

THE OPENUNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 –Continuous Assessment Test 1– 2015 / 2016



CMU 3123/CME 5123 – Analytical Chemistry

Duration: One hour

Date and time: 03rd April, 2016. From 9.00 a.m. to 10.00 a.m.

Reg. No.....

Question number	Max. marks	marks
1	100	
2	100	
Total		

Instructions to students

Answer all questions in the spaces given. Additional sheets will not be marked.

1. A water sample (100.0 cm^3) from an industrial effluent was given to a student to analyze Pb^{2+} using gravimetry by adding only a slight excess of K_2CrO_4 solution. The precipitate was digested overnight, filtered, washed and dried. The weight of the precipitate obtained was 2.864 g. ($\text{Pb} = 207.2$, $\text{Cr} = 52.0$, $\text{O} = 16.0$)

- (i) What is the precipitate formed in the above gravimetric analysis? Why is it suitable for gravimetric analysis? (15 marks)

- (ii) From the procedure given above, identify a **good practice** that had been followed to obtain a pure precipitate and explain briefly how it happens. (20 marks)

- (iii) Give two important factors that you should consider when selecting a washing solvent. (10 marks)

(iv) What is the concentration of Pb^{2+} in the water sample according to the results of the above analysis? (15 marks)

(v) Comment on the following statement.
“By adding very low concentrations of K_2CrO_4 solution, larger particles of the precipitate can be obtained “.
(10 marks)

(vi) It was found that Ba^{2+} also had been present in the effluent. At the completion of precipitation of lead chromate, the concentration of the chromate ion in the solution was 10^{-5} M but was not interfered by the presence of Ba^{2+} .

(a) What do you understand by interference in the above analysis?

(b) Calculate the maximum possible concentration of Ba^{2+} in that the solution.
(solubility product of $\text{BaCrO}_4 = 1.8 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$). (30 marks)

2. A sample of a factory effluent (20.0 cm^3) containing Zn^{2+} was titrated with 0.1 M EDTA using Eriochrome Black T as the indicator at pH 7 and the end point reading was 30.00 cm^3 . ($\alpha_{\text{Y}^{4-}} = 0.64$ at pH=9, $K_{\text{ZnY}} = 2.3 \times 10^{16}$)

(i) Write down the equation for $\alpha_{\text{Y}^{4-}}$ and define the terms in the equation. If you decrease the pH, what do you expect to happen to $\alpha_{\text{Y}^{4-}}$? Give reasons for your answer. (25 marks)

(ii) Calculate the molar concentration of ZnY^{2-} at equilibrium at the end point. State the assumptions you made. (20 marks)

(iii) Draw the titration curve for the above titration. (10 marks)

- (iv) It was decided to carry out a titration for another 20.0 cm³ of the effluent with 0.1 M X²⁺ (a standard reducing agent) in order to determine the concentration of Zn²⁺. The reaction between X²⁺ and Zn²⁺ is fast and stoichiometric.

$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.763 \text{ V}$$

$$E_{\text{X}^{2+}/\text{X}}^{\circ} = -0.91 \text{ V}$$

- (a) State all the requirements of a titration and comment on the possibility of carrying out a titration between Zn²⁺ and X²⁺. (35 marks)

- (b) What is the basis of selecting a suitable redox indicator a redox titration? (10 marks)

Name

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THE OPEN UNIVERSITY OF SRI LANKA
Level 5 – Continuous Assessment Test I – 2015/2016
CMU3123/CME5123 – Analytical Chemistry
Answer Guide

1. (i) PbCrO_4 is the precipitate. It is suitable for gravimetric analysis because it

- 1) has a low K_{sp} value.
- 2) can be obtained in pure form.
- 3) can wash and filter easily.

(ii) It should be from the procedure given,

- 1) Adding only a slight excess of K_2CrO_4

Relative super saturation also low Because of this, rate of nucleation is low.. This results in small number of large particles, which is easy to wash, filter and dry.

- 2) Digestion

Occluded foreign ions go back in to the solution thus the precipitate becomes more pure.

(iii) Washing solvent,

- 1) Should dissolve the impurities but not the precipitate.
- 2) Should not react with the precipitate.
- 3) Should be easily volatile.
- 4) Should not lead to peptisation.

(iv) Molecular weight of $\text{PbCrO}_4 = 323.2 \text{ g mol}^{-1}$

$$\text{Weight of PbCrO}_4 = 2.864 \text{ g}$$

$$\text{Mole of PbCrO}_4 = \frac{2.864 \text{ g}}{323.2 \text{ g mol}^{-1}} = 0.00886 \text{ mol}$$

$$\text{Mole of Pb}^{2+} = 0.00886 \text{ mol}$$

$$[\text{Pb}^{2+}] = \frac{0.00886 \text{ mol}}{100 \times 10^{-3} \text{ dm}^{-3}} = 0.08861 \text{ mol dm}^{-3}$$

(v) Very low concentration will make relative super saturation low, resulting decrease of nucleation (increase of growth rate). This results in formation of larger particles.

(vi) a) Interference – Precipitation of Ba^{2+} along with Pb^{2+} .

$$\text{b) } K_{sp}(\text{BaCrO}_4) = [\text{Ba}^{2+}] [\text{CrO}_4^{2-}]$$

$$[\text{Ba}^{2+}] = \frac{K_{sp}}{[\text{CrO}_4^{2-}]} = \frac{1.8 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}}{10^{-5} \text{ mol dm}^{-3}} = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$$

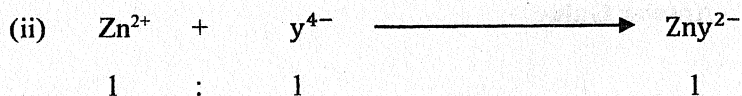
2. (i) $\alpha_{y^{4-}} = \frac{[y^{4-}]}{[y']}$ $[y^{4-}]$ = Concentration of y^{4-} in equilibrium with metal EDTA complex.

$[y^{4-}]$ = All form of EDTA that are not coordinated with the metal ion (Zn^{2+}).

At low pH, $\alpha_{Y^{4-}}$ also decreases.

Reason : $[Y'] = [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}] + [H_4Y^-]$.

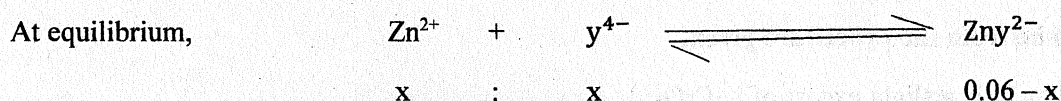
At low pH (high H^+ concentration) $[Y']$ increases thus $\alpha_{Y^{4-}}$ decreases.



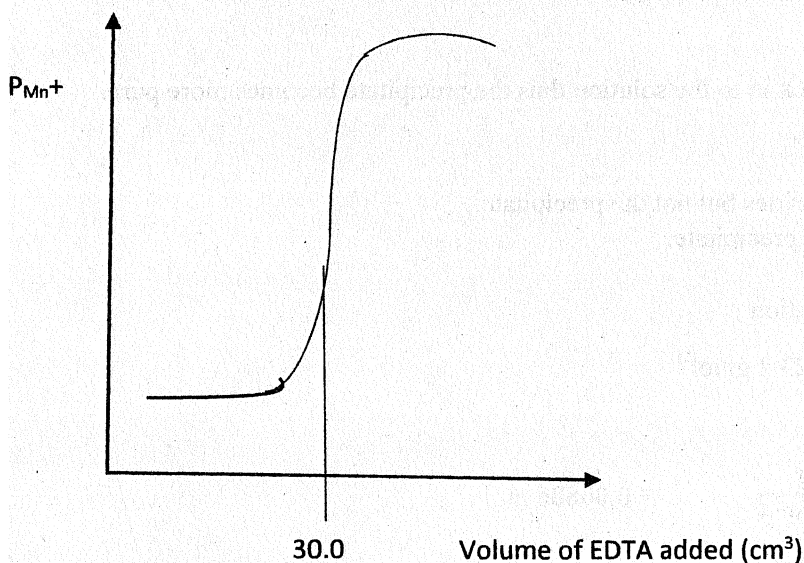
No of moles of Y^{4-} added $= 0.1 \text{ M} \times 30 \times 10^{-3} \text{ dm}^{-3} = 0.1 \times 30 \times 10^{-3} \text{ mol}$

No of moles of ZnY^{2-} formed $= 0.1 \times 30 \times 10^{-3} \text{ mol}$

$$[ZnY^{2-}] = \frac{0.1 \times 30 \times 10^{-3} \text{ mol}}{30 \times 10^{-3} \text{ dm}^{-3}} = 0.06 \text{ M}$$



Assumption: Since x (the dissociated amount) is very small compared to 0.06 M , $0.06 - x \approx 0.06$. Therefore, we can consider that the concentration of ZnY^{2-} is 0.06



(v) a) Requirements:

- 1) Reaction must be fast
- 2) Reaction must be stoichiometric
- 3) Reaction should be feasible. i.e ΔG is negative or ΔE^0 is positive.

$$\begin{aligned} \Delta E^0 &= E^0_{\text{Reduction}} - E^0_{\text{oxidation}} \\ &= E^0_{Zn^{2+}/Zn} - E^0_{X^{4+}/X^{2+}} \\ &= -0.763 - (-0.91) \\ &= +0.147 \text{ V} \end{aligned}$$

4) To use as visual indicator $\Delta E^0 > 0.4 \text{ V}$, Therefore we cannot use as visual indicator.

b) The formal potential of the indicator (E^0_{In}) should be within the potential change (ΔE^0_{cell}) taking place at the end point.