



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 2012/13

Date: 2013.06.17

Duration: Two hours

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

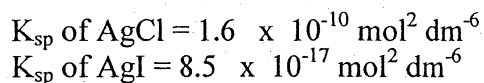
Instructions to students

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

1. (a) A waste water sample was given to a student to analyse lead (Pb) in the sample using gravimetry. He was provided with a sulphate ion solution and a sample of dimethyl sulphate, $(\text{CH}_3\text{O})_2\text{SO}_2$. In addition he was given the following information.



- (i) What is the precipitate expected to form for gravimetric analysis? Why is it suitable for gravimetric analysis?
 - (ii) Write down the essential steps that the student should follow in order to obtain the precipitate.
 - (iii) Explain why you have chosen this particular method over other methods to obtain the precipitate.
 - (iv) Another student suggested that it is possible to recover more precipitate if more sulfate ions are added to the filtrate. Do you agree with his suggestion? Explain your answer.
 - (v) State three qualities of a good washing solvent and suggest a suitable washing solvent to wash the above precipitate.
- (70 marks)
- (b) $0.20 \text{ mol dm}^{-3} \text{ AgNO}_3$ solution was added to a solution having $0.02 \text{ mol dm}^{-3} \text{ Cl}^-$ and $0.02 \text{ mol dm}^{-3} \text{ I}^-$. What will be the concentration of I^- in the solution at the point AgCl begins to precipitate?



(30 marks)

2. (a) A 25.00 cm³ portion of sodium carbonate sample solution was titrated with 0.05 M HCl using methyl orange and phenolphthalein as indicators.
- Draw and label the titration curve and explain the information (using proper equations) you could obtain by the end points of the indicators mentioned above.
 - What would you expect to observe in the titration curve if the concentration of HCl and sodium carbonate was increased?
 - Another 25.00 cm³ portion of 0.01 M NaHCO₃ was added to the flask having 25.00 cm³ of sodium carbonate sample solution and titrated with 0.05 M HCl using methyl orange as the indicator. The end point obtained was 20.00 cm³. Find concentration of sodium carbonate that was present in the sample solution.

(50 marks)

- (b) Silver forms the complex [Ag (trien)]⁺ with triethylenetetramine (trien). A 10.0 cm³ portion of 0.020 M AgNO₃ was added to a 25.0 cm³ of 0.050 M trien solution.

- Assuming that all silver ions are complexed, calculate the molar concentration of the silver ions present after equilibration. The formation constant for the formation of [Ag (trien)]⁺ complex is 4.89 x 10⁷ mol⁻¹ dm³.
- The metal ion X⁺ also forms a complex with trien. If there is a little amount of the metal ion X⁺ present in the solution with trien, what can you say about the formation constant for the reaction between silver ion and trien? (explain your answer using proper equations)

(50 marks)

3. (a) Compare redox titrations with EDTA titrations with respect to feasibility, titration curve, selectivity (assuming that suitable indicators are available) and indicators. (40 marks)

- (b) A 25.0 cm³ of a sample solution having Sn²⁺ and Fe²⁺ in a 0.1 M H₂SO₄ was titrated with 0.02 M KMnO₄.

$$E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ} = +1.51 \text{ V}$$

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = +0.77 \text{ V}$$

$$E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^{\circ} = +0.15 \text{ V}$$

- Comment on the feasibility of the above titration.
- Sketch and explain the titration curve of the above titration.

- (iii) Write down the balanced equations of the reactions taking place during the titration.
- (iv) When 20.00 cm^3 of 0.02 M KMnO_4 solution was added to the sample solution, the potential of the resulting mixture was 0.15 V . What was the initial concentration of Sn^{2+} in the sample solution?
(60 marks)
4. (a) Describe the following terms in brief.
- (i) Distribution coefficient
 - (ii) Isocratic elution
 - (iii) Capacity factor (15 marks)
- (b) (i) Write down the expressions for the partition coefficient (k_d) and distribution ratio (D) for benzoic acid in water and diethyl ether.
- (ii) Benzoic acid (2 g) was dissolved in water (200 cm^3) and extracted with 200 cm^3 of diethyl ether. Distribution coefficient (k_d) of benzoic acid is 100 and its dissociation constant is $6.5 \times 10^{-5} \text{ mol dm}^{-3}$. Calculate the distribution ratio (D) of benzoic acid at pH 2 and 5 .
- (iii) Explain why you observe such a change in distribution coefficient at higher pH in the system.
(65 marks)
- (c) List the major differences in the pairs given below.
- (i) Normal phase chromatography and reverse phase chromatography
 - (ii) Sorption processes in paper chromatography and thin layer chromatography with silica as the stationary phase.
 - (iii) Factors affecting the solute separations in ion exchange chromatography and size exclusion chromatography
 - (iv) Agarose and polyacrylamide (20 marks)
5. (a) Sketch and explain the conductometric titration curve of a titration of 25.0 cm^3 of 0.01 M acetic acid with 0.01 M NaOH .
(20 marks)
- (b) Explain how non linear conductometric titration curves are resulted and state ways of minimizing this error.
(20 marks)

- (c) Compare the principle of Thermogravimetry (TG) and Differential thermal analysis (DTA) as analytical methods. (20 marks)
- (d) A mixture of CaCO_3 and CaO was analysed using Thermogravimetry. Only one decomposition was observed. It was between $600^\circ\text{C} - 900^\circ\text{C}$ and the weight was decreased from 150.6 mg to 106.6 mg. (C = 12.00g, O = 16.00 g, Ca = 40.00g)
- (i) Draw the Thermo Gravimetric curve.
- (ii) Calculate the weight of CaO in the mixture. (40 marks)
6. (a) What is the difference between “sensitivity” and the “minimum detection limit” of an analytical method? (10 marks)
- (b) (i) Draw and label the main components of a UV-Visible spectrophotometer.
- (ii) Name two components used in Atomic Absorption Spectrophotometer which are not used in UV-Visible spectrophotometer and explain the function of the two components. (30 marks)
- (c) A 10.0 cm^3 sample of water containing both Fe^{2+} and Fe^{3+} was determined using spectroscopy. Fe^{2+} forms Fe(II) ortho phenanthroline complex with ortho phenanthroline. Excess ortho phenanthroline was added to the sample and the transmittance measured at 512 nm was 72%. To another 10.0 cm^3 of the same sample water a reducing agent was added to reduce Fe^{3+} to Fe^{2+} , before adding ortho phenanthroline and then the transmittance was 55% at 512 nm. What was the concentration of Fe^{2+} and Fe^{3+} in the sample?
(path length of the cell = 1 cm, molar absorptivity co-efficient of the Fe(II) ortho phenanthroline complex = $1.25 \times 10^4 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$) (30 marks)
- (d) Name two main interference types of Atomic Absorption Spectroscopy. Give one example for each type and a way of eliminating the interference given in the example. (30 marks)