NAMIBIA UNIVERSITY
OF SCIENCE AND TECHNOLOGY

FACULTY OF HEALTH, APPLIED SCIENCES AND NATURAL RESOURCES

DEPARTMENT OF NATURAL AND APPLIED SCIENCES

QUALIFICATION: BACHELOR OF SCIENCE	
QUALIFICATION CODE: 07BOSC	**LEVEL:** 6
COURSE CODE: APP601S	**COURSE NAME:** ANALYTICAL PRINCIPLES AND PRACTICE
SESSION: JUNE 2022	**PAPER:** THEORY
DURATION: 3 HOURS	**MARKS:** 100

FIRST OPPORTUNITY EXAMINATION QUESTION PAPER	
EXAMINER(S)	DR JULIEN LUSILAO
MODERATOR:	DR MARIUS MUTORWA

INSTRUCTIONS

1. Answer ALL the questions in the answer book provided.
2. Write and number your answers clearly.
3. All written work MUST be done in blue or black ink.

PERMISSIBLE MATERIALS

Non-programmable Calculators

ATTACHMENTS

List of useful tables, formulas and constants

THIS QUESTION PAPER CONSISTS OF 11 PAGES (Including this front page and attachments)

Question 1: Multiple Choice Questions [20]

1.1 How many moles of Na^+ ions are in 20 mL of 0.40 M Na_3PO_4? (2)

(A) 0.0080
(B) 0.050
(C) 0.024
(D) 0.20

1.2 A mass of 5.4 grams of Al reacts with an excess of $CuCl_2$ in solution, as shown below:

$$3CuCl_2 + 2Al \longrightarrow 2AlCl_3 + 3Cu$$

What mass of solid copper (Cu) is produced? (2)

(A) 0.65 g
(B) 8.5 g
(C) 13 g
(D) 19 g

1.3 For the reaction

$$2C(s) + O_2(g) \longrightarrow 2CO(g)$$

What are the signs of ΔH and ΔS? (2)

(A) They are both negative
(B) They are both positive
(C) ΔH is positive and ΔS is negative
(D) ΔH is negative and ΔS is positive

1.4 The ion-product constant for water (K_w) at 45 °C is 4.0×10^{-14}. What is the pH of pure water at this temperature? (2)

(A) 7.0
(B) 6.7
(C) 7.3
(D) 13.4

1.5 The amount of chloride ion in a water sample is to be determined by adding excess silver nitrate (MW $AgNO_3$: 169.91 g·mol^{-1}).

$$Cl^-(aq) + AgNO_3(aq) \longrightarrow AgCl(s) + NO_3^-(aq)$$

If 1.0 g of silver chloride (MW $AgCl$: 143.25 g·mol^{-1}) is precipitated, what mass of chloride ion is in the original sample? (2)

(A) 0.34 g
(B) 0.50 g
(C) 0.25 g
(D) 0.75 g

1.6 The ionization of benzoic acid is represented by this equation.

$$C_6H_5COOH(aq) \leftrightarrow H^+(aq) + C_6H_5COO^-(aq)$$

If a 0.045 M solution of benzoic acid has an $[H^+] = 1.7 \times 10^{-3}$, what is the K_a of benzoic acid? (2)

(A) 7.7×10^{-5}
(B) 6.4×10^{-5}
(C) 3.8×10^{-2}
(D) 8.4×10^{-1}

1.7 $Mg_3N_2(s) + 6H_2O(l) \longrightarrow 2NH_3(aq) + 3Mg(OH)_2(s)$

If 54.0 grams of water are mixed with excess magnesium nitride, then how many grams of ammonia are produced? (2)

(A) 1.00
(B) 17.0
(C) 51.0
(D) 153

1.8 For the reaction

$$C_6H_5OH(aq) + CN^-(aq) \leftrightarrow HCN(aq) + C_6H_5O^-(aq)$$

The equilibrium constant for this reaction is less than 1. What is the strongest base in this system? (2)

(A) $C_6H_5OH(aq)$
(B) $CN^-(aq)$
(C) $C_6H_5O^-(aq)$
(D) $HCN(aq)$

1.9 The solubility product constant, K_{sp}, of Ag_3PO_4 is 1.8×10^{-18}. What is the molar solubility of Ag_3PO_4 in water? Neglect any hydrolysis. (2)

(A) 1.6×10^{-5}
(B) 8.4×10^{-7}
(C) 1.3×10^{-9}
(D) 4.5×10^{-19}

1.10 The balanced equation for the reduction of the nitrate anion by the Fe(II) ion in an acidic solution is (2)

(A) $3Fe^{2+}(aq) + NO_3^-(aq) + 4H^+(aq) \longrightarrow 3Fe^{3+}(aq) + NO(g) + 2H_2O(l)$

(B) $Fe^{2+}(aq) + NO_3^-(aq) + 8\ H+(aq) \longrightarrow Fe^{3+}(aq) + NO(g) + 4H_2O(l)$

(C) $2Fe^{2+}(aq) + 2NO_3^-(aq) + 4H^+(aq) \longrightarrow 2Fe^{3+}(aq) + 2NO(g) + 4H_2O(l)$

(D) $3Fe^{3+}(aq) + NO(g) + 2H_2O(l) \longrightarrow 3Fe^{3+}(aq) + NO_3^-(aq) + 4H+(aq)$

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.

0.639 0.638 0.640 0.639 0.640 0.639 0.638

(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? (3)

(b) What calibration method has been used here? (2)

(c) Briefly explain your choice of the calibration method. (2)

Question 4 [20]

4.1 For the following unbalanced reaction at 25°C

$$Fe^{2+} + MnO_4^- \leftrightarrow Fe^{3+} + Mn^{2+} \text{ (acidic medium)}$$

$$(E^0_{Fe3+/Fe2+} = 0.771 \text{ V}; E^0_{MnO4-/Mn2+} = 1.51 \text{ V})$$

(a) Write the balanced oxidation and reduction half reactions as well as the overall reaction. (3)

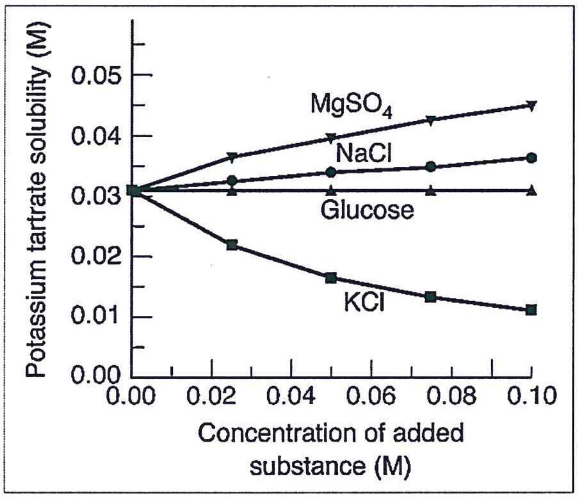
(b) Calculate the standard potential, E^0, of the reaction. (1)

(c) Calculate the equilibrium constant, K, of the reaction. (2)

(d) Calculate the potential, E, under the following conditions: $[Fe^{2+}] = 0.50$ M, $[Fe^{3+}] = 0.10$ M, $[MnO_4^-] = 0.025$ M, $[Mn^{2+}] = 0.015$ 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_3 to a buffer made by combining 0.500 L of 0.380 M $HC_3H_5O_2$ ($K_a = 1.30 \times 10^{-5}$) and 0.500 L of 0.380 M $NaC_3H_5O_2$. Assume addition of the nitric acid has no effect on volume. (5)

4.3 The following diagram shows the variation of the solubility of potassium tartrate ($K_2C_4H_4O_6$) when adding different concentrations of several substances.



(a) Explain the trend observed with the addition of $MgSO_4$ and NaCl. (2)

(b) Why $MgSO_4$ produces a higher solubility than NaCl? (1)

(c) Explain the trend observed with the addition of glucose. (2)

(d) Why does the solubility of potassium tartrate decrease with the addition of KCl? (2)

Question 5 [30]

5.1 50.0 mL of 0.0400 M formic acid (HCOOH, $K_a = 1.80 \times 10^{-4}$) was titrated with 0.120 M NaOH.

(a) Write the balanced reaction of the titration. (1)

(b) calculate the volume of added titrant at the equivalence point. (2)

(c) Calculate the pH after addition of the following volumes of the titrant

(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 V; $E^0_{Ce4+/Ce3+}$ = + 1.72 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

(i) 15.0 mL Ce^{4+} (5)

(ii) 25.0 mL Ce^{4+} (5)

TOTAL MARK = [100]

Data Sheet

$$t_{calculated} = \frac{|\bar{x}-\mu|}{s}\sqrt{N} \qquad t_{calculated} = \frac{\bar{d}}{s_d}\sqrt{n} \qquad t_{calculated} = \frac{|\bar{x}_a - \bar{x}_b|}{s_{pooled}} \times \sqrt{\frac{n_a \times n_b}{n_a + n_b}}$$

$$s_{pooled} = \sqrt{\frac{s_a^2(N_a-1)+s_b^2(N_b-1)+........}{N_a+N_b+......-N_{\text{sets of data}}}}$$

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

Confidence				
degrees Freedom	50%	90%	95%	99%
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_{crit} (Reject if $Q_{exp} > Q_{crit}$)		
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, σnum, σdenom) for a Two-Tailed F-Test													
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^{-1} mol^{-1}
		= 8.315 kPa dm^3 K^{-1} mol^{-1}
		= 8.315 Pa m^3 K^{-1} mol^{-1}
		= 8.206 x 10^{-2} L atm K^{-1} mol^{-1}
Boltzmann constant	k	= 1.381 x 10^{-23} J K^{-1}
Planck constant	h	= 6.626 x 10^{-34} J K^{-1}
Faraday constant	F	= 9.649 x 10^4 C mol^{-1}
Avogadro constant	L or N_A	= 6.022 x 10^{23} mol^{-1}
Speed of light in vacuum	c	= 2.998 x 10^8 m s^{-1}
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 273.15 K)		
Elementary charge	e	= 1.602 x 10^{-19} C
Rest mass of electron	m_e	= 9.109 x 10^{-31} kg
Rest mass of proton	m_p	= 1.673 x 10^{-27} kg
Rest mass of neutron	m_n	= 1.675 x 10^{-27} kg
Permitivity of vacuum	ε_o	= 8.854 x 10^{-12} C^2 J^{-1} m^{-1} (or F m^{-1})
Gravitational acceleration	g	= 9.807 m s^{-2}

Conversion Factors

1 W	= 1 J s^{-1}
1 J	= 0.2390 cal = 1 N m = 1 V C
	= 1 Pa m^3 = 1 kg m^2 s^{-2}
1 cal	= 4.184 J
1 eV	= 1.602 x 10^{-19} J
1 L atm	= 101.3 J
1 atm	= 1.013 x 10^5 N m^{-2} = 1.013 x 10^5 Pa = 760 mmHg
1 bar	= 1 x 10^5 Pa
1 L	= 10^{-3} m^3 = 1 dm^3
1 Angstrom	= 1 x 10^{-10} m = 0.1 nm = 100 pm
1 micron (μ)	= 10^{-6} m = 1 μm
1 Poise	= 0.1 Pa s = 0.1 N sm^{-2}
1 ppm	= 1 μg g^{-1} = 1 mg kg^{-1}
	= 1 mg L^{-1} (dilute aqueous solutions only)

$$\frac{S_{\mathrm{samp}}}{C_A \dfrac{V_o}{V_f}} = \frac{S_{\mathrm{spike}}}{C_A \dfrac{V_o}{V_f} + C_{\mathrm{std}} \dfrac{V_{\mathrm{std}}}{V_f}}$$

$$\frac{S_{\mathrm{samp}}}{C_A} = \frac{S_{\mathrm{spike}}}{C_A \dfrac{V_o}{V_o + V_{\mathrm{std}}} + C_{\mathrm{std}} \dfrac{V_{\mathrm{std}}}{V_o + V_{\mathrm{std}}}}$$

$\Delta G^0 = -RT \ln K$

$$E^{\circ} = \frac{0.05916}{n} \log K \qquad E^{\circ} = E^{\circ}_{\mathrm{red}} - E^{\circ}_{\mathrm{ox}} \qquad E = E^{\circ} - \frac{0.05916}{n} \log Q$$

Atomic Number — 2 **He** 4.0026 — Atomic Weight

1 **H** 1.0079																	2 **He** 4.0026
3 **Li** 6.941	4 **Be** 9.0122											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.179
11 **Na** 22.990	12 **Mg** 24.305											13 **Al** 26.982	14 **Si** 28.086	15 **P** 30.974	16 **S** 32.064	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.098	20 **Ca** 40.078	21 **Sc** 44.956	22 **Ti** 47.88	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.847	27 **Co** 58.933	28 **Ni** 58.69	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.723	32 **Ge** 72.61	33 **As** 74.922	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57 **La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.03	89 **Ac** 227.03															

58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** 146.92	62 **Sm** 150.36	63 **Eu** 151.97	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	94 **Pu** (244)	95 **Am** (234)	96 **Cm** (247)	97 **Bk** 247	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)