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: JUNE 2023	**PAPER:** THEORY
DURATION: 3 HOURS	**MARKS:** 100

FIRST OPPORTUNITY EXAMINATION QUESTION PAPER	
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ATTACHMENT
List of Useful Tables, Formulas and Constants

THIS EXAMINATION PAPER CONSISTS OF 9 PAGES (Including this front page and attachments)

Question 1: Multiple Choice Questions [30]

1.1 Which of the following glassware is not recommended for accurate measurements of volumes? (2)

(A) A graduated cylinder
(B) A volumetric flask
(C) A volumetric pipette
(D) A measuring pipette

1.2 A chemical or physical principle that can be used to study an analyte is called (2)

(A) A technique
(B) A procedure
(C) A protocol
(D) A method

1.3 The ability of an analytical balance to measure the smallest detectable increment of mass is called (2)

(A) The balance accuracy
(B) The balance precision
(C) The balance sensitivity
(D) None of the above

1.4 In statistics, the precision of repeated measurements is characterised by (2)

(A) The standard deviation
(B) The relative standard deviation
(C) The variance
(D) All of the above

1.5 An amphoteric substance (2)

(A) Has neither acid or base properties
(B) Turns litmus paper red and blue
(C) Is insoluble in base, but dissolves in an acid
(D) Reacts with both an acid and a base

1.6 Consider the equilibrium reaction

$$4NH_3(g) + 3O_2(g) \square \quad 2N_2(g) + 6H_2O(g) \qquad \Delta H = -1268 \text{ kJ}$$

Which change will cause the reaction to shift to the right? (2)

(A) Increase the temperature
(B) Decrease the volume of the container.
(C) Add a catalyst to speed up the reaction.

(D) Remove the gaseous water by allowing it to react and be absorbed by KOH.

1.7 Sodium nitrate, heated in the presence of an excess of hydrogen, forms water according to the two-step process

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

From the reactions above, how many grams of sodium nitrate are required to form 9 grams of water? (2)

(A) 21.3
(B) 42.5
(C) 69.0
(D) 85.0

1.8 What is the molarity of the sulphate ion in a solution prepared by dissolving 17.1 g of aluminium sulphate, $Al_2(SO_4)_3$, in enough water to prepare 1.00 L of solution? Neglect any hydrolysis. (2)

(A) 1.67×10^{-2} M
(B) 5.00×10^{-2} M
(C) 1.50×10^{-1} M
(D) 2.50×10^{-1} M

1.9 A reaction for which $\Delta H < 0$ and $\Delta S < 0$ is most likely to have which of these thermodynamic properties? (2)

(A) The reaction cannot be spontaneous at any temperature.
(B) The reaction will tend to be spontaneous at low temperatures.
(C) The reaction will tend to be spontaneous at high temperatures.
(D) The spontaneity of the reaction will be independent of temperature.

1.10 Consider the equilibrium reaction

$$Cd^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cd(NH_3)_4^{2+}(aq)$$

The equilibrium constant of the reaction is called (2)

(A) Overall formation constant
(B) Stepwise formation constant
(C) Cumulative formation constant
(D) Both (A) and (C)

Question 2 [20]

A researcher at NUST investigated the quantitative determination of Cr in high-alloy steels using a potentiometric titration of Cr(VI). Before the titration, samples of the steel were dissolved in acid and the chromium oxidized to Cr(VI) using peroxydisulfate. Shown here are the results (as %w/w Cr) for the analysis of a reference steel.

16.968; 16.922; 16.840; 16.883; 16.887; 16.977; 16.857; 16.728

2.1 Calculate the mean of the measurements (to 5 significant figures). (2)
2.2 Determine the median of the measurements (2)
2.3 Calculate the standard deviation (2 significant figures). (2)
2.4 Calculate the relative standard deviation (in %) (2)
2.5 Comment on the precision of the measurements (2)
2.6 Calculate the 95% confidence interval about the mean. (4)
2.7 What does this confidence interval mean? (2)
2.8 One of the measured values appears to be an outlier. Identify that value and use The Dixon Q test to confirm whether that measurement is reliable at 95% confidence level. (4)

Question 3 [10]

A 10.0-g sample containing an analyte is transferred to a 250-mL volumetric flask and diluted to volume. When a 10.0 mL aliquot of the resulting solution is diluted to 25.0 mL it gives signal of 0.235 (arbitrary units). A second 10.0-mL portion of the solution is spiked with 10.0 mL of a 1.0-ppm standard solution of the analyte and diluted to 25.0 mL. The signal for the spiked sample is 0.502.

3.1 What type of standardisation is used in this analysis? Explain your answer. (2)
3.2 Express ppm in gram per litre (g/L) (1)
3.3 Calculate the analyte concentration (in g/L) in the 10.00 ml aliquot. (3)
3.4 Calculate the gram of analyte in the 250 mL solution. (2)
3.5 Calculate the weight percent of analyte in the original sample. (2)

Question 4 [20]

4.1 Write equilibrium constant expressions for the following reactions.

(a) $AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$ (1)

(b) $BaCO_3(s) + H_3O^+(aq) \rightleftharpoons Ba^{2+}(aq) + H_2CO_3(aq) + H_2O(\ell)$ (1)

4.2 Calculate the standard state potential and the equilibrium constant for the following

redox reaction: $MnO_4^-(aq) + H_2SO_3(aq)$ □ $Mn^{2+}(aq) + SO_4^{2-}(aq)$ acidic solution. Assume that $[H_3O^+]$ is 1.0 M.
E^0 (MnO_4^-/ Mn^{2+}) = +1.51 V and $E^0(SO_3^{2-}/SO_4^{2-})$ = +0.172 V (8)

4.3 Calculate the ionic strength of a 0.050 M NaCl solution. (2)

4.4 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. (8)

Question 5 [20]

Calculate the pH at each point listed below for the titration of 100.0 mL of 0.100 M cocaine, symbolised as "B", ($K_b = 2.6 \times 10^{-6}$) with 0.200 M HNO_3. The points to calculate are at added HNO_3 volumes of 0.0, 10.0, 25.0, 50.0 and 60.0 mL.

5.1 0.0 mL of added HNO_3 (4)
5.2 10.0 mL of added HNO_3 (4)
5.3 25.0 mL of added HNO_3 (4)
5.4 50.0 mL of added HNO_3 (4)
5.5 60.0 mL of added HNO_3 (4)

END

Data Sheet

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

$$s_{pooled} = \sqrt{\frac{s_a^2(N_a - 1) + s_b^2(N_b - 1) + \ldots\ldots}{N_a + N_b + \ldots\ldots - N_{\text{sets of data}}}} \qquad \mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

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)

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

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

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

$$E^o = \frac{0.05916}{n}\log K \qquad E^o = E^o_{red} - E^o_{ox} \qquad E = E^o - \frac{0.05916}{n}\log Q$$

PERIODIC TABLE OF THE ELEMENTS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 1.00794																	2 **He** 4.00260
3 **Li** 6.941	4 **Be** 9.01218											5 **B** 10.81	6 **C** 12.011	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.9984	10 **Ne** 20.179
11 **Na** 22.9898	12 **Mg** 24.305											13 **Al** 26.9815	14 **Si** 28.0855	15 **P** 30.9738	16 **S** 32.06	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.0983	20 **Ca** 40.08	21 **Sc** 44.9559	22 **Ti** 47.88	23 **V** 50.9415	24 **Cr** 51.996	25 **Mn** 54.9380	26 **Fe** 55.847	27 **Co** 58.9332	28 **Ni** 58.69	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.8
37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.9059	40 **Zr** 91.22	41 **Nb** 92.9064	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.906	46 **Pd** 106.42	47 **Ag** 107.868	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.69	51 **Sb** 121.75	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.29
55 **Cs** 132.905	56 **Ba** 137.33	71 **Lu** 174.967	72 **Hf** 178.49	73 **Ta** 180.948	74 **W** 183.85	75 **Re** 186.207	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.967	80 **Hg** 200.59	81 **Tl** 204.383	82 **Pb** 207.2	83 **Bi** 208.908	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.025	103 **Lr** (260)	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (264)	108 **Hs** (265)	109 **Mt** (268)	110 Uun (269)	111 Uuu (272)	112 Uub (269)		114 Uuq		116 Uuh		118 Uuo

Lanthanides:

57 **La** 138.906	58 **Ce** 140.12	59 **Pr** 140.908	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.925	66 **Dy** 162.50	67 **Ho** 161.930	68 **Er** 167.26	69 **Tm** 166.934	70 **Yb** 173.04

Actinides:

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