CHUKA  **UNIVERSITY**

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN INDUSTRIAL CHEMISTRY

CHIN 101: QUANTITATIVE CHEMICAL ANALYSIS

STREAMS: BSC. CHIN **TIME: 2 HOURS**

DAY/DATE: WEDNESDAY 16/04/2025 **11.30 A.M. – 1.30 P.M.**

INSTRUCTIONS

- Answer Question **ONE** and any other **TWO** questions.
- Useful data are provided

General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.997 925 58*	10^{8}	$m\ s^{-1}$
Elementary charge	e	1.602 176	10^{-19}	C
Faraday's constant	$F = N_A e$	9.648 53	10^{4}	$C\ mol^{-1}$
Boltzmann's constant	k	1.380 65	10^{-23}	$J\ K^{-1}$
Gas constant	$R = N_A k$	8.314 47		$J\ K^{-1}\ mol^{-1}$
		8.314 47	10^{-2}	$dm^3\ bar\ K^{-1}\ mol^{-1}$
		8.205 74	10^{-2}	$dm^3\ atm\ K^{-1}\ mol^{-1}$
		6.236 37	10	$dm^3\ Torr\ K^{-1}\ mol^{-1}$
Planck's constant	h	6.626 08	10^{-34}	J s
	$\hbar = h/2\pi$	1.054 57	10^{-34}	J s
Avogadro's constant	N_A	6.022 14	10^{23}	mol^{-1}
Atomic mass constant	m_u	1.660 54	10^{-27}	kg
Mass				
electron	m_e	9.109 38	10^{-31}	kg
proton	m_p	1.672 62	10^{-27}	kg
neutron	m_n	1.674 93	10^{-27}	kg
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	8.854 19	10^{-12}	$J^{-1}\ C^2\ m^{-1}$
	$4\pi\varepsilon_0$	1.112 65	10^{-10}	$J^{-1}\ C^2\ m^{-1}$
Vacuum permeability	μ_0	4π	10^{-7}	$J\ s^2\ C^{-2}\ m^{-1}\ (= T^2\ J^{-1}\ m^3)$
Magneton				
Bohr	$\mu_B = e\hbar/2m_e$	9.274 01	10^{-24}	$J\ T^{-1}$
nuclear	$\mu_N = e\hbar/2m_p$	5.050 78	10^{-27}	$J\ T^{-1}$
g value	g_e	2.002 32		
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	5.291 77	10^{-11}	m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 35	10^{-3}	
	α^{-1}	1.370 36	10^{2}	
Second radiation constant	$c_2 = hc/k$	1.438 78	10^{-2}	m K
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3c^2$	5.670 51	10^{-8}	$W\ m^{-2}\ K^{-4}$
Rydberg constant	$R = m_e e^4/8h^3 c\varepsilon_0^2$	1.097 37	10^{5}	cm^{-1}
Standard acceleration of free fall	g	9.806 65*		$m\ s^{-2}$
Gravitational constant	G	6.673	10^{-11}	$N\ m^2\ kg^{-2}$

Exact value

QUESTION ONE (30 MARKS)

a) i) One quantitative analytical method for tetraethylthiuram disulfide, $C_{10}H_{20}N_2S_4$ (Antabuse), requires oxidizing the sulfur to SO_2, and bubbling the resulting SO_2 through H_2O_2 to produce H_2SO_4. The H_2SO_4 is then reacted with NaOH according to the reaction

$$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(\ell)$$

Using appropriate conservation principles, derive an equation relating the moles of $C_{10}H_{20}N_2S_4$ to the moles of NaOH. Determine the weight percent $C_{10}H_{20}N_2S_4$ in a sample of Antabuse if the H_2SO_4 produced from a 0.4613-g portion reacts with 34.85 mL of 0.02500 M NaOH. (3 marks)

iii) The %w/w Na_2CO_3 in soda ash can be determined by an acid–base titration. The results obtained by two analysts are shown here. Determine whether the difference in their mean values is significant at a = 0.05.

Analyst A	Analyst B
86.82	81.01
87.04	86.15
86.93	81.73
87.01	83.19
86.20	80.27
87.00	83.94

(3 marks)

b) i) Lord Rayleigh, John William Strutt (1842–1919) was one of the most well-known scientists of the late nineteenth and early twentieth centuries, publishing over 440 papers and receiving the Nobel Prize in chemistry in 1904 for the discovery of argon. An important turning point in the discovery of Ar was Rayleigh's experimental measurements of the density of N_2. Rayleigh approached this experiment in two ways: first by taking atmospheric air and removing any O_2 and H_2 that was present; and second, by chemically producing N_2 by decomposing nitrogen-containing compounds (NO, N_2O, and NH_4NO_3) and again removing any O_2 and H_2. His results for the density of N_2, published in *Proc. Roy. Soc.* 1894, *LV,* 340 (publication 210), follow (all values are for grams of gas at equivalent volume, pressure, and temperature).

Atmospheric	2.31017	2.30986	2.31010	2.31001
Origin:	2.31024	2.31010	2.31028	
Chemical	2.30143	2.29890	2.29816	2.30182
Origin:	2.29869	2.29940	2.29849	2.29889

Explain why these data led Rayleigh to look for and discover Ar. (3 marks)

ii) Using a ladder diagram, explain why the following reaction

$$H_3PO_4(aq) + F^-(aq) \rightleftharpoons HF(aq) + H_2PO_4^-(aq)$$

Is favorable, whereas

$$H_3PO_4(aq) + 2F^-(aq) \rightleftharpoons 2HF(aq) + H_2PO_4^{2-}(aq)$$

Is unfavorable. Determine the equilibrium constant for these reactions, and verify that they are consistent with your ladder diagram. (2 marks)

iii) When solutions of 1.5 M KNO_3 and 1.5 M $HClO_4$ are mixed, a white precipitate of $KClO_4$ is formed. If traces of MnO_4^- are present, an inclusion of $KMnO_4$ is possible. Impure precipitates of

$KClO_4$ are colored purple by the included $KMnO_4$. Following are the descriptions and results for two experiments in which $KClO_4$ is precipitated in the presence of MnO_4^-. Explain why the two experiments lead to different results.

Experiment 1. Place 1 mL of 1.5 M KNO_3 in a test tube, add 3 drops of 0.1 M $KMnO_4$, and swirl to mix. Add 1 mL of 1.5M $HClO_4$ drop wise, agitating the solution between drops.

Destroy the excess $KMnO_4$ by adding 0.1 M $NaHSO_3$ drop wise. The resulting precipitate of $KClO_4$ has an intense purple color.

Experiment 2. Place 1 mL of 1.5 M $HClO_4$ in a test tube, add 3 drops of 0.1 M $KMnO_4$, and swirl to mix. Add 1 mL of 1.5M KNO_3 drop wise, agitating the solution between drops.

Destroy the excess $KMnO_4$ by adding 0.1 M $NaHSO_3$ drop wise. The resulting precipitate of $KClO_4$ is pale purple or white in color. (2.5 marks)

c) i) Aluminum can be determined gravimetrically by precipitating as $Al(OH)_3$ and isolating as Al_2O_3. A sample containing approximately 0.1 g of Al is dissolved in 200 mL of H_2O and 5 g of NH_4Cl and a few drops of methyl red indicator is added (methyl red is red at pH levels below 4 and yellow at pH levels above 6). The solution is heated to boiling, and 1:1 NH_3 is added drop wise till the indicator turns yellow, precipitating $Al(OH)_3$. The precipitate is held at the solution's boiling point for several minutes, filtered, and washed with a hot solution of 2%, w/v NH_4NO_3. The precipitate is then ignited at 1000–1100 °C, forming Al_2O_3.

I. Cite two ways in which this procedure has been designed to encourage the formation of larger particles of precipitate. (2 marks)

II. The ignition step must be carried out carefully to ensure that $Al(OH)_3$ is quantitatively converted to Al_2O_3. What effect would an incomplete conversion have on the reported %w/w Al? (1 mark)

III. What role do NH_4Cl and methyl red indicator play in this procedure? (1 mark)

IV. An alternative procedure involves isolating and weighing the precipitate as the 8-hydroxyquinolate, $Al(C_9H_6ON)_3$. Why might this be a more advantageous form of Al for a gravimetric analysis? (1 mark)

ii) Calcium is determined gravimetrically by precipitating it as $CaC_2O_4.H_2O$, followed by isolating the precipitate as $CaCO_3$. The sample to be analyzed is dissolved in 10 mL of water and 15 mL of 6 M HCl. After dissolution, the resulting solution is heated to boiling, and a warm solution of

excess ammonium oxalate is added. The solution is maintained at 80 °C, and 6 M NH_3 is added drop wise with stirring, until the solution is faintly alkaline. The resulting precipitate and solution are removed from the heat and allowed to stand for at least 1 h. After testing the solution for completeness of precipitation, the sample is filtered, washed with 0.1% w/v ammonium oxalate, and dried at 100–120 °C for 1 h. The precipitate is then transferred to a muffle furnace where it is converted to $CaCO_3$ by drying at 500 ± 25 °C until a constant weight.

I. Why is the precipitate of $CaC_2O_4.H_2O$ converted to $CaCO_3$? (1.5 marks)

II. In the final step, if the sample is heated at high temperatures, some $CaCO_3$ may be converted to CaO. What effect would this have on the reported %w/w Ca? (1 mark)

III. Why is the precipitant, $(NH_4)_2C_2O_4$, added to a hot, acidic solution rather than to a cold, alkaline solution? (1 mark)

iii) Discuss the characteristics of a quality assurance unit. (3 marks)

iv) Distinguish among repeatability, ruggedness, robustness and reproducibility of a method. (4 marks)

v) Would it be possible to estimate sodium hydroxide and ammonia in a solution of the two in water by direct titration with hydrochloric acid using two indicators, one of pK 11 and the other of pK 4?

QUESTION TWO (20 MARKS)

a) i) Discuss the two aspects of the validation process. (5 marks)

ii) The following data were obtained for the duplicate analysis of a stable standard

Sample	X_1 (ppm)	X_2 (ppm)	Sample	X_1 (ppm)	X_2 (ppm)
1	50	46	14	36	36
2	37	36	15	47	45
3	22	19	16	16	20
4	17	20	17	18	21
5	32	34	18	26	22
6	46	46	19	35	36
7	26	28	20	26	25
8	26	30	21	49	51
9	61	58	22	33	32
10	44	45	23	40	38
11	40	44	24	16	13
12	36	35	25	39	42
13	29	31			

Construct a precision control chart for these data, and evaluate the state of statistical control.

(4 marks)

Statistical factors for the upper warning limit and upper control limit

Replicates	fuwl	fucl
2	2.512	3.267
3	2.050	2.575
4	1.855	2.282
5	1.743	2.115
6	1.669	2.004

iii) I. Explain the term Z score as used in quality assurance. (1 mark)

II. You participate in a collaborative study for measuring lead in leaves. A homogeneous standard reference material of ground leaves, certified to contain 10.3 ± 0.5 ppm lead, is given to the participating labs. You analyze the sample, using acid digestion and atomic absorption spectrometry. You report 9.8 ± 0.3 ppm for seven analyzed aliquots. Determine the *z* value for your laboratory. (1 mark)

iv) The quantity of charge, *Q*, in coulombs passing through an electrical circuit is

$$Q = I \times t$$

where I is the current in amperes and t is the time in seconds. When a current of 0.15 ± 0.01 A passes through the circuit for 120 ± 1 s, the total charge is

$$Q = (0.15\ \text{A}) \times (120\ \text{s}) = 18\ \text{C}$$

Calculate the absolute and relative uncertainties for the total charge. (1 mark)

b) i) Describe how you can determine copper in a mixture of nitric and sulphuric acid solutions, include the reaction at cathode and anode using electro gravimetric at a constant current. (2 marks)

ii) A 0.1475-M solution of $Ba(OH)_2$ was used to titrate the acetic acid (60.05 g/mol) in a dilute aqueous solution. The following results were obtained.

Sample	Sample Volume, mL	$Ba(OH)_2$ Volume, mL
1	50.00	43.17
2	49.50	42.68
3	25.00	21.47
4	50.00	43.33

I. Calculate the mean w/v percentage of acetic acid in the sample. (2 marks)

II. Calculate the standard deviation for the results. (1 mark)

III. Calculate the 90% confidence interval for the mean. (1 mark)

IV. At the 90% confidence level, could any of the results be discarded? (1 mark)

iii) Account why acid/base indicator exhibit its color change over a range of about 2 pH units. (1 mark)

QUESTION THREE (20 MARKS)

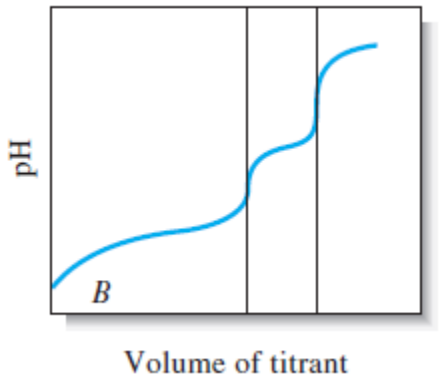
a) i) Tartaric acid, $H_2C_4H_4O_6$, is a diprotic weak acid with a pK_{a1} of 3.0 and a pK_{a2} of 4.4. Suppose you have a sample of impure tartaric acid (%purity > 80) and that you plan to determine its purity by titrating with a solution of 0.1 M NaOH using a visual indicator to signal the end point. Describe how you would carry out the analysis, paying particular attention to how much sample you would use, the desired pH range over which you would like the visual indicator to operate, and how you would calculate the %w/w tartaric acid. (4 marks)

ii) Suggest with explanation an indicator that could be used to provide an end point for the titration of;

I. The first proton in H_3AsO_4. (1 mark)

II. The first two protons in H_3AsO_4 (1 mark)

iii) Briefly explain why curve *B cannot* describe the titration of a mixture consisting of H_3PO_4 and NaH_2PO_4. (1 mark)



b) i) Explain why nitric acid is seldom used to prepare standard acid solutions. (1 mark)

ii) Describe how Na_2CO_3 of primary-standard grade can be prepared from primary-standard $NaHCO_3$. (1 mark)

iii) The boiling points of HCl and CO_2 are nearly the same (285°C and 278°C). Explain why CO_2 can be removed from an aqueous solution by boiling briefly while essentially no HCl is lost even after boiling for 1 h or more. (1 mark)

c) i) Discuss determination of copper ion in water sample using spectrophotometric titration with EDTA. (3 marks)

ii) A 0.5000-g sample containing $NaHCO_3$, Na_2CO_3, and H_2O was dissolved and diluted to 250.0 mL. A 25.00-mL aliquot was then boiled with 50.00 mL of 0.01255 M HCl. After cooling, the excess acid in the solution required 2.34 mL of 0.01063 M NaOH when titrated to a phenolphthalein end point. A second 25.00-mL aliquot was then treated with an excess of $BaCl_2$ and 25.00 mL of the base. All the carbonate precipitated, and 7.63 mL of the HCl was required to titrate the excess base. Determine the composition of the mixture. (3 marks)

iii) Describe three general methods for performing EDTA titrations. State the advantages of each. (4 marks)

QUESTION FOUR (20 MARKS)

a) i) While working as a laboratory assistant you prepared 0.4 M solutions of $AgNO_3$, $Pb(NO_3)_2$, $BaCl_2$, KI, and Na_2SO_4. Unfortunately, you became distracted and forgot to label the solutions before leaving the laboratory. Realizing your error, you labeled the solutions A–E and performed all possible binary mixings of the five solutions. The following results were obtained where NR means no reaction was observed, W means a white precipitate formed, and Y means a yellow precipitate formed.

	A	B	C	D	E
A		NR	Y	NR	W
B			Y	W	W
C				NR	NR
D					W

Identify solutions A–E. (2.5 marks)

ii) Explain using a suitable example the mechanism of adsorption indicator during titration. (2 marks)

b) (i) Discuss the advantages of spectrophotometric titrations. (2 marks)

ii) Distinguish between acid-base, metal-ion and adsorption indicators. (3 marks)

iii) Critically discuss gravimetric method. (2.5 marks)

c) i) I. Explain how a particle size can be controlled during gravimetric analysis. (3 marks)

II. Discuss how gravimetric method is useful in the industries. (2 marks)

ii) A 1.217-g sample of commercial KOH contaminated by K_2CO_3 was dissolved in water, and the resulting solution was diluted to 500.0 mL. A 50.00-mL aliquot of this solution was treated with 40.00 mL of 0.05304 M HCl and boiled to remove CO_2. The excess acid consumed 4.74 mL of 0.04983 M NaOH (phenolphthalein indicator). An excess of neutral $BaCl_2$ was added to another 50.00-mL aliquot to precipitate the carbonate as $BaCO_3$. The solution was then titrated with 28.56 mL of the acid to a phenolphthalein end point. Calculate the percentage KOH, K_2CO_3, and H_2O in the sample, assuming that these are the only compounds present. (3 marks)

Table 3.1

Values of t for ν Degrees of Freedom for Various Confidence Levels[a]

	Confidence Level			
ν	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

[a] $\nu = N - 1$ = degrees of freedom.