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. (Pb = 207.2, Cr = 52.0, 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 $BaCrO_4 = 1.8 \times 10^{-10} mol^2 dm^{-6}$). (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 and the end point reading was 30.00 cm^3. ($\alpha_{Y^{4-}}$ = 0.64 at pH =9, $K_{ZnY} = 2.3 \times 10^{16}$)

(i) Write down the equation for $\alpha_{Y^{4-}}$ and define the terms in the equation. If you decrease the pH, what do you expect to happen to $\alpha_{Y^{4-}}$? 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 cm^3 of the effluent with 0.1 M X^{2+} (a standard reducing agent) in order to determine the concentration of Zn^{2+}. The reaction between X^{2+} and Zn^{2+} is fast and stoichiometric.

$E^o_{Zn^{2+}/Zn} = -0.763\ V$ $\qquad$ $E^o_{X^{4+}/X^{2+}} = -0.91\ V$

(a) State all the requirements of a titration and comment on the possibility of carrying out a titration between Zn^{2+} and X^{2+}. (35 marks)

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

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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 Ksp 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 $PbCrO_4$ = 323.2 $gmol^{-1}$

   Weight of $PbCrO_4$ = 2.864 g

   Mole of $PbCrO_4$ $= \frac{2.864\ g}{323.2\ gmol^{-1}}$ = 0.00886 mol

   Mole of Pb^{2+} = 0.00886 mol

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

   (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+}.

   b) Ksp (BaCrO4) = $[Ba^{2+}]\ [CrO_4^{2-}]$

   $$[Ba^{2+}] = \frac{Ksp}{[CrO_4^{2-}]}$$

   $$= \frac{1.8 \times 10^{-10}\ mol^2dm^{-6}}{10^{-5} mol\ dm^{-3}} = 1.8 \times 10^{-5}\ moldm^{-3}$$

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, α_{y4^-} also decreases.

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

At low pH (high H^+ concentration) $[y']$ increases thus α_{y4^-} decreases.

(ii) $Zn^{2+} + y^{4-} \longrightarrow Zny^{2-}$

1 : 1 1

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

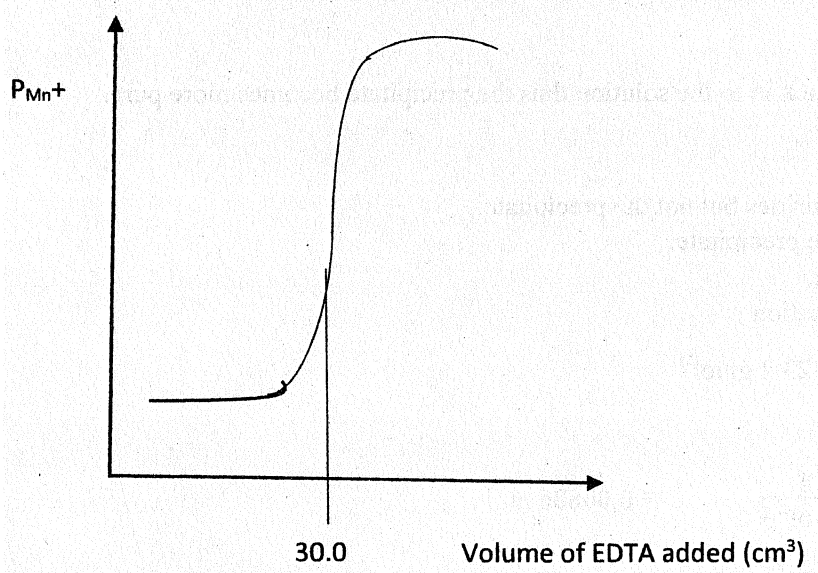
No of moles of Zny^{2-} formed $= 0.1 \times 30 \times 10^{-3}$ mol

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

At equilibrium, $Zn^{2+} + y^{4-} \rightleftharpoons Zny^{2-}$

x : x 0.06 – x

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.

$\Delta E^0 = E^0_{Reduction} - E^0_{oxidation}$

$= E^0_{Zn^{2+}/Zn} - E^0_{X^{4+}/X^{2+}}$

$= -0.763 - (-0.91)$

$= +0.147$ V

4) To use as visual indicator $\Delta E^0 > 0.4$ 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.