00173

THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 4

Final Examination Paper

CYU4302— Practical Chemistry II

(2 *hours*)

14th June 2019 (Friday) 9.30 a.m. — 11.30 a.m.

- There are four (04) questions and six (06) pages (including the first page) in the paper.
- Answer **ALL FOUR** (04) questions.
- The use of a non-programmable calculator is permitted
- Mobile phones are **not** allowed.

Gas constant (R)	=	$8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$
Avogadro constant (N_A)	=	$6.023\times10^{23}\ \mathrm{mol^{-1}}$
Faraday constant (F)	=	$96,500\ \mathrm{C\,mol^{-1}}$
Planck constant (h)	=	$6.63\times10^{-34}\ \mathrm{J\,s}$
Velocity of light (c)	=	$3.0\times10^{8}\ \mathrm{m\,s^{-1}}$
Standard atmospheric pressure	=	$10^5\ \mathrm{Pa}\left(\mathrm{N\,m^{-2}}\right)$
π	=	3.14159
$\mathrm{Log}_e(X)$	=	$2.303\ \mathrm{Log}_{10}(X)$

Some equations used in chemistry are given below in standard notation.

For $W=\frac{ab}{c}$; $\left(\frac{\delta W}{W}\right)^2=\left(\frac{\delta a}{a}\right)^2+\left(\frac{\delta b}{b}\right)^2+\left(\frac{\delta c}{c}\right)^2$

$$-\frac{d[A]}{dt}=k[A] \qquad \int_{[A]_0}^{[A]_t}\frac{d[A]}{[A]}=\ln[A]_t-\ln[A]_0 \qquad A=-\log_{10}\left(\frac{I}{I_0}\right)=\varepsilon C l$$

$$\Lambda_Y=\frac{\kappa_Y}{C_Y} \qquad \Lambda_{MX_2}=\lambda_{M^{Z+}}+2\lambda_{X^{Z-}} \qquad \log_{10}(\gamma_\pm)=-\frac{A\left|Z_+Z_-\right|\sqrt{I}}{1+aB\sqrt{I}}$$

1. (a) (i) Define the error in an experimentally determined value of a physical quantity.
(ii) Briefly explain why the error cannot be determined exactly.

(10 marks)

(b) A student was asked to measure the electromotive force (emf), E_A, of a Galvanic cell A using a potentiometer. With cell A connected, he measured the length, X, of the potentiometer resistor wire when there is no current through the galvanometer to be $122.3\ cm$. Then he repeated the experiment with a standard cell, B. With cell B connected, the length, Y, of the potentiometer resistor wire when there is no current through the galvanometer was $157.8\ cm$. The manufacturer has indicated that the emf, E_B, of B to be $1.25\ V$. The student observed that the smallest graduation of the ruler (used to measure the length of the resistor wire) to be $1\ mm$. [You are reminded that $E_A/E_B = X/Y$ and as usual the potentiometer resistor wire has a constant resistance per unit length.]

(i) Giving reasons state the maximum random error in E_B.

(ii) Giving reasons state the maximum random error the student may have made in each of the length measurements if he was using the correct technique in measuring using a ruler.

(iii) Calculate E_A and its error.
State E_A to the correct number of significant figures and indicate its uncertainty (in standard form).

(40 marks)

(c) Answer **either** Part (A) **or** Part (B) (but **NOT** both).

Part A

In the experiment, in determining the rate constant of acid catalysed hydrolysis of methyl acetate, you extracted a $5.00\ cm^3$ sample of the reaction mixture (using a pipette) at reaction time = t, and transferred it into a conical flask having ice. Then quickly titrated it with NaOH solution and determined the volume, V_t, of NaOH required to neutralise it. Show that the relationship among the reaction time, t, V_t and the rate constant, k, is given by

$$t = \frac{2.303}{k}\log_{10}(V_\infty - V_0) - \frac{2.303}{k}\log_{10}(V_\infty - V_t).$$

Here, V_0 and V_∞ are the volumes of NaOH required to titrate with $5.00\ cm^3$ sample of the reaction mixture at time = 0 and ∞, respectively.
The above mentioned reaction is first order in methyl acetate.

(50 marks)

Part B

In the experiment to find the rate law of acid catalysed iodination of acetone, a student placed $5.00\ ml$ of acetone, $10.00\ ml$ of HCl and $75.00\ ml$ of distilled water in a stoppered bottle and stirred well. She labelled it as "Solution A". Then using a pipette, she added $10.00\ ml$ of $0.05\ mol\,dm^{-3}$ iodine solution (Solution B) into the stoppered bottle (Solution A) and stirred well to obtain Solution C. She started the stop watch (i.e. time = t_{ini}) the moment she started draining the pipet into the stoppered bottle. The student performed the experiment at $25^{\circ}C$. [Density of acetone at $25^{\circ}C$ is $0.78\ g\,cm^{-3}$ and its molar mass is $58.08\ g\,mol^{-1}$]

(i) What is meant by the *half draining time* of a pipette.

(ii) Briefly explain why reaction starting time should be taken as $t_{inl} + t_{1/2}$ where

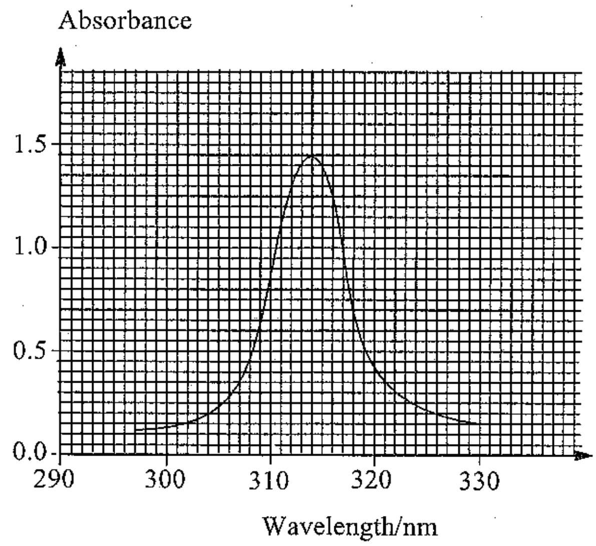
t_{inl} = time at which the draining of the iodine solution in the pipette started (this may be zero) and

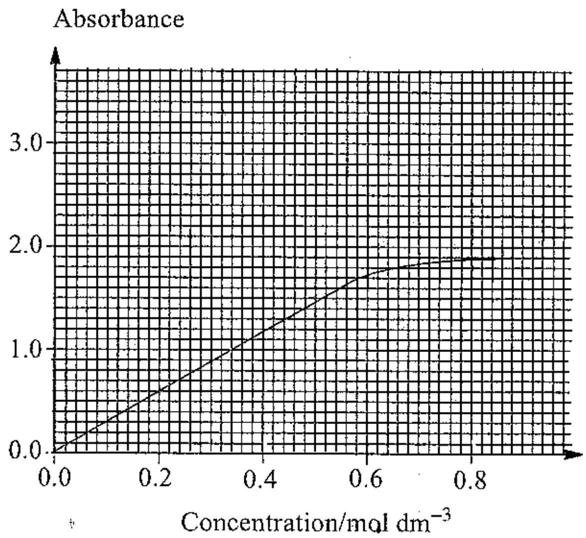
$t_{1/2}$ = time after half of the contents in the pipette has drained.

(iii) Calculate the molar concentration of acetone in solution A.
State any assumptions you make.

(50 marks)

2. (a) A student was asked to determine the range of validity of Beer-Lambert law for a chemical species X in aqueous solution. Using an aqueous solution of X of concentration $0.4\ mol\ dm^{-3}$, she first determined the wavelength, λ_0, at which the sensitivity of the spectrometer is maximum for X. Then she determined the absorbance of X, at radiation wavelength λ_0, in a series of solutions of different concentration. The path length of the cell used was 1.5 cm. Her results are shown below.





(i) What do you understand by the phrase "*the wavelength at which the sensitivity of the spectrometer is maximum for X*"?

(ii) Determine λ_0.

(iii) Write down the Beer-Lambert law and identify all the parameters in it.

(iv) Determine the range of validity of Beer-Lambert law for X using the above results.
Briefly explain your answer.

(v) Determine the molar extinction coefficient of X at wavelength λ_0.

(50 marks)

(b) Answer **either** Part (A) **or** Part (B) (but **NOT** both).

Part A

Calcium fluoride (CaF_2) is a sparingly soluble salt which behaves as a strong electrolyte in aqueous medium. In a conductometric experiment, a student determined the conductivity of calcium fluoride (CaF_2) in a saturated solution to be $4.67 \times 10^{-3}\ \mathrm{S\,m^{-1}}$ at $25^0\mathrm{C}$ and 1 atm. You are given that at $25^0\mathrm{C}$ and 1 atm $\lambda^0_{Ca^{2+}} = 118.0 \times 10^{-4}\ \mathrm{S\,m^2\,mol^{-1}}$ and $\lambda^0_{F^-} = 55.0 \times 10^{-4}\ \mathrm{S\,m^2\,mol^{-1}}$.

(i) Write down the definition of the solubility product of CaF_2 and identify all the terms in it.

(ii) For CaF_2, write down the relationship among the molar conductivity, conductivity and concentration and identify all the terms in it.

(iii) Write down the relationship among the molar conductivity of CaF_2 and the molar conductivities of calcium and fluoride ions and identify all the terms in it.

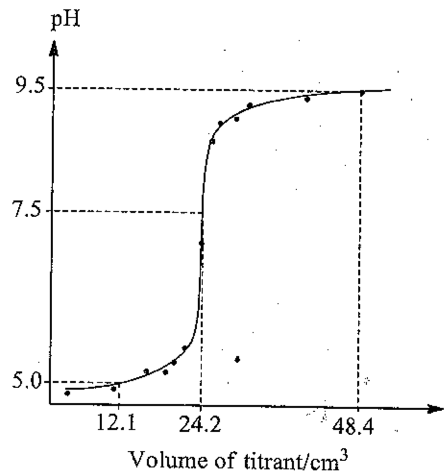
(iv) Derive a relationship among the solubility product of CaF_2, conductivity of a saturated solution of CaF_2 and the limiting molar conductivities of calcium and fluoride ions.

(v) Calculate the solubility product of calcium fluoride at $25^0\mathrm{C}$ and 1 atm.

(50 marks)

Part B

A student performed a weak acid (HA) - strong base (BOH) titration. To determine the end point, he measured the pH (of the reaction mixture) after the addition of known volumes of titrant. His plot of pH versus the volume of titrant added is shown in the figure. The experimental values he got are shown as black dots in the plot. The volume of titrand used was $30.00\ \mathrm{cm^3}$ and its concentration was $0.10\ \mathrm{mol\,dm^{-3}}$.



(i) Giving reasons, state whether titrant is the acid or the base.

(ii) Determine the concentration of titrant.

(iii) Explain why the student has taken pH readings by adding smaller portions of titrant (compared to that at the beginning and at end of the experiment) when the volume of the titrant added in close to $24.2\ \mathrm{cm^3}$.

(iv) Determine the dissociation constant, K, of the acid at the temperature the experiment was performed.
Briefly explain your answer.

(50 marks)

3. (a) A benzoic acid sample (1.00 g) dissolved in water (100 mL) is extracted with chloroform (100 mL). Partition coefficient of benzoic acid between water and chloroform is 49.

   (i) Write an expression for the partition of benzoic acid between water and chloroform defining all the terms.

   (ii) Calculate the amount of benzoic acid extracted into chloroform.

   (iii) Show that extraction efficiency is more when two 50 mL portions of chloroform is used for the extraction.

(50 marks)

(b) Given below are some problems faced by students when recrystallizing an impure solid. Indicate the remedial measures that should be taken in each situation.

   (i) The filtrate in the flask solidified during 'hot filtration'.

   (ii) Instead of well-formed crystals, a fine powder is obtained.

(20 marks)

(c) Answer **either** Part (A) **or** Part (B) (but **NOT** both).

Part A

A student needs to carry out a reaction under reflux. Reaction mixture contains a flammable liquid. Draw a completely labelled diagram of the set up to be assembled for this purpose.

(30 marks)

Part B

A can of solvent grade dichloromethane is contaminated. Draw a fully labeled diagram of the set up that can be used to purify it.

(30 marks)

4. (a) Given in the figure is the pattern of spots visualized by a student in a TLC experiment using 5% methanol in dichloromethane.

   (i) What is the purpose of doing this type of a TLC?

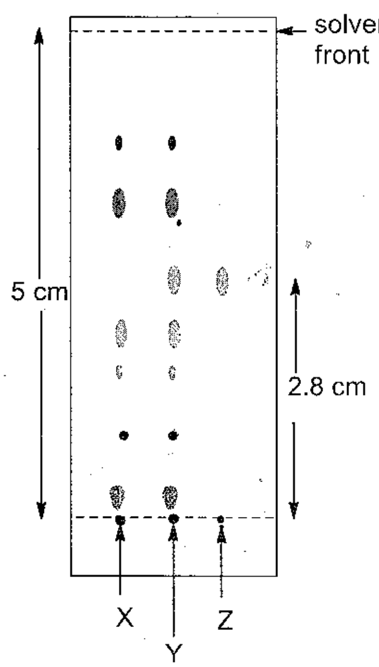
   (ii) What has he applied in the spot labelled as Y?

   (iii) What is the conclusion he can arrive at, in this experiment?

   (iv) Calculate the R_f value of the spot given by Z.

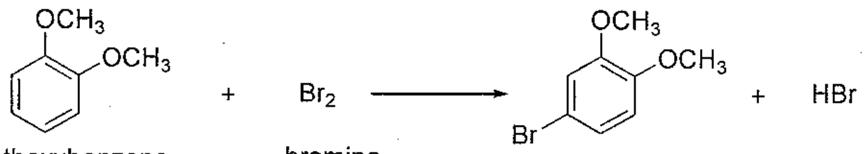
   (v) What would you expect to happen to the R_f value if you decrease the percentage of methanol in the developing solvent?

   (vi) Give reasons for your answer in v.



(50 marks)

(b) Bromination of 4.0 g of 1,2- dimethylbenzene was carried out using 5.0 mL of bromine liquid. Find out the limiting reagent in this reaction.



1,2-dimethoxybenzene — m. w. = 138.2 g/mol

bromine — m.w = 159.9 g/mol, density = 3.1 g/mL

(20 marks)

(c) Answer **either** Part (A) **or** Part (B) (but **NOT** both).

Part A

A slightly impure unknown solid **P** is suspected to be benzamide (m. p. 129°C). Write down the steps in point form for the procedure to confirm it as benzamide by mixed melting point determination.

(30 marks)

Part B

A two-component mixture contains cinnamic acid (m. p. 133°C) and cinnamaldehyde (m. p. -7.5°C). Draw a flow chart to show the method you will adopt to separate out the two components. Indicate how the two components can be purified.

(30 marks)

The END