00244

THE OPEN UNIVERSITY OF SRI LANKA

B.Sc/B.Ed DEGREE/STAND ALONE COURSES IN SCIENCE - Level 5

FINAL EXAMINATION – 2017/2018

ANALYTICAL CHEMISTRY CYU5302/CMU3123/CME5123

(2 hours)

3rd October 2018 1.30 p.m.- 3.30 p.m.

Answer any **four** questions.

1.Effluent from an industry is collected into a tank for treatment before being discharged. A random sample of this industrial effluent (100.0 cm^3) was subjected to gravimetric analysis to determine the concentration of Pb^{2+}. A student prepared $PbCrO_4$ precipitate by adding only a slight excess of K_2CrO_4 solution. The precipitate was digested for 2-3 hours, cooled to room temperature, filtered, washed and dried.

(i) What do you mean by a random sample?
(ii) Assuming that the effluent contains only dissolved matter, suggest how you would obtain a random sample.
(iii) Comment on the suitability of the precipitate for gravimetric analysis.
(iv) Identifying the good practices that have been followed by the student, explain how these will affect the quality of the precipitate and hence the accuracy of the method.
(v) Write down **two** properties of a good washing solvent.
(vi) Explaining the terms 'selectivity' and 'sensitivity', comment on these in relation to gravimetry.
(vii) If the weight of the precipitate was 0.3232 g, calculate the concentration of Pb^{2+} in the effluent sample. (Pb = 207.2; Cr = 52.0; O = 16.0).
(viii) If the same concentration of Ba^{2+} as in (vii) was found in the effluent, which ion will precipitate first? (K_{sp} of $PbCrO_4 = 1.8x10^{-14}$ mol^2 dm^{-6}; K_{sp} of $BaCrO_4 = 1.8x10^{-10}$ mol^2 dm^{-6}). How will you achieve selectivity in this case? (100 marks)

2.(a) A sample of a dibasic weak acid (H_2A) is believed to be adulterated with a small amount of strong acid (HB). A Laboratory Technician was curious to find out if there was such adulteration and attempted to carry out acid- base titrations in his laboratory. A 100.0 cm^3 of the mixture was titrated with 0.1 M NaOH and the end point obtained using methyl orange as indicator was 20.00 cm^3 while that using phenolphthalein was 35.00 cm^3.
For H_2A, $K_{a1} = 2.0x10^{-2}$ mol dm^{-3} and $K_{a2} = 2.0x10^{-8}$ mol dm^{-3}.

(i) What are the factors that need to be satisfied to use a reaction for a titration?
(ii) Draw and label the titration curve for the above titration using phenolphthalein. Give reasons for your answer.
(iii) Calculate the concentrations of H_2A and HB.
(iv) What do you mean by 'titration error'?
(v) If the weak acid is citric acid (H_3C), deduce the shape of the titration curve for the titration of citric acid with 0.1 M NaOH using phenolphthalein.
For citric acid, $K_{a1} = 9.2\text{x}10^{-4}$ mol dm^{-3}, $K_{a2} = 2.7\text{x}10^{-5}$ mol dm^{-3}; $K_{a3} = 1.3\text{x}10^{-6}$ mol dm^{-3}.
(75 marks)

(b) Briefly explaining the term 'buffer action', write down the essential steps in the preparation of a buffer of pH 4.50. (25 marks)

3.(a) In a student project, a random sample of water from a selected well in a village was analysed for Mg^{2+} by titrating 25.0 cm^3 of the sample solution with 0.02 M EDTA at pH 9.0 using Eriochrome Black T as the indicator. The volume of EDTA used was 22.00 cm^3.

(i) How would you obtain a random sample of water from a well?
(ii) Why was the pH maintained at 9.0?
(iii) Calculate the concentration of Mg^{2+} in the sample.
(iv) Giving reason(s), briefly explain the colour change at the end point.
(v) Derive an expression to show the relationship between the formation constant (K_{MgY}) and the conditional formation constant ($K'_{Mg'Y'}$) of magnesium EDTA complex.
Calculate the conditional formation constant of Mg- EDTA complex at pH 9.0.
($K_{MgY} = 5.01\text{x}10^8$ dm^3 mol^{-1}; at pH 9.0, $\alpha_{Y4-} = 5.2\text{x}10^{-2}$).
Write any assumption that you make.
(vi) Sketch the titration curves for the titration of Mg^{2+} with EDTA when $\alpha_{Y4-} = 5.2\text{x}10^{-2}$ and 1.0.
(vii) How would you achieve selectivity in complexometric titration? (75 marks)

(b) Water from an effluent was found to contain Al^{3+}. To a 25.0 cm^3 portion of the sample, 50.0 cm^3 of 0.02 M EDTA was added at pH 7 and the excess EDTA was titrated against 0.02 M Mg^{2+} solution using Eriochrome Black T as indicator. The volume of Mg^{2+} used was 26.50 cm^3.

(i) Calculate the concentration of Al^{3+} in the sample.
(ii) Give two possible reasons why direct titration of Al^{3+} with EDTA is unsuccessful.
(25 marks)

4.(a) In a titration to determine the amount of Fe^{2-} in a sample, it was found that 25.0 cm^3 of the sample required 20.00 cm^3 0.05 M Ce^{4+} solution. $E^0_{Ce^{4+}/Ce^{3+}} = 1.44\ V$; $E^0_{Fe^{3+}/Fe^{2+}} = 0.70\ V$.
Calculate
(i) the concentration of Fe^{2+}.
(ii) the potential at the equivalence point (35 marks)

(b) In an attempt to determine the constituents in a mineral sample containing Ti(III) and Fe(II), a sample was digested and a solution containing Ti(III) and Fe(II) was prepared and an aliquot was titrated against Ce(IV). Choice of an indicator should be made from X ($E^0_X = 0.76\ V$) and Y ($E^0_Y = 1.06\ V$) given to you.
$E^0_{Ce^{4+}/Ce^{3+}} = 1.44\ V$; $E^0_{Ti^{4+}/Ti^{3+}} =$ $0.10\ V$; $E^0_{Fe^{3+}/Fe^{2+}} = 0.70\ V$.

(i) Deduce whether it is possible to determine the concentration of Ti(III) and Fe(II) separately by titrating against Ce(IV). If so, which one will be oxidized first?
(ii) Sketch and label the expected titration curve.
(iii) Select a suitable redox indicator for this titration. What is the basis of selecting a suitable indicator in a redox titration? (45 marks)

(c) Compare and contrast redox titrations with complexometric titrations. (20 marks)

5. A factory effluent was analysed for the heavy metal ion X^{2+} before being discharged into the water body. The allowable limit of X^{2+} for discharging is 20 ppm. X^{2+} can be oxidised to X^{3+} and X^{3+} is not toxic. Both X^{2+} and X^{3+} were expected to be present in the effluent. X^{2+} can undergo the following reaction.

X^{2+} + R (complexing agent) ⟶ XR (water soluble red coloured complex of which the λ_{max} = 440 nm)

A sample of 5.00 mL of the effluent was diluted to 100.0 mL after adding 5.00 mL of the complexing agent R. The resultant solution was analysed using UV/Visible spectroscopy in a cell of 1 cm. It gave an absorbance of 0.235 at 440 nm and the molar absorptivity coefficient of X^{2+} is 17,500 $mol^{-1}cm^{-1}$.

(a) Can the effluent be discharged without treating to reduce of X^{2+}? Justify your answer with suitable calculations. (At. wt. of X = 29.1 g) (15 marks)

(b) Suggest a way to improve the accuracy of absorbance obtained. (10 marks)

(c) Another 5.00 mL sample of the effluent was analysed using Atomic Absorption Spectroscopy (AAS) at 193 nm and the absorbance obtained was 0.435 and the standard of X^{2+} (20 ppm) gave an absorbance of 0.645 when it was subjected to the same procedure.
(i) Calculate the composition of X^{3+} in the effluent.
(ii) Some other ions which were present in the effluent seemed to be interfering the results. How can you correct it and analyse using AAS? (20 marks)

(d) Do you think it is a good idea to carry out a classical redox titration using a suitable titrant and an indicator to analyse X^{2+}? Justify your answer. (10 marks)

(e) Suggest a method to overcome the disadvantage of classical redox titrimetry in this particular analysis? (06 marks)

(f) State two differences in the instruments used in the above two methods. (12 marks)

(g) A thermometric titration was carried out between a standard solution of R and X^{2+}.
(i) What is the principle behind thermometric titrations?
(ii) Sketch and label the expected titration curve. (27 marks)

6. (a) Briefly describe the following terms.
(i) Distribution coefficient (ii) Distribution ratio (20 marks)

(b) During a liquid -liquid extraction, 0.48 g of a substance X was extracted to 20 mL of 1-octanol from 50 mL of an aqueous plant extract at pH 7. Distribution ratio (K_d) of X for this system is 9.80.

(i) Calculate the amount of X present in aqueous plant extract before extraction.
(ii) Calculate the volume(V) of 1-octanol needed to effect 98% extraction in a single extraction.
(iii) Show that the extraction efficiency is more when extraction is done twice with half of volume V (i.e. V/2) each time.
(iv) If X is a weak base, giving reasons predict what happens to K_d when pH is decreased to 5.
(40 marks)

(c) Compare and contrast paper chromatography and thin layer chromatography.
(20 marks)

(d) Describe the mechanism of the separation process in ion exchange chromatography.
(20 marks)

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