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THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme
Level 5 –CYU 5302–ANALYTICAL CHEMISTRY
FINAL EXAMINATION PAPER 2024/25

Date: 202~~3~~4.12.10 Duration: Two hours
Time: 1.30 p.m.- 3.30 p.m.

Instructions to students

Answer all four questions.

1. (A) In the Gravimetric determination of the metal M, to a 100.0 mL of $M(OH)_2$ solution, A 20.00 mL of 1.000 M HCl was added until all the metal ion formed the precipitate MCl_2. The weight of the precipitate was 1.110 g. (O=16.00 g, H=1.008 g, Cl=35.45 g)

(i) Describe briefly (how, what happens and why) all the important steps that must be followed in the correct order, after getting the precipitate but before weighing, in Gravimetry. (20 marks)

(ii) Find the weight of M in the solution. (20 marks)

(iii) Suggest a way of improving the accuracy of the above determination. (10 marks)

(iv) Do you agree with the following statement? Justify.
"Selectivity in Gravimetry can be achieved if the ratio of the solubility products is more than 10^5." (10 marks)

(B) To determine X^{4+} in a 20.0 mL of a sample solution, 20.0 mL of 0.10 M, Z^{-} solution (in excess) was added. The resultant solution was titrated with 0.05 M solution of A^{2-}. The end point obtained was 16.00 mL.

$A^{3+} + e \leftrightarrow A^{2+}$ $E^\circ = 0.261$ V
$X^{4+} + 2e \leftrightarrow X^{2+}$ $E^\circ = 1.281$ V
$Z^{2+} + e \leftrightarrow Z^{+}$ $E^\circ = 0.761$ V

(i) Give one possible reason for not titrating X^{4+} directly with Z^{+}? (05 marks)

(ii) Write the balanced equations for the feasible reactions that have taken place showing that they are feasible. Calculate the concentration of X^{4+} in the sample solution. (15 marks)

(iii) What would have been the cell potential when 8.00 mL of A^{2+} was added? justify your answer. (10 marks)

(iv) Do you agree with the following statement? Justify.
"It is not the standard electrode potential but the formal electrode potential that is important when deciding on feasibility of a redox reaction" (10 marks)

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2. **Titration I**-The weight of W g of a sample containing $NaHCO_3$ and $CaCO_3$ was dissolved in 100.0 mL of 0.020 M HCl and the solution was boiled to remove carbon dioxide. The excess unreacted HCl was titrated with 0.020 M NaOH. The end point obtained was 40.00 mL. **Titration II**-Another sample with the same weight was dissolved in HCl but adjusted the pH to 10 with a buffer and was titrated with 0.020 M EDTA. The end point obtained was 30.00 mL. (Na=23 g, H=1 g, C=12 g, O=16 g, Ca=40 g)

(i) What is the reason behind removing carbon dioxide? (10 marks)

(ii) Calculate the weights of $NaHCO_3$ and $CaCO_3$ in the sample. (25 marks)

(iii) Sketch and label the titration curve of the titration II. (10 marks)

(iv) Do you agree with the following statement? Justify.
"The above EDTA titration was done at pH 10 to have a higher conditional formation constant" (10 marks)

(v) Sketch and label the titration curve of the titration I. Show the changes in the titration curve with a dotted line if HCl and NaOH concentrations were higher than what was really used. (15 marks)

(vi) Since the colour change at the end point of the titration II was not sharp, it was decided to carry out a back titration. Suggest briefly how you would carry out the back titration. State the required conditions and how to do the calculation.
(15 marks)

(vii) The buffer used was made with a weak base BOH (0.1 M) and its salt BCl (0.1 M). What is the dissociation constant (K_b) of the weak base? Suggest a way of increasing the capacity of the buffer. (15 marks)

3. A) 5.520 g of AX in 50.0 mL of aqueous solution was extracted to 75.0 mL (extracted Using 25.0 mL, three times) of diethyl ether using a separatory funnel. After the third extraction, diethyl ether was evaporated and the dry weight of the AX in this layer was 1.780 g. The molecular weight of AX and the distribution ratio between the two layers are 92 g mol^{-1} and 4.0 respectively.

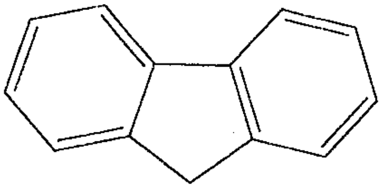
(i) Define all the parameters and derive the following relationship. (15 marks)

$$a_1 = \left(\frac{V_{aq}}{DV_{org}+V_{aq}}\right) a_0$$

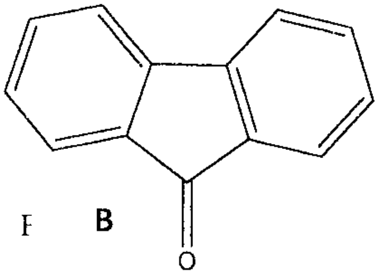
(ii) Determine the remaining concentration of AX in the aqueous layer after all three extractions. (15 marks)
(Hint: Use the expanded form of the above equation for n number of extractions)

(iii) Predict at least two reasons for selecting diethyl ether as a solvent. (10 marks)

B) A mixture of the following two compounds were separated by a silica column using hexane as a mobile phase.



A



B

(i) Briefly explain which compound elutes first from the column (A or B). (15 marks)

(ii) During the elution, one compound eluted first and the other one remained in the silica column for a long time. So how can you adjust the mobile phase to elute the second compound without any delay? Give an example. (10 marks)

(iii) Briefly explain a classical method that you can use to check whether the two compounds are separated while elution. (10 marks)

C) The unknown sample with two compounds (P and Q) was quantified using a reverse phase liquid chromatography using water: methanol (1:4) as a solvent. Further, 2.00 ppm standard solutions of P and Q were used for quantification. The chromatogram results are given below.

Peak	Retention time (t_r)/ min	Peak area (arbitrary unit)		
		Unknown sample	Standard P	Standard Q
1	1.2	60	40	40
2	8.4	360	-	240
3	9.6	200	354	-

(i) "Q is more polar than P." justify. (08 marks)

(ii) Determine the selectivity factor for the two compounds P and Q. (08 marks)

(iii) Determine the concentration of Q in the sample mixture. (09 marks)

4. A) A student wanted to determine the concentration of Mn^{2+} in an effluent sample released during steel production. For this purpose, he pipetted out 10.0 mL of effluent sample into a beaker and added 10 mL of 50% nitric acid and heated for 15 minutes. After cooling the mixture, potassium periodate (2.0 g) was added and heated again for 15 minutes. Then the sample solution was transferred to 100.0 mL of volumetric flask and diluted to the mark using deionized water. Finally, the absorbance was measured at 520 nm using a double-beam UV/Visible spectrometer and the absorbance was 0.224.

Then he made another mixture by transferring 10.0 mL of the prepared solution from the volumetric flask into a conical flask having10.0 mL of 2.00 ppm standard potassium permanganate solution. The absorbance at the same wavelength was 0.672 with the same spectrophotometer.

The molecular mass of potassium permanganate and the atomic mass of manganese are 158 g mol^{-1} and 55.0 g mol^{-1} respectively.

(i) What is the reason for adding potassium periodate? (05 marks)

(ii) What was the concentration of Mn^{2+} (ppm) present in the sample? (25 marks)

(iii) Briefly explain the advantage of using a double-beam spectrometer compared to a single-beam spectrometer. (10 marks)

(iv) Suggest a way to further improve the accuracy of this method. (10 marks)

B) Another student standardized the potassium permanganate solution using photometry titration. For this purpose, he titrated the 10.0 cm^3 of potassium permanganate with 2.0 ppm oxalic acid while measuring the absorbance at 520 nm.

(i) Write down the balanced chemical reaction for this titration. (05 marks)

(ii) Sketch the expected titration curve and briefly explain. (15 marks)

(iii) Even very dilute solutions of potassium permanganate can be used for photometric titrations. Explain briefly. (10 marks)

C) A student performed a potentiometric titration to determine the concentration of NH_4OH by titrating 20.0 mL of it with 0.01 M CH_3COOH. The endpoint reading was 42.20 mL.

(i) What is the most suitable indicator electrode for this titration? (05 marks)

(ii) What is the concentration of NH_4OH solution? (08 marks)

(iii) Can you do this titration using a classical titrimetric method? Justify the answer.
(07 marks)