**UNIVERSITY OF RUHUNA**

**Bachelor of Science in Marine and Freshwater Sciences Degree**

**Bachelor of Science in Fisheries and Marine Sciences Degree**

**Examination-July/August 2017**

**Level I, Semester I**

**CHM 1122: Analytical Chemistry I**

Time: 1 ½ hrs

Answer only **three (03)** questions

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(01) Answer **all** parts

(a) Define briefly each of the following terms.

(i) Buffer solution

(ii) Buffer capacity

(iii) Primary standard substance

**(15 marks)**

(b) Consider the ethanoic acid ($CH_3COOH$) / sodium ethanoate ($CH_3COO^-Na^+$) buffer system.

(i) Calculate the pH of a buffer solution where [$CH_3COOH$] is 0.1 mol $dm^{-3}$ and [$CH_3COO^-$] is 0.2 mol $dm^{-3}$. The $K_a$ of the weak acid $CH_3COOH$ is $1.8 \times 10^{-5}$ mol $dm^{-3}$.

(ii) If you add 2.00 mL of 0.10 M HCl to 100 mL of the above buffer solution, what will be the new pH?

(iii) If you add 2.00 mL of 0.10 M HCl to 100 mL of distilled water calculate pH of the resultant solution.

**(55 marks)**

(c) Sketch the titration curves for the following acid-base mixtures. Clearly label the axes in your drawing. (Assume base is always in the titration flask)

(i) Strong acid- Strong base

(ii) Strong acid- weak base

(iii) Titration of a $Na_2CO_3$ solution with standard HCl

**(30 marks)**

**(02)** (a) Briefly explain the following terms pertaining to the complexometric titrations.

(i) Auxiliary complexing agents

(ii) Masking and demasking

(20 marks)

(b) In the determination of hardness of water and wastewater small amount of Mg-EDTA complex is added to the sample. Explain chemistry pertaining to this statement.

(20 marks)

(c) A student titrated 50.00 mL of $Ca^{2+}$ ion solution buffered to pH 10 with 0.0600 mol $dm^{-3}$ EDTA solution in the presence of calmagite indicator. He observed a sharp colour change from blue to wine red when 25.00 mL 0.0600 mol $dm^{-3}$ EDTA solution was reacted with the $Ca^{2+}$ solution.

(i) What is the $Ca^{2+}$ ion concentration of the solution?

(ii) Calculate the conditional formation constant $K_f'$ for the $CaY^{2-}$complex at pH =10

Note: For $Ca^{2+}$ $\log K_f = 10.65$, $\alpha_{Y4-} = 0.30$for EDTA at pH = 10

(iii) Calculate the concentration of $CaY^{2-}$ at the equivalence point

(iv) Calculate the pCa at the equivalence point. (Assume that the dissociation of $CaY^{2-}$ at pH = 10 is very small)

(35 marks)

(d) A 25.00 mL aliquot of a solution containing $Cu^{2+}$ and $Fe^{3+}$ was titrated with 16.06 mL of 0.0508 M EDTA. A second 25.00 mL aliquot of the $Cu^{2+}/Fe^{3+}$ mixture was treated with NaF to form a stable iron-fluoride complex. This mixture was then titrated with 0.0508 M EDTA and the endpoint volume was found to be 5.43 mL. Calculate the molar concentrations of $Cu^{2+}$ and $Fe^{3+}$in the aliquot.

(25 marks)

**(03)** **(a)** Explain the chemistry pertaining to the following statements

(i) $Na_2CrO_4$ can be used as an indicator in the determination of $Cl^-$ ions by precipitation titration with $AgNO_3$

(ii) $K_2Cr_2O_7$is widely used in redox titrations.

(20 marks)

(b) Sodium thiosulfate is used as a topical antifungal agent in medicine. Concentration of thiosulfate is determined by reacting it with $KIO_3$and $I_2$. During this titration KI reacts with $KIO_3$ in acidic medium to yield $I_2$. Liberated $I_2$ then reacts with sodium thiosulfate solution. A student dissolved 0.1322 g of $KIO_3$ (FW 214 g/mol) in water adding large excess of KI and acidifying with $H_2SO_4$ acid. The liberated $I_2$ consumed 28.50 mL of the sodium thiosulfate solution at the end point.

(i) Write down balanced chemical equations for the reactions between,

(I) $KIO_3$ and KI in acidic medium

(II) $I_2$ and $S_2O_3^{2-}$

(ii) Calculate the concentration of sodium thiosulfate solution.

(iii) Explain how you would detect the end point of the above titration.

(iv) Discuss briefly the possible errors associated with the above titration and how you would minimize them.

(50 marks)

(c) (i) State desired properties of a precipitate product in gravimetric analysis

(ii) What steps would you take to maximize crystal growth in gravimetric analysis?

(30 marks)

**(04)** Answer **all** parts

(a) Briefly discuss the following terms.

(i) Systematic errors

(ii) Random errors

(iii) Relative Uncertainty

(25 marks)

(b) The Hg content of five different fish verities was measured with two different experimental methods and the results are shown in the following table.

| Fish verity | Hg content (wt %) by Method 1 | Hg content (wt %) by Method 2 |
|---|---|---|
| A | 0.0134 | 0.0135 |
| B | 0.0144 | 0.0156 |
| C | 0.0126 | 0.0137 |
| D | 0.0125 | 0.0137 |
| E | 0.0137 | 0.0136 |
| Standard deviation | 0.00079 | 0.00089 |

(i) Calculate the average Hg content of the data measured by the two methods.

(ii) Do the two analytical methods give results that are significantly different at the 95% confidence level?

(40 marks)

(c) A student titrated commercially available vinegar sample with 0.01 M NaOH to determine acetic acid percentage present in the sample and the results are shown in the following table.

| Sample | Acetic acid (w %) |
|---|---|
| 1 | 4.4 |
| 2 | 4.6 |
| 3 | 4.1 |
| 4 | 5.2 |

(ii) Calculate the average, standard deviation and coefficient of variation.

(iii) Identify any rejectable data point at the 95% confidence level.

(35 marks)

Note :

(i) For two sets of data consisting of $n_1$ and $n_2$ and measurements (with averages $\overline{X}1$ and $\overline{X}2$ ), *t*value is calculated with the formula

$$t_{calculated} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{pooled}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}} \qquad \text{S pooled} = \sqrt{\frac{s_1^2 (n_1 - 1) + s_2^2 (n_2 - 1)}{n_1 + n_2 - 2}}$$

$s_1$ and $s_2$ are the standard deviations of the two sets of data with $n_1$ and $n_2$ measurements.

$t_{calculated}$ is compared with for $n_1 + n_2 - 2$ degrees of freedom.

(ii) Qcrit = ($|Xq-Xn|/X_{highest}-X_{lowest}$) where Xq is the questionable result and Xn is the nearest neighbor of the questionable result

## Values of $t$ for Various Levels of Probability

| Degrees of Freedom | 80% | 90% | 95% | 99% | 99.9% |
|---|---|---|---|---|---|
| 1 | 3.08 | 6.31 | 12.7 | 63.7 | 637 |
| 2 | 1.89 | 2.92 | 4.30 | 9.92 | 31.6 |
| 3 | 1.64 | 2.35 | 3.18 | 5.84 | 12.9 |
| 4 | 1.53 | 2.13 | 2.78 | 4.60 | 8.61 |
| 5 | 1.48 | 2.02 | 2.57 | 4.03 | 6.87 |
| 6 | 1.44 | 1.94 | 2.45 | 3.71 | 5.96 |
| 7 | 1.42 | 1.90 | 2.36 | 3.50 | 5.41 |
| 8 | 1.40 | 1.86 | 2.31 | 3.36 | 5.04 |
| 9 | 1.38 | 1.83 | 2.26 | 3.25 | 4.78 |
| 10 | 1.37 | 1.81 | 2.23 | 3.17 | 4.59 |
| 15 | 1.34 | 1.75 | 2.13 | 2.95 | 4.07 |
| 20 | 1.32 | 1.73 | 2.09 | 2.84 | 3.85 |
| 40 | 1.30 | 1.68 | 2.02 | 2.70 | 3.55 |
| 60 | 1.30 | 1.67 | 2.00 | 2.62 | 3.46 |
| ∞ | 1.28 | 1.64 | 1.96 | 2.58 | 3.29 |

## Rejection Quotient, $Q$, at Different Confidence Limits[a]

| 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 |