.51	39.00	39.17	39.25	39.30	39.33	39.36	39.37	39.39	39.40	39.43	39.45	39.50
3	17.44	16.04	15.44	15.10	14.88	14.73	14.62	14.54	14.47	14.42	14.25	14.17	13.90
4	12.22	10.65	9.979	9.605	9.364	9.197	9.074	8.980	8.905	8.444	8.657	8.560	8.257
5	10.01	8.434	7.764	7.388	7.146	6.978	6.853	6.757	6.681	6.619	6.428	6.329	6.015
6	8.813	7.260	6.599	6.227	5.988	5.820	5.695	5.600	5.523	5.461	5.269	5.168	4.894
7	8.073	6.542	5.890	5.523	5.285	5.119	4.995	4.899	4.823	4.761	4.568	4.467	4.142
8	7.571	6.059	5.416	5.053	4.817	4.652	4.529	4.433	4.357	4.259	4.101	3.999	3.670
9	7.209	5.715	5.078	4.718	4.484	4.320	4.197	4.102	4.026	3.964	3.769	3.667	3.333
10	6.937	5.456	4.826	4.468	4.236	4.072	3.950	3.855	3.779	3.717	3.522	3.419	3.080
11	6.724	5.256	4.630	4.275	4.044	3.881	3.759	3.644	3.588	3.526	3.330	3.226	2.883
12	6.544	5.096	4.474	4.121	3.891	3.728	3.607	3.512	3.436	3.374	3.177	3.073	2.725
13	6.414	4.965	4.347	3.996	3.767	3.604	3.483	3.388	3.312	3.250	3.053	2.948	2.596
14	6.298	4.857	4.242	3.892	3.663	3.501	3.380	3.285	3.209	3.147	2.949	2.844	2.487
15	6.200	4.765	4.153	3.804	3.576	3.415	3.293	3.199	3.123	3.060	2.862	2.756	2.395
16	6.115	4.687	4.077	3.729	3.502	3.341	3.219	3.125	3.049	2.986	2.788	2.681	2.316
17	6.042	4.619	4.011	3.665	3.438	3.277	3.156	3.061	2.985	2.922	2.723	2.616	2.247
18	5.978	4.560	3.954	3.608	3.382	3.221	3.100	3.005	2.929	2.866	2.667	2.559	2.187
19	5.922	4.508	3.903	3.559	3.333	3.172	3.051	2.956	2.880	2.817	2.617	2.509	2.133
20	5.871	4.461	3.859	3.515	3.289	3.128	3.007	2.913	2.837	2.774	2.573	2.464	2.085
∞	5.024	3.689	3.116	2.786	2.567	2.408	2.288	2.192	2.114	2.048	1.833	1.708	1.000

## **Physical Constants**

,		
Gas constant	R	= 8.315 J K <sup>-1</sup> mol <sup>-1</sup>
		= 8.315 kPa dm³ K <sup>-1</sup> mol <sup>-1</sup>
		= 8.315 Pa m <sup>3</sup> K <sup>-1</sup> mol <sup>-1</sup>
		= 8.206 x 10 <sup>-2</sup> L atm K <sup>-1</sup> mol <sup>-1</sup>
Boltzmann constant	k	= 1.381 x 10 <sup>-23</sup> J K <sup>-1</sup>
Planck constant	h	= 6.626 x 10 <sup>-34</sup> J K <sup>-1</sup>
Faraday constant	F	= 9.649 x 10 <sup>4</sup> C mol <sup>-1</sup>
Avogadro constant	L or NA	= 6.022 x 10 <sup>23</sup> mol <sup>-1</sup>
Speed of light in vacuum	С	= 2.998 x 10 <sup>8</sup> m s <sup>-1</sup>
Mole volume of an ideal gas	$V_m$	= $22.41 L mol^{-1}$ (at 1 atm and 273.15 K)
$= 22.71 L mol^{-1}$ (at 1 bar and 2	273.15 K)	
Elementary charge	е	= 1.602 x 10 <sup>-19</sup> C
Rest mass of electron	m <sub>e</sub>	$= 9.109 \times 10^{-31} \text{ kg}$
Rest mass of proton	$m_p$	$= 1.673 \times 10^{-27} \mathrm{kg}$
Rest mass of neutron	$m_n$	$= 1.675 \times 10^{-27} \mathrm{kg}$
Permitivity of vacuum	$\epsilon_{o}$	= $8.854 \times 10^{-12} \mathrm{C}^2 \mathrm{J}^{-1} \mathrm{m}^{-1} \mathrm{(or F m}^{-1)}$
Gravitational acceleration	g	= 9.807 m s <sup>-2</sup>

#### **Conversion Factors**

 $\frac{S_{\text{samp}}}{C_{A} \frac{V_{o}}{V_{o}}} = \frac{S_{\text{spike}}}{C_{A} \frac{V_{o}}{V_{o}} + C_{\text{gd}}}$ 

$$\frac{S_{\text{samp}}}{C_{\text{A}}} = \frac{S_{\text{spike}}}{C_{\text{A}} \frac{V_{\text{o}}}{V_{\text{o}} + V_{\text{std}}} + C_{\text{std}} \frac{V_{\text{std}}}{V_{\text{o}} + V_{\text{std}}}}$$

= 1 mg L<sup>-1</sup> (dilute aqueous solutions only)

$$E^{o} = \frac{0.05916}{n} \log K \quad E^{o} = E^{o}_{\text{sed}} - E^{o}_{\text{ox}} \quad E = E^{o} - \frac{0.05916}{n} \log Q$$

## PERIODIC TABLE OF THE ELEMENTS

1																	18
1																	2
<b>H</b> 1.00794	2											13	14	15	16	17	<b>He</b> 4.00260
3	4											5	6	7	8	9	10
Li	Be											В	C	N	O	F	Ne
6.941	9.01218											10.81	12.011	14.0067	15.9994	18.9984	20.179
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
22.9898	24.305	3	4	5	6	7	8	9	10	11	12	26.9815	28.0855	30.9738	32.06	35.453	39.948
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co.	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.0983	40.08	44.9559	47.88	50.9415		54.9380	55.847	58.9332	58.69	63.546	65.38	69.72	72.59	74.9216	78.96	79.904	83.8
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
85.4678	87.62	88.9059	91.22	92.9064	95.94	(98)	101.07	102.906	106.42	107.868	112.41	114.82	118.69	121.75	127.6	126.9	131.29
55	56	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
132.905	137.33	174.967	178.49	180.948	183.85	186.207	190.2	192.22	195.08	196.967		204.383	207.2	208.908	(209)	(210)	(222)
87	88	103	104	105	106	107	108	109	110	111	112		114		116		118
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq		Uuh		Uuo
(223)	226.025	(260)	(261)	(262)	(263)	(264)	(265)	(268)	(269)	(272)	(269)						

Lanthanides: 59 60 62 63 64 65 66 67 68 69 58 61 La Ce Pr Nd Pm 
 Sm
 Eu
 Gd
 Tb
 Dy
 Ho
 Er
 Tm
 Yb

 150.36
 151.96
 157.25
 158.925
 162.50
 161.930
 167.26
 166.934
 173.04
 (145)

Actinides:

89	90	91	92	93	94	95	96	97	98	99	100	101	102
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
227.028	232.038	231.036	238.029	237.048	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)

70