

**UNIVERSITY OF SWAZILAND  
SUPPLEMENTARY EXAMINATION 2005**

**TITLE OF PAPER:    INTRODUCTORY ANALYTICAL  
                          CHEMISTRY**

**COURSE NUMBER:    C204**

**TIME ALLOWED:     THREE (3) HOURS**

**INSTRUCTIONS:     ANSWER ANY FOUR(4) QUESTIONS. EACH  
                          QUESTION CARRIES 25 MARKS**

**A periodic Table and other useful data have been attached with this  
Paper.**

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Granted by the Chief Invigilator.***

**Question 1 (25 marks)**

- (a). (i). Define a 'Gaussian error curve'. (1)  
 (ii). Give four of the main features of a 'Gaussian curve' (4)  
 (iii). State the percentage of the area under a normalized Gaussian curve covered by the following:

$$\mu \pm 1\sigma, \quad \mu \pm 2\sigma, \quad \text{and} \quad \mu \pm 3\sigma \quad (3)$$

- (iv). Give the expression that describes a Gaussian curve, and define all the parameters contained in it. Under what condition is the equation applicable to a given set of data? (4)

- (b). Given the following calculation:

$$(9.23 \pm 0.03) + (4.21 \pm 0.02) - (3.26 \pm 0.06)$$

Calculate the absolute and relative errors, and express your answers with reasonable number of significant figures. (5)

- ©. The following expression can be used to calculate the formula weight(F.W.), of a gas:

$$\text{F.W.} = \frac{mRT}{PV}$$

Where:  $m = (0.118 \pm 0.002)$

$T = (298.2 \pm 0.1)$

$P = (0.724 \pm 0.005)$

$V = (0.250 \pm 0.005)$

$R = (0.082056 \pm 0.0000001)$

- (i). Determine the formula weight of the compound. (2)  
 (ii). Calculate the absolute error, the % relative error and the %<sub>o</sub> relative errors in the formula. (6)

**Question 2 (25 marks)**

An old method and a new one were used for the determination of the Ca levels in a given set of biological samples. The data obtained are tabulated below:

NEW METHOD (mg/dL)	OLD METHOD (mg/dL)
10.1	9.7
12.5	11.2
9.7	10.6
10.2	10.0
9.5	10.9
10.5	10.1

- (a). Calculate the pooled mean and the pooled standard deviation for the two sets of data. (8)
- (b). Employ both the paired t-test and the F-test to determine if there are significant differences in the means and precisions of the two methods respectively at the 95% Confidence Level. (10)
- (c). For the new method, identify any questionable datum and determine if it should be discarded at the 95% Confidence Level. (7)

### Question 3 (25 marks)

- (a). Offer a brief explanation for the following terms:
- A normal calibration curve. (2)
  - Matrix matching (for external standardization process). (2)
- (b). Briefly describe how you would use the principles of the multiple/graphical standard addition method for the analysis of copper in a given sample. (6)
- (c). Standard solutions of an element X, containing 1.00 mg of X per L were mixed with an unknown sample containing X. The absorbance of the final solutions obtained from an Atomic Absorption Spectrometer are shown in the table below:

Vol. of the Unknown (mL)	Vol. of Standard (mL)	Total Volume (mL)	Absorbance
10.00	0.0	100.00	0.163
10.00	1.0	100.00	0.240
10.00	2.0	100.00	0.319
10.00	3.0	100.00	0.402
10.00	4.0	100.00	0.478

- Determine the final concentration of the added standard in each solution in mg/L. (5)
- Employ the multiple point (Graphical) method to determine the concentration of X in the unknown sample. (10)

**Question 4 (25 marks)**

- (a). Define the term, 'Distribution Ratio'  $D$ , for a given system. Differentiate it from the 'Distribution coefficient' for such a system. (3)
- (b). (i). A weak acid,  $HB$ , is distributed between an organic and an aqueous phase. If the acid is monomeric in both phases and without its anion penetrating the organic phase, obtain an expression for the distribution ratio,  $D$ , of the acid between the two phases. (7)
- (ii). Based on the expression obtained for  $D$  above, give the factors that influence  $D$ . (2)
- (iii). By rearranging the expression for  $D$  above, show how the values of the  $K_a$  and  $K_D$  for the weak acid can be estimated graphically. (6)
- ©. The distribution coefficient for an acid,  $HB$ , between an organic solvent and water is 9.8. At pH 5.00, half of the material is extracted into the organic layer from an equal volume of the aqueous phase. Calculate  $K_a$  for the weak acid,  $HB$ . (7)

**Question 5 (25 marks)**

- (a). (i). Explain the term 'Homogeneous precipitation'. What necessitates this method and what are its unique advantages? (5)
- (ii). With the aid of appropriate reaction equation illustrate this principles with an example. Identify the generated precipitating reagent and give an example of a process in which it has been used for precipitation. (3)
- (b). Describe the different ways by which 'Coprecipitation can occur during gravimetric analysis. How would you minimize or treat the sample against each of them? (9)
- (c). A 4.0 mg mixture of  $AgBr$  and  $AgCl$  was quantitatively treated, reducing to 2.6 g of pure silver metal. Calculate the % of the  $AgBr$  and  $AgCl$  in the original sample. (5)
- (d). Calculate the solubility product of  $Al(OH)_3$ , given that its solubility at  $25^\circ C$  is 0.137 g/L. (3)

**Question 6 (25 marks)**

- (a). Define the following:
- (i). A primary standard for titrimetric analysis.
  - (ii). A secondary standard for titrimetric analysis. (2)
- (b). Give seven of the requirements a compound must satisfy before it can be used as a primary standard. (7)
- ©. Give one primary standard that can be used for each of the following titrations, and give one specific example of such a titration reaction respectively.
- (i). Acid – base
  - (ii). Complex formation (Or Complexiometric titration).
  - (iii). Precipitation
  - (iv). Oxidation – Reduction. (6)
- (d). Define a p-function and give two advantages of using it. (3)
- (e). A sample which weighed 0.300g was a mixture of phosphoric acid and an inert substance. The mixture was diluted with distilled water and then titrated with  $5.0 \times 10^{-2}$  M NaOH according to the following reaction:



If 29.00 mL of the titrant was required to reach the end point, calculate the %  $\text{H}_3\text{PO}_4$  in the sample. (7)

Values of Student's *t*

Degrees of freedom	Confidence level (%)				
	50	80	90	95	99
1	1.000	3.078	6.314	12.706	63.657
2	0.816	1.886	2.920	4.303	9.925
3	0.765	1.638	2.353	3.182	5.841
4	0.741	1.533	2.132	2.776	4.604
5	0.727	1.476	2.015	2.571	4.032
6	0.718	1.440	1.943	2.447	3.707
7	0.711	1.415	1.895	2.365	3.500
8	0.706	1.397	1.860	2.306	3.355
9	0.703	1.383	1.833	2.262	3.250
10	0.700	1.372	1.812	2.228	3.169
15	0.691	1.341	1.753	2.131	2.947
20	0.687	1.325	1.725	2.086	2.845
∞	0.674	1.282	1.645	1.960	2.576

Values of *t* for *v* Degrees of Freedom for Various Confidence Levels<sup>a</sup>

<i>v</i>	Confidence Level, 90%	95%	99%	99.5%
1	6.314	12.706	63.657	127.32
2	2.920	4.303	9.925	14.089
3	2.353	3.182	5.841	7.453
4	2.132	2.776	4.604	5.598
5	2.015	2.571	4.032	4.773
6	1.943	2.447	3.707	4.317
7	1.895	2.365	3.500	4.029
8	1.860	2.306	3.355	3.832
9	1.833	2.262	3.250	3.690
10	1.812	2.228	3.169	3.581
15	1.753	2.131	2.947	3.252
20	1.725	2.086	2.845	3.153
25	1.708	2.060	2.787	3.078
∞	1.645	1.960	2.576	2.807

<sup>a</sup>*v* = *N* - 1 = degrees of freedom.

Values of *F* at the 95% Confidence Level

$\nu_2 =$	$\nu_1 = 2$	3	4	5	6	7	8	9	10	15	20	30
2	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.70	8.66	8.62
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.86	5.80	5.75
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.62	4.56	4.50
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	3.94	3.87	3.81
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.51	3.44	3.38
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.22	3.15	3.08
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.01	2.94	2.86
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.85	2.77	2.70
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.40	2.33	2.25
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.20	2.12	2.04
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.01	1.93	1.84

Rejection Quotient, *Q*, at Different Confidence Limits<sup>a</sup>

No. of Observations	Confidence level		
	$Q_{90}$	$Q_{95}$	$Q_{99}$
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
15	0.338	0.384	0.475
20	0.300	0.342	0.425
25	0.277	0.317	0.393
30	0.260	0.298	0.372

<sup>a</sup>Adapted from D. B. Rorabacher, *Anal. Chem.*, 63 (1991) 139.

Quantity	Symbol	Value	General data and fundamental constants.
Speed of light†	$c$	$2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$	
Elementary charge	$e$	$1.602\,177\,3 \times 10^{-19} \text{ C}$	
Faraday constant	$F = eN_A$	$9.6485 \times 10^4 \text{ C mol}^{-1}$	
Boltzmann constant	$k$	$1.380\,66 \times 10^{-23} \text{ J K}^{-1}$	
Gas constant	$R = kN_A$	$8.314\,51 \text{ J K}^{-1} \text{ mol}^{-1}$ $8.205\,78 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ $62.364 \text{ L Torr K}^{-1} \text{ mol}^{-1}$	
Planck constant	$h$ $\hbar = h/2\pi$	$6.626\,08 \times 10^{-34} \text{ J s}$ $1.054\,57 \times 10^{-34} \text{ J s}$	
Avogadro constant	$N_A$	$6.022\,14 \times 10^{23} \text{ mol}^{-1}$	
Atomic mass unit	$u$	$1.660\,54 \times 10^{-27} \text{ kg}$	
Mass of electron	$m_e$	$9.109\,39 \times 10^{-31} \text{ kg}$	
proton	$m_p$	$1.672\,62 \times 10^{-27} \text{ kg}$	
neutron	$m_n$	$1.674\,93 \times 10^{-27} \text{ kg}$	
Vacuum permeability†	$\mu_0$	$4\pi \times 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$ $4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^2$	
Vacuum permittivity	$\epsilon_0 = 1/c^2\mu_0$ $4\pi\epsilon_0$	$8.854\,19 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$ $1.112\,65 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$	
Bohr magneton	$\mu_B = eh/2m_e$	$9.274\,02 \times 10^{-24} \text{ J T}^{-1}$	
Nuclear magneton	$\mu_N = eh/2m_p$	$5.050\,79 \times 10^{-27} \text{ J T}^{-1}$	
Electron $g$ value	$g$	2.002 32	
Bohr radius	$a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$	$5.291\,77 \times 10^{-11} \text{ m}$	
Rydberg constant	$R_\infty = m_e e^4/8h^3 c$	$1.097\,37 \times 10^5 \text{ cm}^{-1}$	
Fine structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$	
Gravitational constant	$G$	$6.672\,59 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2}$	
Standard acceleration of free fall†	$g$	$9.806\,65 \text{ m s}^{-2}$	

† Exact (defined) values

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



## PERIODIC TABLE OF ELEMENTS

PERIODS	GROUPS																		
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	
1	IA H 1.008	IIA He 4.001																	IIIA Li 6.941
2	IA Li 3	IIA Be 4																	IIIA B 10.811
3	IA Na 11	IIA Mg 12	TRANSITION ELEMENTS																IIIA Al 13
4	IA K 19	IIA Ca 20																	IIIA Ga 31
5	IA Rb 37	IIA Sr 38																	IIIA In 49
6	IA Cs 55	IIA Ba 56																	IIIA Tl 81
7	IA Fr 87	IIA Ra 88																	IIIA Pb 82
																			IIIA Bi 83
																			IIIA Po 84
																			IIIA At 85
																			IIIA Rn 86

Atomic mass →  
Symbol ←  
Atomic No.

\*Lanthanide Series

\*\*Actinide Series

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

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