00159

The Open University of Sri Lanka
Faculty of Natural Sciences
B.Sc. / B.Ed. Degree Programme

Course Code	**: CYU5302/CMU3123/CME5123**
Title	: Analytical Chemistry
Department	: Chemistry
Level	: 05
Name of the Examination	: Final Examination
Academic Year	: 2019 /2020
Date	: 12. 01. 2020
Time	: 1.30 pm – 3.30 pm.
Duration	: Two Hours

General Instructions

1 This question paper consists of 06**(Six)** questions in **05 (five)** pages.

2. Read all instructions carefully before answering the questions.

3. Answer any **04(Four)** questions. All questions carry equal marks.

4. Having any unauthorized documents/ mobile phones/any other electronic equipment's in your possession is a punishable offence.

7. Use blue or black ink to answer the questions.

8. Clearly state your index number in all pages of your answer script.

9. The use of a non-programmable electronic calculator is permitted.

Relative atomic mass **H=1; C=12; O=16; Na=23; S=32; Ca=40; Mn=54.9; Ni=58.7; Co=58.9; Cu=63.5; Zn=65.4; Ba=137; Pb=207.**

1.(a) 100.0 ml of an equimolar solution containing X^{2+} and Y^{2+} was treated with H_2S after acidification. The metal ions precipitated as XS and YS from the solution. The solubility product of XS and YS are 8×10^{-36} mol^2 dm^{-6} and 6×10^{-10} mol^2 dm^{-6} respectively.

(i) Which metal ion will precipitate as sulphide first? Explain your answer

(ii) Write three essential properties that a precipitate should have in order to use gravimetry for its determination

(b) In a similar precipitation of Cu^{2+} from a solution, 0.0191 g of CuS dry precipitate was obtained from 50.0 ml of an unknown Cu^{2+} solution Calculate the Cu^{2+} ion concentration in ppm of the starting solution. (50 marks)

(c) (i) Explain briefly, what will happen if $C_2O_4^{2-}$ is added to the solution containing Pb^{2+} and Ba^{2+} having different concentration of lead and barium ions. K_{sp} of lead and barium as 4.8×10^{-12} mol^2 dm^{-6} and 2.4×10^{-8} mol^2 dm^{-6} respectively.

(ii) Showing the relevant calculation, explain how you can achieve selectivity.

(iii) What concentrations of Pb^{2+} and Ba^{2+} should be present in the solution in order to precipitate both ions together?

(30 marks)

(d) (i) What is the difference between accuracy and precision?

(ii) The sample of metal ion concentration was determined the results were obtained as 0.382, 0.411, 0.402, 0.408, 0.410, 0.415, and 0.403 The critical Q values for different sample sizes are given in the table

Number of observations	Critical Q values (p=0.05)
5	0.717
6	0.621
7	0.570
8	0.524

Use the suitable method and determine the concentration of metal ion of 0.382 can rejected? (20 marks)

2.(a) A student was given a bottle of vinegar to find out its acetic acid composition. He carried out acid- base titrations in the laboratory: A 25.0 cm^3 portion of a random sample of vinegar was titrated with 0.5 M NaOH using phenolphthalein as the indicator and the end point obtained was 25.30 cm^3.

(i) Explaining what is meant by a 'random sample', briefly describe how you would obtain a random sample from the bottle of vinegar.

(ii) Draw and label the titration curve for the above titration.

(iii) Briefly explaining what is meant by 'titration error', indicate it on the titration curve.

(iv) Calculate the percentage (w/w) of acetic acid in the vinegar sample.

(v) Deduce and draw the shape of the titration curve for the titration of phosphoric acid with 0.1 M NaOH using phenolphthalein as the indicator.
For phosphoric acid, $K_{a1} = 7.5 \times 10^{-4}$ mol dm^{-3}, $K_{a2} = 6.2 \times 10^{-8}$ mol dm^{-3};
$K_{a3} = 4.8 \times 10^{-13}$ mol dm^{-3}.

(70 marks)

(b) A buffer solution maintains a relatively constant pH when a small amount of acid or base is added to it. Buffering is important in living systems as a means of maintaining a fairly constant internal environment, also known as *homeostasis*. Bicarbonate, phosphate and proteins are examples of buffers in living systems.

(i) Derive the Henderson- Hasselbalch equation for the acetic acid (HA) and sodium acetate (NaA) buffer.

(ii) Calculating the strength and volume of NaOH required, show how you would prepare 100.0 cm^3 of a buffer of pH 4.50 using 50.0 cm^3 of 0.4 M acetic acid ($pK_a = 4.76$).

(30 marks)

3.(a) Chronic Kidney Disease of unknown aetiology (CKDu) is a major health concern in the North Central Province (NCP) of Sri Lanka. Studies to identify the causative factors of CKDu point to hardness of ground water, among others, in the areas. In an effort to determine hardness of water, complexometric titrations were carried out with EDTA using Eriochrome Black T (EBT) as the indicator. For this purpose, random water samples were collected from shallow wells in a selected area.

(i) 1 dm^3 of well water sample was concentrated to 100.0 cm^3 and a 25.0 cm^3 portion of it was titrated against 0.02 M EDTA at pH 10.0 using EBT, the volume of EDTA used was 22.00 cm^3.
(α) Why was the pH maintained at 10.0?
(β) Giving reason(s), briefly explain the colour change at the end point.
(γ) Estimate total hardness of water in ppm (or mg dm^{-3}) in terms of $CaCO_3$.

(ii) Derive the expression for conditional formation constant (K'_{CaY}) of calcium EDTA complex in terms of fractions (α) of calcium ion and EDTA in equilibrium with calcium-EDTA complex.

(iii) Calculate the conditional formation constant of Ca- EDTA complex at pH 10.0.
($K_{CaY} = 5.0 \times 10^{10}$ dm^3 mol^{-1}; at pH 10.0, $\alpha_{Y^{4-}} = 0.35$).
Write any assumption(s) that you make.

(iv) Briefly explaining the variation, sketch the titration curves for the titration of Ca^{2+} with EDTA when the pH increases.

(v) How would you achieve selectivity in complexometric titration? (75 marks)

(b) The effluent from a nickel plating industry needs to be analyzed for Ni^{2+} to make sure that the levels of Ni^{2+} are not excessive according to guidelines. Acceptable levels of nickel for freshwater is <100 μg/L. If Ni^{2+} levels are higher, the effluent must be treated before being discharged into the nearby water body. 1 dm^3 of effluent sample was digested and re-dissolved in a suitable reagent and the solution was made up to 100.0 cm^3. To a 25.0 cm^3 portion of the prepared solution, 50.0 cm^3 of 0.02 M EDTA was added and the excess EDTA was titrated against 0.02 M Zn^{2+} solution at pH 5.5 using xylenol orange indicator. The volume of Zn^{2+} used was 46.75 cm^3.

(i) Calculate the concentration (mg dm^{-3}) of Ni^{2+} in the effluent sample. is the Ni^{2+} level in the effluent acceptable for discharge into the water body?

(ii) Why was back titration used to determine Ni^{2+}? (25 marks)

4. (a) Describe the following terms in brief.

i. Distribution coefficient ($\mathbf{k_d}$)
ii. Distribution ratio (**D**)
iii. Retention factor (Retardation factor; $\mathbf{R_f}$ value)

(15 marks)

(b) At 25°C, two immiscible layers containing an organic acid **A** are in equilibrium. Diethyl ether layer (20 mL) contained 0.54 g of **A** while water layer (100 mL) contained 0.24 g of **A**.

i. Calculate the distribution coefficient (k_d) of **A** in water and diethyl ether at 25°C.
ii. In a separate extraction at the same temperature, 1.35 g of **A** was extracted into 100 mL of diethyl ether from a 100 mL aqueous solution. Calculate the percentage of extraction.
iii. Calculate the volume of diethyl ether needed for an 85% extraction from a solution of 3.0 g of **A** in 100 mL water.
iv. Calculate the total amount of **A** extracted from the above solution (3.0 g of **A** in 100 mL water) if two successive extractions with 50 mL portions of diethyl ether is done.
v. Calculate the extraction efficiency for the two successive extractions described in above

(60 marks)

(c) Compare the similarities/differences between ascending development and descending development techniques and their efficiencies in relation to planar chromatography,

(25 marks)

5. (a) A complex of Ni^{2+} has an ϵ value of 3529 at 365 nm and 0 at 700 nm respectively while that of Co^{2+} has an ϵ value of 3228 at 365 nm and 429 at 700 nm respectively. (unit for ϵ values are in $dm^3\ mol^{-1}\ cm^{-1}$) When a solution containing these complexes are placed in a cell 1.0 cm path length, the absorbance at 700 nm was 0.0954 and that at 365 nm was 0,930. Calculate the concentration of Ni^{2+} and Co^{2+} ions in the solution (20 marks)

(b) The absorbance of a solution prepared by dissolving 1.000 g of an unknown manganese sample was found to be 0.700 at 550 nm. A 1.52×10^{-4} mol dm^{-3} manganese solution showed an absorbance of 0.350 at 550 nm with the same optical path of 1 cm. Calculate

(i) the concentration of manganese in the prepared solution.

(ii) % of the manganese in the unknown sample. (20 marks)

(c) Briefly explain the difference between a line spectrum and a band spectrum (20 marks)

(d) The 1.2456 gram of rubidium salt was dissolved, and it was diluted to 100 ml and analyzed using atomic absorbance technique at 780 nm. The absorbance reading against amount of rubidium was mg/ml (absorbance):

Concentration/(mg/ml)	0.5	1.0	2.0	2.5	4.0	Unknown
Absorbance	0.240	0.490	1.030	1.200	1.900	1.210

(i) Draw the suitable graph

(ii) Determine the concentration of unknown rubidium solution

(iii) Calculate the rubidium % percentage in rubidium salt sample (40 marks)

6. (a) (i) What is conductometric titration?

(ii) Give two limitations of Hydrogen electrode.

(iii) State two differences in the instrumentation of Atomic absorption spectrophotometer compared to UV-Visible spectrophotometer.

(iv) What is the principle behind thermometric titration?

(v) Give two major differences between electrophoresis and paper chromatography. (40 marks)

(b) 30.0 cm^3 of solution containing an equimolar mixture of Sn^{2+} and Z^{2+} ions in 0.15 mol dm^{-3} H_2SO_4 solution was titrated with 0.02 mol dm^{-3} $KMnO_4$ solution

(i) Determine the feasibility and selectivity of the above titration

(ii) Sketch and label the titration curve for the above titration

$E^{\theta}_{MnO_4^-/Mn^{2+}} = 1.51V$; $E^{\theta}_{Sn^{2+}/Sn^{3+}} = 0.15\ V$ $E^{\theta}_{Z^{3+}/Z^{2+}} = 0.27\ V$ (30 marks)

(d) A solution contained 1.0×10^{-3} mol dm^{-3} in $Cr_2O_7^{2-}$ and 1.0×10^{-2} mol dm^{-3} in Cr^{3+}. If the pH is equal 2.0 What is the potential of the half reaction. $E^{\theta}_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\ V$ (15 marks)

(d) Calculate the potential of a solution obtained by reacting 10 ml each of 0.2 mol dm^{-3} Fe^{2+} and 0.2 mol dm^{-3} Ce^{4+}. $E^{\theta}_{Fe^{2+}/Fe^{3+}} = 0.77\ V$; $E^{\theta}_{Ce^{4+}/Ce^{3+}} = 1.61\ V$ (15 marks)

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