OPENUNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 –Continuous Assessment Test 1– 2016 / 2017

CMU 3123/CME 5123 – Analytical Chemistry

Duration: One hour
Date and time: 29th April, 2017. From 9.00 a.m. to 10.00 a.m.

Reg. No.....

Question number	Max. marks	marks
1	34	
2	38	
3	28	
Total		

Instructions to students

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

1. The pH of a 25.00 cm^3 of sample solution containing 0.1 M Fe (III) was buffered at 2 and 2 cm^3 of salicylic acid in methanol was added. The solution was titrated with 0.02 M EDTA and the end point was 20.10 cm^3. Fe (III) precipitates as ferric hydroxide when the pH is above 6.

   (i) Why do you think that the solution was buffered at pH 2?

(10 marks)

   (ii) This buffer was made out of the acid HX where the concentrations of HX and X^- were 0.040 M and 0.150 M respectively. Calculate the pK_a of the acid HX.

(10 marks)

(iii) What will happen to the conditional formation constant value of the Fe (III)-EDTA complex if the pH is raised to 7. Justify your answer using suitable equations.

(14 marks)

2. 25.00 cm^3 of a solution containing an equimolar mixture of Sn^{2+} and Z^{2+} in 0.1 M H_2SO_4 was titrated with 0.02 M $KMnO_4$ solution.

$E^\circ (MnO_4^-/Mn^{2+}) = 1.51$ V $\quad E^\circ (Sn^{4+}/Sn^{2+}) = 0.15$ V $\quad E^\circ (Z^{3+}/Z^{2+}) = 0.27$ V

(i) Comment on the feasibility and selectivity of the above titration.

(20 marks)

(ii) Sketch and label the titration curve for the above titration.

(10 marks)

(iii) Give one significant difference between acid- base titration and redox titrations.

(08 marks)

3. (i) State two major disadvantages of gravimetry compared to other methods of analysis.

(08 marks)

(ii) To a 30.0 cm^3 of a solution having Ba^{2+}, a 20.0 cm^3 of 0.0100 M sulfuric acid solution was added **dropwise** while **stirring**. 1.202 g of barium sulphate was obtained.

(a) Explain briefly why sulfuric acid was added dropwise while stirring.

(10 marks)

(b) Calculate the concentration of Ba^{2+} in the original solution assuming that barium was precipitated completely.
(Ba =137.33, S= 32.06, O= 16.00)

(10 marks)

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CMU 3123 - Assignment Test I- Answer Guide

01) (i) The formation constant (K_{Fey}) is high at pH = 2 and at pH = 2, Fe^{3+} reacts with EDTA selectively.

(ii) $HX \rightleftharpoons H^+ + X^-$

If the dissociation constant is K_a

$$Ka = \frac{[H^+][X^-]}{[HX]}$$

$$-log\ Ka = -log[H^+] + \{-log\frac{[X^-]}{[HX]}\}$$

$$pKa = pH + \{-log\frac{[X^-]}{[HX]}\}$$

$$pH = pKa + log\frac{[X^-]}{[HX]}$$

$$2 = pKa + log\frac{(0.150)}{(0.04)}$$

$$pKa = 1.42$$

(iii) When Fe^{3+} precipitates, $\alpha_{Fe^{3+}}$ (fraction of Fe^{3+} in equilibrium with EDTA) reduces.

$K'_{Fe'y'} = \alpha_{y^{4-}} . \alpha_{Fe^{3+}} . \alpha_{Fey}$

Therefore, Confidential formation constant ($K'_{Fe'y'}$) also reduces.

02) (i) For the titration between MnO_4^- and Sn^{2+}

$\Delta E^o_{cell\ 1} = E^o (MnO_4^-/ Mn^{2+}) - E^o (Sn^{4+}/ Sn^{2+})$

$= 1.51 - 0.15 = 1.36V$

Since ΔE^o is positive and high ΔG^o will a high negative value. Therefore, the titration between MnO_4^- and Sn^{2+} is feasible ($\Delta G^o = - n F \Delta E^o$)

For the titration between MnO_4^- and Z^{2+}

$\Delta E^o_{cell\ 2} = E^o (MnO_4^-/ Mn^{2+}) - E^o (Z^{3+}/ Z^{2+})$

$= 1.51 - 0.27 = 1.24V$

Since ΔE^o is positive and high ΔG^o will a high negative value. Therefore, the titration between MnO_4^- and Z^{2+} is feasible.

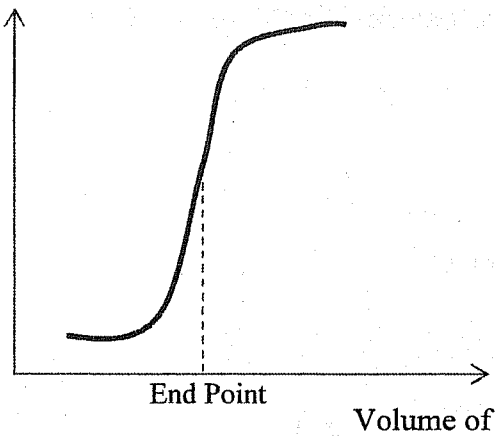
<u>Selectivity</u>

$\Delta E^o_{cell\ 1} - \Delta E^o_{cell\ 2} = 1.36 - 1.24 = 0.12V$

$= 0.12V < 0.4V$

Since the difference of $\Delta E^o_{cell\ 1}$ and $E^o_{cell\ 2}$ is less than 0.4V, selective titration of Sn^{2+} and Z^{2+} is not possible.

(ii) $E^{o'}$



(iii) Any one difference from the Table given below.

Acid - Base	Redox
1. Feasibility depends on the k_a and k_b values of the acid and the base	Feasibility depends on the difference of the potential of two half cell reactions.
2. pH varies with titrant added	E^{oll} varies with the titrant added
3. Stoichiometry is 1:1	Stoichiometry varies
4. $pk_{a1}/pk_{a2} > 4$ selective	$\Delta E^o_{cell\ 1} - \Delta E^o_{cell\ 2} > 0.4V$ selective
5. Colour change of the indicator depends on the pH	Colour change of the indicator depends on the change of the potential at the end point of the titration when redox indicators are used.

03) (i) Any two from the following.

1. Polar sensitivity
2. Low accuracy for trace analysis
3. Time consuming
4. High minimum detection limit

(ii) a) Drop wise addition – Absolute super saturation is low.
Stirring – Prevents momentary high super saturation.
These actions results in poor nucleation and high growth rate which results fewer number of large particles.

b) Molecular weight of $BaSO_4$ = 2333.3g

No. of moles of $BaSO_4$ in 1.202g = 1.202g / 233.3g mol^{-1}

No. of moles of Ba in it = 1.202g / 233.3g mol^{-1}

$[Ba^{2+}]$ $= \frac{1000ml}{30ml} x \frac{1.202g}{233.3g\ mol-1}$

$= 0.1717 molL^{-1}$