

**DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SWAZILAND**

C204

INTRODUCTION TO ANALYTICAL CHEMISTRY

MAY 2011 FINAL EXAMINATION

Time Allowed:

Three (3) Hours

Instructions:

- 1. This examination has six (6) questions and one (1) data sheet. The total number of pages is four (4), including this page.**
- 2. Answer any four (4) questions fully; diagrams should be clear, large and properly labeled. Marks will be deducted for improper units and lack of procedural steps in calculations.**
- 3. Each question is worth 25 marks.**

Special Requirements

- 1. Data sheet.**
- 2. Graph paper.**

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Question 1[25]

- (a) A new microwave method for the analysis of carbon dioxide is being evaluated by comparing the results obtained using it with that of the standard method. The results of the concentrations of the gas (in $\mu\text{L}/\text{m}^3$), by the two methods are as shown in the table below:

Standard Method	Microwave Method
216	215
242	223
216	215
235	213
231	257
243	246

- (i) Calculate the pooled standard deviation from the two data sets (2)
- (ii) Employ the paired t-test to determine whether there is a significant difference between the two methods at the 95% confidence Level. (3)
- (iii) Comment on the precision of the microwave method relative to the standard one at 95% confidence level. (2)
- (b) For random errors:
- (i) Draw the Gaussian curve (2)
- (ii) Indicate clearly the position of 1σ (2)
- (iii) Indicate clearly the position of μ (1)
- (iv) Write down the equation that describes the curve, and explain all terms appearing in it (3)
- (c) Of the standardization data set for NaOH solution:

0.5365M 0.5295M 0.5466M 0.5344M 0.5545M 0.5366M

- (i) Calculate the coefficient of variation (2)
- (ii) Would the data point 0.5545 be considered an outlier at the 90% confidence level? (3)
- (iii) If the standardized solution in (v) above yielded the following results for alkalinity of waste water in 4 subsamples as follows:

53.55 mg/mL 54.21 mg/mL 49.65 mg/mL 50.22 mg/mL

Calculate the error due to the subsampling the waste water in mg/mL (5)

Question 2 [25]

- (a) For ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, as a non-aqueous solvent, write down the:
- (i) Autoprotolysis equation. (1)
 - (ii) Expression for the equilibrium constant for autoprotolysis. (1)
 - (iii) Calculate the pH of a "neutral" solution, given that the autoprotolysis constant is 5×10^{-16} . (2)
- (b) (i) Calculate the pH of a 400-mL buffer solution containing 0.200M NH_3 and 0.300M NH_4Cl (2)
(ii) Calculate the change in pH of the buffer system in b(i) above upon addition of 100mL of 0.05M HCl (4)
- (c) (i) A 0.1000M solution of HCl is used to titrate 25.00 ml of 0.0100M $\text{Ba}(\text{OH})_2$. Calculate the pH at the following volumes of HCl added during that titration (5)
- 2.00ml, at equivalence point, 5.00ml, 5.01ml, 10.00ml
- (ii) Plot the titration curve. (2)
 - (iii) Use the Henderson Equation to suggest a suitable indicator for the titration. (3)
 - (iv) Sketch the plot expected if 0.1000M HCl above is replaced with 0.1000M CH_3COOH , and state the difference between these two curves. (2)
 - (v) State the difference between "end point" and "equivalence" point in acid-base titrations (3)

Question 3 [25]

- (a) In the technique of gravimetric analysis,
- (i) State the Von Weimarn Ratio, and define all the terms in it. (3)
 - (ii) Using the Von Weimarn Ratio as reference, discuss the effects of relative supersaturation of a solution on the size of the crystalline precipitate formed in the solution concerned. (2)
 - (iii) What are the three ideal characteristics of a good analytical precipitate? (3)
- (b) (i) Define "titration error" in precipitation titrations (2)
(ii) In precipitation titrations, AgNO_3 , though not a primary standard, is universally used. What is meant by a "primary standard" (2)
- (c) (i) Consider the titration of 50 ml of 0.0100M KBr with 0.025M AgNO_3 , and calculate the pAg at the following volumes of AgNO_3 added: (5)
- 5ml, 19ml, 19.9ml, 20ml, 35ml
- (ii) Draw the titration curve for (i) above. (2)
 - (iii) On one graph, sketch three curves that you would expect to get for the system in (i) above for the following KBr concentrations:

0.005M , 0.01M , 0.015M
clearly label each one. (3)
 - (iv) On one graph, sketch three curves that you would expect to get for the system in (i) above for the following salts:

0.01M KBr , 0.01M KCl , 0.01M KI
Clearly label each one. (3)

Question 4 [25]

- (a) In complexometric titrations,
- What does the acronym "EDTA" stand for, and draw its chemical structure (2)
 - Explain what is meant by the "Chelate Effect" (3)
 - Explain what is meant by an "Indirect Titration" (3)
 - Explain what is meant by a "Back Titration" (3)
 - Draw the chemical structure of the indicator calmagite, and explain how it works in the titration of Mg^{2+} ions with EDTA (4)
- (b) Calculate pFe given that $\log K_f$ for the $(EDTA)^{4-}$ is 25.1 for a solution of 0.10M $Fe(EDTA)^{-}$ in pH=8 (3)
- (c) Suppose a 25.00ml solution of 0.02026M Co^{2+} is titrated with 0.03855M EDTA at pH = 6.00. Calculate the pCo at the following volumes of EDTA added:
- 0.10ml 12.00ml equivalence point volume 14.00ml
- and plot the titration curve. (5)
- (d) Explain the role of an auxiliary complexing reagent in EDTA titrations. (2)

Question 5[25]

- (a) (i) Use a chemical equation to state the difference between an oxidizing agent and a reducing agent.(2)
- (ii) Suppose that electrons are forced into a Pt wire immersed in a solution containing Sn^{4+} , which undergoes a two-electron change to Sn^{2+} at a constant rate of 4.24 mmol/hr. How much current in mA, flows into the solution? (5)
- (b) An acid solution of $Na_2Cr_2O_7$ is mixed with a solution of KBr. A redox reaction occurs, resulting in Br_2 and Cr^{3+} . Write a balanced equation for the redox reaction. (3)
- (c) For the redox system $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$, in which 0.58g of Fe^{3+} is starting material,
- How much charge should be applied to completely reduce the Fe^{3+} ? (3)
 - If the process in (i) above were to take place in 10 minutes, how much constant current should be applied ($F=9.648 \times 10^4 C$)? (2)
- (d) The standard hydrogen electrode (SHE) is the electrode against which all electrode potentials are referenced.
- Draw the SHE and label all its components. (3)
 - Write down the half cell reaction taking place in the SHE, and state the electrode potential.(2)

- (iii) State the function of a salt bridge and explain how it works. (1)
- (e) Suppose a 10ml solution of 0.05M Fe^{2+} is titrated with 0.100 M Ce^{4+} in 1M HClO_4 and the potential measured relative to the saturated calomel electrode (SCE, $E = 0.241\text{V}$). Calculate the measured potential at the following values of 0.100 M Ce^{4+} added:
- 2.50ml 4.99ml 5.0ml 7.00ml
- And plot the titration curve. (4)

Question 6[25]

- (a) Ammonia, NH_3 , is allowed to distribute between water at pH=5 and carbon tetrachloride, CCl_4 .
- (i) Write down the equilibrium equation in the aqueous phase (1)
- (ii) Write down the distribution ratio expression for this solvent extraction system. (2)
- (iii) Write down the distribution coefficient expression for this solvent extraction system(2)
- (b) Describe four desirable properties of an ideal choice of solvent in liquid-liquid extraction(4)
- (c) Extractions are enhanced through the use of chelation. Write down the chemical structures of the following chelating agents
- (i) Oxime (2)
- (ii) Dithizone (2)
- (d) In the determination of trace nickel by liquid-liquid extraction, several reagents are added prior to the extraction step.
- (i) Name and write chemical structure of the compound used to form the nickel complex that extracts into chloroform (3)
- (ii) Explain the role of hydroxylamine hydrochloride in the analysis (2)
- (iii) Explain the role of pH 6.5 acetate buffer in this analysis (2)
- (e) The distribution ratio of iodine gas (at. Wt. = 126.9045) between water and carbon tetrachloride is 85. A 50-mL solution containing 0.35 grams of iodine and 75 ppm of Cd is mixed with 25 mL of carbon tetrachloride in order to remove the iodine into the organic phase. Calculate the number of times that the extraction needs to be performed in order to get 99.999% of the iodine into the organic phase. (5)

Table 4-4
Values of \bar{Q} for rejection of data

Number of observations	\bar{Q} (90% confidence)
3	0.94
4	0.76
5	0.64
6	0.56
7	0.51
8	0.47
9	0.44
10	0.41

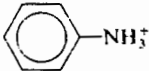
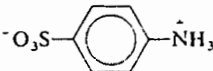
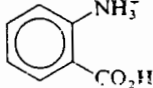
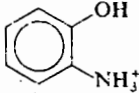
Table 4-2
Values of Student's t

Degrees of freedom	99	95	90	80	50
1	6.3657	12.706	6.314	3.078	1.000
2	9.925	4.303	2.920	1.886	0.816
3	5.841	3.182	2.353	1.638	0.765
4	4.604	2.776	2.132	1.533	0.741
5	4.032	2.571	2.015	1.476	0.727
6	3.707	2.447	1.943	1.440	0.718
7	3.500	2.365	1.895	1.415	0.711
8	3.355	2.306	1.860	1.397	0.706
9	3.250	2.262	1.833	1.383	0.703
10	3.169	2.228	1.812	1.372	0.700
15	2.947	2.131	1.753	1.341	0.691
20	2.845	2.086	1.725	1.325	0.687
∞	2.576	1.960	1.645	1.282	0.674

Table 26-5
VALUES OF F AT THE
95% CONFIDENCE LEVEL

v_2	v_1	2	3	4	5	6	∞
2	19.00	19.16	19.25	19.30	19.33	19.50	19.50
3	9.55	9.28	9.12	9.01	8.94	8.53	8.53
4	6.94	6.59	6.39	6.26	6.16	5.63	5.63
5	5.79	5.41	5.19	5.05	4.95	4.36	4.36
6	5.14	4.76	4.53	4.39	4.28	3.67	3.67
∞	3.00	2.60	2.37	2.21	2.10	1.00	1.00

G / Acid Dissociation Constants

Name	Structure [†]	pK _a [‡]	K _a
Acetic acid (ethanoic acid)	CH ₃ CO ₂ H	4.757	1.75 × 10 ⁻⁵
Alanine	$\begin{array}{c} \text{NH}_3^+ \\ \\ \text{CHCH}_3 \\ \\ \text{CO}_2\text{H} \end{array}$	2.348 (CO ₂ H) 9.867 (NH ₃)	4.49 × 10 ⁻³ 1.36 × 10 ⁻¹⁰
Aminobenzene (aniline)		4.601	2.51 × 10 ⁻⁵
4-Aminobenzenesulfonic acid (sulfanilic acid)		3.232	5.86 × 10 ⁻⁴
2-Aminobenzoic acid (anthranilic acid)		2.08 (CO ₂ H) 4.96 (NH ₃)	8.3 × 10 ⁻³ 1.10 × 10 ⁻⁵
2-Aminoethanethiol (2-mercaptoethylamine)	HSCH ₂ CH ₂ NH ₃ ⁺	8.21 (SH) (μ = 0.1) 10.71 (NH ₃) (μ = 0.1)	6.2 × 10 ⁻⁹ 1.95 × 10 ⁻¹¹
2-Aminoethanol (ethanolamine)	HOCH ₂ CH ₂ NH ₃ ⁺	9.498	3.18 × 10 ⁻¹⁰
2-Aminophenol		4.78 (NH ₃) (20°) 9.97 (OH) (20°)	1.66 × 10 ⁻⁵ 1.05 × 10 ⁻¹⁰
Ammonia	NH ₄ ⁺	9.244	5.70 × 10 ⁻¹⁰
Arginine	$\begin{array}{c} \text{NH}_3^+ \\ \\ \text{CHCH}_2\text{CH}_2\text{CH}_2\text{NHC} \begin{array}{l} \text{=NH}_2^+ \\ \text{NH}_2 \end{array} \\ \\ \text{CO}_2\text{H} \end{array}$	1.823 (CO ₂ H) 8.991 (NH ₃) (12.48) (NH ₂)	1.50 × 10 ⁻² 1.02 × 10 ⁻⁹ 3.3 × 10 ⁻¹³
Arsenic acid (hydrogen arsenate)	$\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{As}-\text{OH} \\ \\ \text{OH} \end{array}$	2.24 6.96 11.50	5.8 × 10 ⁻³ 1.10 × 10 ⁻⁷ 3.2 × 10 ⁻¹²

[†] Each acid is written in its protonated form. The acidic protons are indicated in bold type.

[‡] pK_a values refer to 25°C and zero ionic strength unless otherwise indicated. Values in parentheses are considered to be less reliable. Data are from A. E. Martell and R. M. Smito, *Critical Stability Constants* (New York: Plenum Press, 1974).

$$N = 14.01$$

$$u = 35.45$$

$$H = 1.0079$$

pH	$\alpha_{Y^{4-}}$
0	1.3×10^{-23}
1	1.9×10^{-18}
2	3.3×10^{-14}
3	2.6×10^{-11}
4	3.8×10^{-9}
5	3.7×10^{-7}
6	2.3×10^{-5}
7	5.0×10^{-4}
8	5.6×10^{-3}
9	5.4×10^{-2}
10	0.36
11	0.85
12	0.98
13	1.00
14	1.00

Table 14-2
Formation constants for metal-EDTA complexes

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li ⁺	2.79	Mn ²⁺	25.3 (25 C)	Ce ³⁺	15.98
Ni ²⁺	1.66	Fe ³⁺	25.1	Pt ²⁺	16.40
K ⁺	0.8	Co ³⁺	41.4 (25 C)	Nd ³⁺	16.61
Rc ³⁺	9.2	Zr ⁴⁺	29.5	Pm ³⁺	17.0
Mg ²⁺	8.79	Hf ⁴⁺	29.5 ($\mu = 0.2$)	Sm ³⁺	17.14
Cu ²⁺	10.69	VO ²⁺	18.8	Eu ³⁺	17.35
Sr ²⁺	8.73	VO ₂ ⁺	15.55	Gd ³⁺	17.37
Bar ²⁺	7.86	Ag ⁺	7.32	Tb ³⁺	17.93
Ra ²⁺	7.1	Tl ⁺	6.54	Dy ³⁺	18.30
Sc ³⁺	23.1	Pd ²⁺	18.5 (25 C)	Ho ³⁺	18.62
			$\mu = 0.2$		
Y ³⁺	18.09			Er ³⁺	18.85
La ³⁺	15.50			Tm ³⁺	19.32
V ²⁺	12.7	Zn ²⁺	16.50	Yb ³⁺	19.51
Cr ²⁺	13.6	Cd ²⁺	16.46	Lu ³⁺	19.83
Mn ²⁺	13.87	Hg ²⁺	21.7	Am ³⁺	17.8 (25 C)
Fe ²⁺	14.32	Sn ²⁺	18.3 ($\mu = 0$)	Cm ³⁺	18.1 (25 C)
Co ²⁺	16.31	Pb ²⁺	18.04	Bk ³⁺	18.5 (25 C)
Ni ²⁺	18.62	Al ³⁺	16.3	Cf ³⁺	18.7 (25 C)
Cu ²⁺	18.80	Ga ³⁺	20.3	Th ⁴⁺	23.2
Ti ³⁺	21.3 (25 C)	In ³⁺	25.0	U ⁴⁺	25.8
V ³⁺	26.0	Tl ³⁺	37.8 ($\mu = 1.0$)	Np ⁴⁺	24.6 (25 C, $\mu = 1.0$)
Cr ³⁺	23.4	Bi ³⁺	27.8		

Note: The stability constant is the equilibrium constant for the reaction $M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$. Values in table apply at 20 C, and ionic strength 0.1 M, unless otherwise noted.
Source: Data from A. F. Martell and R. M. Smith, *Critical Stability Constants*, Vol. 1 (New York: Plenum Press, 1974), pp. 204-211.