THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone course – Level 4

CHU 2125/CHE 4125 – Analytical Chemistry I - 2008/2009

Duration: One and half-hours   Date: 25th September from 3.30 p.m. to 5.00 p.m.

Reg. No. ....

Question No.	Marks
1	
2	
3	
Total	
Percentage	

Instructions to candidates

* Answer all questions.
* Write down answers on this paper itself, attached sheets will not be graded.

1.(a)(i) What do you mean by a 'buffer solution'?

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(ii) Derive the expression $pH = pK_a + \log\dfrac{[A^-]}{[HA]}$ for the pH of a buffer solution that

consists of a weak acid (HA) and a conjugate base of the acid (A$^-$).

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(iii) Calculate the pH of a HCOOH- HCOO$^-$ buffer that is 0.200 mol dm^{-3} in HCOO[H] acid and 0.100 mol dm^{-3} in HCOO$^-$. (40 mark[s])

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(b) The fraction of EDTA in the form Y^{4-}, $\alpha_{y^{4-}}$, is given by

$$\frac{1}{\alpha_{y^{4-}}} = \frac{[H^+]^4}{K_1 K_2 K_3 K_4} + \frac{[H^+]^3}{K_2 K_3 K_4} + \frac{[H^+]^2}{K_3 K_4} + \frac{[H^+]}{K_4} + 1$$

Calculate $\alpha_{y^{4-}}$ at pH 10. $K_1 = 1.0 \times 10^{-2}$; $K_2 = 2.2 \times 10^{-3}$; $K_3 = 6.9 \times 10^{-7}$; $K_4 = 5.5 \times 10$

(20 ma[rks])

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(c) Considering the formation of EDTA complex with M^{n+} ions,
  (i)   Write down the formation constant K_f for the chelate complex MY$^{(n-4)+}$.
  (ii)   Write down the equation relating K_f to the conditional formation constant $K_{MY'}$.
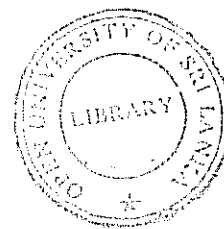
(15 m[arks])

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(d)(i) How do you achieve 'selectivity' in EDTA titration?

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(ii) In complexometric titration, back titration is considered when direct titration becomes unsuccessful. Give **three** reasons that most often make direct titration unsuccessful. (25 marks)

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2.(a)(i) What is meant by the solubility product of a sparingly soluble compound?

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(ii) The solubility product at 25 ^{0}C of lanthanum iodate, $La(IO_3)_3$ is 1.20×10^{-11} $mol^4 \, dm^{-12}$. Calculate the solubility of lanthanum iodate at 25 ^{0}C.

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(iii) In an experiment, sufficient Na_2CrO_4 is added to a solution containing Pb^{2+} and Ba^{2+}, the concentration of each is 0.001 mol dm^{-3}. Indicate, giving reasons, the ion that will precipitate first. K_{sp} $PbCrO_4 = 1.8 \times 10^{-14}$; K_{sp} $BaCrO_4 = 1.8 \times 10^{-10}$ $mol^2 \, dm^{-6}$.

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Can we precipitate the first ion completely before the second ion begins to precipitate? Give reason(s) for your answer. (40 marks)

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(b)(i) What do you understand by term, 'co-precipitation'?

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(ii) Briefly describe the processes involved in co-precipitation.

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(iii) 'Precipitation From Homogeneous Solution' (PFHS) is a method employed to obtain analytical quality precipitate for gravimetry. Briefly describe this method using an example.   (60 marks)

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3.(a)(i) Write the conditions that must be satisfied by a reaction in order for it to be used in a redox titration.

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(ii) Write the three methods by which the end point in a redox titration can be detected.

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(iii) When a solution containing Sn^{2+} was titrated with Ce^{4+}, Sn^{2+} was oxidized to Sn^{4+} while Ce^{4+} was reduced to Ce^{3+}.

Write down equations for the half reactions involved in the titration and hence the balanced equation for the redox reaction .

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Write the Nernst equations for the two half reactions.

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Derive an expression for the potential at equivalence point.   (75 marks)

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(b) The volume of 0.02 mol dm^{-3} $KMnO_4$ solution required to oxidize 25.00 cm^3 of Fe^{2+} solution (X) in acid medium is 23.35 cm^3. calculate the concentration of X.

(25 marks)

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Assignment Test I – Answer Guide

(a) i It is a solution that resists changes in pH when a small amount of acid / base is added or when the solution is diluted.

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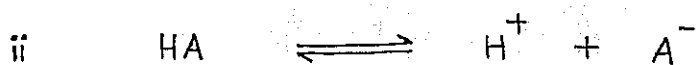
$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad [H^+] = K_a \frac{[HA]}{[A^-]}$$

$$pH = -\log_{10}[H^+] = pK_a - \log_{10}\frac{[HA]}{[A^-]}$$

$$pH = pK_a + \log_{10}\frac{[A^-]}{[HA]}$$

iii

$$pH = pK_a + \log_{10}\frac{[0.100 \ mol \, dm^{-3}]}{[0.200 \ mol \, dm^{-3}]}$$

$$= pK_a + \log_{10}(0.50)$$

(b) $pH = 10$ $[H^+] = 1 \times 10^{-10}$

$$\frac{1}{\alpha^{Y^{4-}}} = \frac{10^{-40}}{(1 \times 2.2 \times 6.9 \times 5.5)10^{23}} + \frac{10^{-30}}{(2.2 \times 6.9 \times 5.5) \times 10^{-24}}$$

$$+ \frac{10^{-20}}{(6.9 \times 5.5) \, 10^{-18}} + \frac{10^{-10}}{5.5 \times 10^{-11}} + 1$$

$$\frac{1}{\alpha^{Y^{4-}}} = 1.2 \times 10^{-19} + 1.2 \times 10^{-11} + 2.6 \times 10^{-4} + 1.82 + 1$$

$$\alpha^{4-} = \underline{0.35}$$

(c)
$$M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+}$$
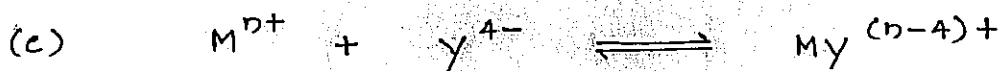
$$K_f = \frac{[MY^{(n-4)+}]}{[M^{n+}][Y^{4-}]} \qquad \alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[Y']}$$

$$K_f = \frac{[MY^{n-4}]}{[M^{n+}] \, \alpha_{Y^{4-}} \, [Y']}$$

$$K_{MY'} = \alpha_{Y^{4-}} K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y']}$$

(d) i By masking (i.e reduction of the conditional formation constant) or by changing pH

ii When the reaction between analyte (M) and EDTA - Slow. Inability to keep soluble the conditions necessary for direct titration, or very small amount of analyte. - Lack of a suita indicator formation.

02 (a) i It is the product of the molar concentrations o the ions of the compound, each raised to the power of its stoichiometric coefficient in the balanced equation.

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$$La(IO_3) \longrightarrow La^{+3}_{(aq)} + 3 IO_3^-{}_{(aq)}$$
$$\qquad\qquad\qquad\qquad x \qquad\qquad 3x$$
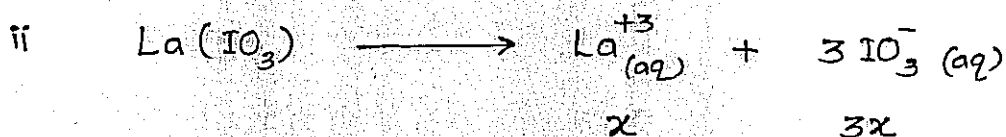
$$K_{sp} = [La^{+3}][IO_3^-]^3$$
$$\qquad = x \qquad (3x)^3$$
$$1.2 \times 10^{-11} = 27 x^4$$
$$x = (4/9)^{1/4} \times 10^{-3} \; mol\,dm^{-3}$$

iii It's $PbCrO_4$ that precipitate first since K_{sp} is
or appropriate calculation.

a) i 1. Reaction should be a rapid one

2. Stoichiometric and quantitative

3. Product formation should be favourable ($-\Delta G$)

ii 1. Potentiometrically

2. Self Indicator

3. Redox indicator

iii $Sn^{2+} \longrightarrow Sn^{4+} + 2e$

$Ce^{4+} + e \longrightarrow Ce^{3+}$

$Sn^{2+} + 2\,Ce^{4+} \longrightarrow Sn^{4+} + 2\,Ce^{3+}$
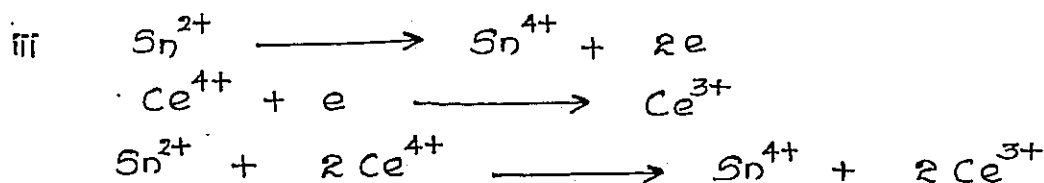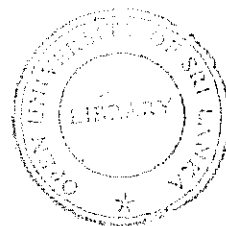
$$E_{cell} = E^{o}_{Sn^{+2},\,Sn^{+4}} - \frac{0.059}{2} \log \frac{[Sn^{2+}]}{[Sn^{4+}]}$$

$$E_{cell} = E^{o}_{Ce^{3+},\,Ce^{4+}} - \frac{0.059}{1} \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$3\,E_{cell} = \left(2\,E^{o}_{Sn^{2+},\,Sn^{4+}} + E^{o}_{Ce^{3+},\,Ce^{4+}}\right) - 0.059 \log \frac{[Sn^{2+}][Ce^{3+}]}{[Sn^{4+}][Ce^{4+}]}$$

b) $8\,H^{+} + 5\,Fe^{+2} + MnO_4^{-} \longrightarrow Mn^{+2} + 5\,Fe^{+3} + 4\,H_2O$
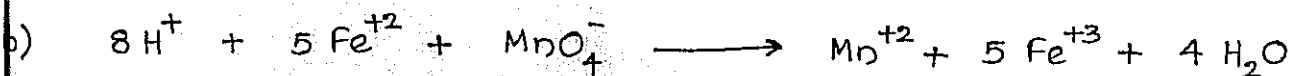
\# MnO_4^{-} moles consumed $= \dfrac{0.02}{1000} \times 23.25$

∴ \# Fe^{2+} moles consumed $= \dfrac{0.02}{1000} \times 23.25 \times 5$

$$[Fe^{+2}] = \frac{0.02}{1000} \times \frac{23.25 \times 5}{25} \times 1000$$

$$= \underline{9.30 \times 10^{-2} \; mol\,dm^{-3}}$$

For PbCrO$_4$

$$[CrO_4^{2-}] = \frac{1.8 \times 10^{-14}}{10^{-3}} = 1.8 \times 10^{-11}$$

For BaCrO$_4$

$$[CrO_4^{2-}] = \frac{1.8 \times 10^{-10}}{10^{-3}} = 1.8 \times 10^{-7}$$

Minimum $[CrO_4^{2-}]$ required to ppt BaSO$_4$ = 1.8×10^{-7} mol

At that moment, $[Pb^{+2}] = \frac{1.8 \times 10^{-14}}{1.8 \times 10^{-7}} = 10^{-7}$ moldm^{-3}

$$10^{-3} \longrightarrow 10^{-7}$$

Initially   at the time BaCrO$_4$ first ppt out

It can be considered that the amount is very low or almost over.

· Marks given for any reasonable explanation.

(b) i The precipitation of impurities along with the pp due to absorption and occlusion. Adsorption an occlusion are described as follows.

ii Surface adsorption — similar ions dislodge ion from the surface of a ppt

Occlusion — compound is trapped within a pocke formed during rapid crystal growth.

iii used in the precipitation of CaC$_2$O$_4$.
Initially the medium is acidic. Ca^{+2} and H$_2$C$_2$O$_4$ are in the sample. Urea is added to give NH$_3$ whi will make the solution basic. Slowly but gradua then the CaC$_2$O$_4$ precipitated out. Here the form -tion of precipitation is slow and relative supe saturation is very low. Therefore coprecipitatio is less.