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THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 –CMU 3123/CME 5123 –ANALYTICAL CHEMISTRY
FINAL EXAMINATION PAPER 2014/15

Date: 2015.05.19
Time: 1.00 p.m.- 3.00 p.m.

Duration: Two hours

Instructions to students

This question paper consists of six questions. Answer any four questions only.

1. A water sample (100.0 cm^3) from a swimming pool was given to a student to analyze Cl^- using gravimetry by adding only a slight excess of AgNO_3 . The precipitate was digested overnight, filtered, washed with dil. HNO_3 and dried at 110°C . The weight of the precipitate obtained was 0.0900 g . ($\text{Ag} = 108$, $\text{Cl} = 35.5$)
- (i) What is the precipitate formed for gravimetric analysis? Why is it suitable for gravimetric analysis? (15 marks)
- (ii) Why only a slight excess of AgNO_3 was added? (10 marks)
- (iii) Give reasons for selecting dil. HNO_3 as the washing solvent. (10 marks)
- (iv) What is the concentration of Cl^- in the water sample? (15 marks)
- (v) If the water sample was containing 0.001 M of I^- ions, is it possible to get the precipitate without any iodine? Justify your answer with proper calculations.
 K_{sp} of $\text{AgCl} = 1.6 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$
 K_{sp} of $\text{AgI} = 8.5 \times 10^{-17} \text{ mol}^2 \text{ dm}^{-6}$ (30 marks)
- (vi) Comment on the following statements.
- (a) Although the sensitivity of gravimetry is low, accuracy is high compared to instrumental methods.
- (b) Digestion of a precipitate minimizes errors. (20 marks)
2. (i) A bottle contains 1.00 dm^3 of NaOH and Na_2CO_3 mixture and the following two titrations were carried out.
- Titration I
A 25.00 cm^3 of this solution was titrated with 0.01 M HCl using phenolphthalein as the indicator and the end point obtained was 35.00 cm^3 .

Titration II

To another 25.00 cm³ of the solution portion 25.00 cm³ of 0.01 M BaCl₂ was added and the filtrate was titrated with 0.01 M HCl using phenolphthalein as the indicator and the end point obtained was 25.00 cm³.

- (a) Draw and label the two titration curves in the same graph and explain the information (using proper equations) you could obtain by the end points of the two titrations.
- (b) Calculate the concentrations of NaOH and Na₂CO₃ in the bottle separately. (50 marks)
- (ii) Compare redox titrations with acid-base titrations with respect to feasibility, titration curve, selectivity (assuming that suitable indicators are available) and selection criteria of indicators. (50 marks)
3. Two 25.0 cm³ samples of a factory effluent containing the metal ions M²⁺ and X²⁺ were taken. To titrate X²⁺, one sample was buffered at pH 7 and titrated with 0.02 M EDTA using Eriochrome Black T as the indicator and the concentration of X²⁺ was found to be 2.00 x 10⁻² M. In order to determine the concentration of M²⁺, to the other sample solution 25.0 cm³ of 0.02 M EDTA was added, the pH was adjusted to 10 before boiling. Then the excess EDTA was titrated with another metal ion solution, 0.02 M D²⁺ and the end point reading obtained was 15.00 cm³.
- (i) Why the two titrations were done at different pH? (10 marks)
- (ii) Give three possible reasons for carrying out a back titration to determine the concentration of M²⁺. (12 marks)
- (iii) Calculate the concentration of M²⁺. (18 marks)
- (iv) Calculate the molar concentration of X²⁺ present at equilibrium after adding 30.00 cm³ of 0.02 M EDTA in the titration buffered at pH 7. (Conditional formation constant of XY = 6.432 x 10¹³ mol⁻¹ dm³) (40 marks)
- (v) A 25.0 cm³ of a sample solution having 0.01 M Fe²⁺ was titrated with 0.02 M Ce⁴⁺ solution.
- $$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = +0.68 \text{ V} \qquad E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ} = +1.44 \text{ V}$$
- (a) What is the potential at the equivalence point of the titration?
- (b) Calculate the equilibrium constant for the reaction between Fe²⁺ and Ce⁴⁺. (20 marks)

4. (i) A 20.0 cm³ sample from a sewage tank was brought to pH 13 with NaOH and was diluted to 100.0 cm³. The voltage across a lead membrane electrode (ion selective electrode) and a calomel electrode immersed in this solution was -0.112 V. To another 20.0 cm³ sample solution from the sewage tank was brought to pH 13 with NaOH and was diluted to 100.0 cm³ after addition of 25.0 cm³ of 100 ppm Pb²⁺ solution. Then the voltage across the lead ion selective electrode and a calomel electrode immersed in this solution was increased to -0.300 V. The lead ion selective electrode obeys $E = \text{constant} - 0.0592 \log [\text{Pb}^{2+}]$

- (a) What is the principle behind the membrane electrode with respect to quantitative analysis?
- (b) What may be the reason for adding standard to the sample solution without measuring the potential of the standard solution only?
- (c) Calculate the concentration of lead ions in the sewage tank.

(35 marks)

- (ii) Compare the principle of conductometric titrations and thermometric titrations as analytical methods.

(20 marks)

- (iii) A CaCO₃ sample contaminated with CaC₂O₄ and some other thermally stable substance was analysed using Thermogravimetry. The first decomposition was observed at 346° C – 420° C and the weight was decreased from 160.00 mg to 157.20 mg. The second decomposition was observed at 660° C – 840° C and the weight was decreased from 157.20 mg to 10.4 mg. (C= 12.00 g, O = 16.00 g, Ca = 40.00 g)

- (a) Draw the first derivative Thermo Gravimetric curve (DTG curve).
- (b) Calculate the weight of CaC₂O₄ and CaCO₃ in the mixture. (45 marks)

5. (i) What do you mean by “Linearity” of an analytical method?

(10 marks)

- (ii) A student wanted to determine the concentration of the compound RCl₂ in a solution using UV-Visible spectrophotometer. RO is a very stable oxide and R is having a low ionization energy. The following information is also given to him.

Compound/ion	λ_{max} (nm)	Molar absorptivity co-efficient (dm ³ mol ⁻¹ cm ⁻¹)
R(OH) ₂	890	5.4 x 10 ⁵
RL ₂	552	1.00 x 10 ³
RCrO ₄	660	1.21 x 10 ²
L ⁻	552	6.40 x 10 ¹

- (a) If chemicals are available, what is the most suitable compound from $R(OH)_2$, RL_2 and $RCrO_4$ in order to determine R using UV-Visible spectrophotometer? Justify your answer. (15 marks)
- (b) To a 10.0 cm^3 of $5.00 \times 10^{-3} \text{ M RCl}_2$ solution, 20.0 cm^3 of $5.00 \times 10^{-2} \text{ M NaL}$ solution was added and diluted to 500 cm^3 after mixing. The absorbance was measured at 552 nm using UV-Visible spectrophotometer at a path length of 1.00 cm . Calculate the Absorbance. (25 marks)
- (c) Another student who works in another laboratory decides to analyze RCl_2 using Atomic Absorption Spectrophotometer. Identify two chemical interferences in the analysis and suggest methods to overcome them. (20 marks)
- (d) Name two components used in Atomic Absorption Spectrophotometer (AAS) which are not in UV-Visible spectrophotometer and explain the function of the two components. (20 marks)
- (e) What is the significant difference in spectra obtained by UV-Visible spectrophotometer and AAS? (10 marks)
6. (i) A divalent metal ion (M^{2+}) is extracted from a 100.0 mL of a $1.0 \times 10^{-6} \text{ M}$ aqueous solution into 100.0 mL of an organic phase containing 0.1 mM of chelating ligand HL. Partition coefficients for the ligand (K_{DHL}) and for the metal - ligand complex (K_{DC}) are 1.0×10^4 and 7.0×10^4 respectively. Acid dissociation constant (K_a) of the ligand is 5.0×10^{-5} while formation constant for the metal - ligand complex (β) is 2.5×10^{16} .
- (a) Write down equations for all the equilibrium reactions involved in the extraction process.
- (b) Derive an expression for the distribution ratio (D) in terms of K_{DHL} , K_{DC} , K_a , β and concentrations of HL and H^+ ions.
- (c) Calculate D when the aqueous solution is buffered to pH 1.0. (55 marks)
- (ii) List down three assumptions you made in deriving the expression for D, in above part (i) (b). (15 marks)
- (iii) Compare and contrast the following pairs. (30 marks)
- (a) Thin layer chromatography and paper chromatography
- (b) Normal phase chromatography and reverse phase chromatography
- (c) Isocratic elution and gradient elution in column chromatography