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

CHU 2125/CHE 4125 – Analytical Chemistry I - 2011/2012

Duration: One and half-hours 27th August 2011 from 2.00 p.m. to 3.30 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 is meant by a 'buffer solution'? Write expressions for 'buffer capacity', β and 'buffer ratio' and identify the terms in it.

(ii) Write down the expression for pH of a buffer solution in terms of pK_a of the weak acid and the concentrations of the weak acid and its conjugate base.

(iii) Calculate the buffer capacity of the buffer that consists of 0.1 mol dm^{-3} CH_3COOH and 0.5 mol dm^{-3} CH_3COONa. (40 marks) (b)(i) Write down the expression for mole fraction ($\alpha_Y{}^{4-}$) of Y^{4-} form of EDTA, in terms of H^+ concentration and the dissociation constants K_1 ,K_2, K_3 and K_4.

(ii) Derive the expression for the conditional formation constants. $K_{MY'}$ in terms of the formation constant K_{MY} and $\alpha_Y{}^{4-}$. Calculate the conditional formation constant Ni-EDTA complex at pH = 4.00. $\alpha_Y{}^{4-} = 3.61 \times 10^{-9}$ at pH 4.00; $K_{NiY}{}^{2-} = 4.2 \times 10^{18}$.

(iii) Calculate the concentration of unreacted Ni^{2+} in a solution that was prepared by mixing 50.0 cm^3 of 0.05 mol dm^{-3} EDTA solution with 50 cm^3 of 0.03 mol dm^{-3} Ni^{2+} solution at pH 4.00. (60 marks)

2.(a)(i) Write **two** advantages and **two** disadvantages of gravimetry.

Advantages

Disadvantages (20 marks)

(ii) Briefly describe two major types of contamination during the precipitation process.

(30 marks)

(b) Briefly explain how each of the following experimental procedures will affect the quality and purity of precipitate for gravimetric analysis.

(i) Rapid addition of reagent

(ii) Precipitation from homogeneous solution (PFHS) (30 marks)

(c) It is often a practice in gravimetry to wash the precipitate with a solution containing a common ion. In a gravimetric analysis where silver ions were precipitated as AgCl, the precipitate was washed with a 0.01 mol dm^{-3} Cl^- solution instead of distilled water. Using calculation(s), briefly explain why this was done so.

The molar solubility of AgCl at 25 ^{0}C is 4.4×10^{-6} mol dm^{-3}. The solubility product K_{sp} of AgCl at 25 ^{0}C is 1.8×10^{-10} mol^2 dm^{-6}. (20 marks)

3.(a) Compare and contrast acid base titration with redox titration. (20 marks)

(b)(i) Reduction potentials of 2 electrodes A and B are -0.325 V and +0.076 V respectively. Which electrode will undergo reduction if used in conjunction in an electrochemical cell?

(ii) If we make an electrochemical cell using the 2 electrodes A and B, what would be the theoretical cell potential?

(c) Given that $UO_2^{2+} + 4H^+ + 2e \leftrightarrow U^{4+} + 2H_2O$ $E^\circ = +0.334$
$Ce^{4+} + e \leftrightarrow Ce^{3+}$ $E^\circ = +1.440$ V

(i) Calculate the E°_{cell} value.

(ii) Comment on the feasibility of the reaction.

(iii) Derive an expression for the potential at equivalence point in the titration of 0.05M U^{4+} with 0.01M Ce^{4+}. (Assume both solution are 1M in H_2SO_4).

(iv) In a titration, if 25.0 cm^3 of 0.01 M U^{4+}solution required 22.50 cm^3 of a Ce^{4+} solution. Calculate the concentration of Ce^{4+} solution.

(v) Write important features of a redox indicator. (80 marks)

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Answer Guide

1.(a) (i) A solution that resist changes in pH when a small amount of an acid, base or water is added in to the solution.

$$\text{Buffer capacity } (\beta) = \frac{db/da}{dpH}$$

$$\text{Buffer ratio} = \frac{[HA]}{A^-}$$

(ii) $$\text{pH} = p^{ka} + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

(b) (i) $$\frac{1}{\alpha_{Y^{4-}}} = \frac{k_{a1}k_{a2}k_{a3}k_{a4} + k_{a1}k_{a2}k_{a3}[H^+] + k_{a1}k_{a2}[H^+]^2 + k_{a1}[H^+]^3 + [H^+]^4}{k_{a1}k_{a2}k_{a3}k_{a4}}$$

(ii) $$M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$$

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

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

$$K'_{MY} = \frac{[MY^{n-4}]}{[M'][Y']} \quad \text{———}(2)$$

By substituting $[Y']$ & $[M']$ from above equations on equation (2),

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

$$K'_{MY} = K_{MY}.\ \alpha_{Y^{4-}}.\alpha_{M^{n+}}$$

assume $\alpha_{M^{n+}} = 1$

$$K'_{MY} = K_{MY}.\alpha_{Y^{4-}}$$

At p^H=4,

$K'_{NiY} = 4.2\times10^{18} \times 3.61\times10^{-9} = 1.516\times10^{10}$

(iii) $\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[Y']}$

$[Y^{4-}] = 3.61\times10^{-9} \times \quad 0.05 \text{ mol dm}^{-3} = 0.181\times10^{-9} \text{ mol dm}^{-3}$

$$Ni^{2+} + Y^{4-} \rightleftharpoons NiY^{2-}$$

0.03x50/1000	0.05x50/1000		
0.15×10^{-2}	0.25×10^{-2}		mol
0.15×10^{-2}	0.15×10^{-2}	0.15×10^{-2}	mol

$[NiY^{2-}] = \frac{0.15\times10^{-2}}{100} \times 1000 \text{ mol dm}^{-3} = 0.015 \text{ mol dm}^{-3}$

$K_{MY} = \frac{[NiY^{2-}]}{[Ni^{2+}][Y^{4-}]}$

$[Ni^{2+}] = \frac{0.015}{4.28\times10^{18} \times 0.181\times10^{-9}} = 0.02\times10^{-9} \text{ mol dm}^{-3}$

2.(a) (i) **Advantages**

- Technique is very accurate and precise
- Reading errors associated with mass are less w.r.t. volumes
- Possible sources of errors are readily checked
- Apparatus are relatively inexpensive

Disadvantages

- For large samples analysis will take more time & consume more reagents
- Purity is less
- The precipitation that satisfies the following conditions only can be determined using gravimetry;

(a) Solubility of the ppt should be negligibly small
(b) It should be filtered and washed easily
(c) It should be in pure form

(ii) Co-precipitation: Contamination by impurities during formation those are soluble in the precipitation medium.

(a) Adsorption – Impurities deposit on the surface of the ppt positive

Therefore ΔG = negative and the reaction is spontaneous.

(iii) $UO_2^{2+} + 4H^+ + \rightleftharpoons 2e \qquad U^{4+} + 2H_2O \qquad E^0 = +0.334V$

$Ce^{4+} + e \rightleftharpoons Ce^{3+} \qquad E^0 = +1.440V$

$$E_{eq} = E^0_{UO_2^{2+}/U^{4+}} - \frac{RT}{F}\ ln\frac{[U^{4+}][H_2O]^2}{[UO_2^{2+}][H^+]^4} \text{ ——— } \quad (1)$$

$$E_{eq} = E^0_{Ce^{4+}/Ce^{3+}} - \frac{RT}{F}\ ln\frac{[Ce^{3+}]}{[Ce^{4+}]} \text{ ——— } \quad (2)$$

(1)x2 + (2),

$$3\ E_{eq} = 3E^0_{UO_2^{2+}/U^{4+}} + E^0_{Ce^{4+}/Ce^{3+}} - 0.059\ ln\frac{[U^{4+}][Ce^{3+}]}{[UO_2^{2+}]\,[Ce^{4+}][H^+]^4}$$

At equivalence point, $\frac{[UO_2^{2+}]}{[U^{4+}]} = \frac{[Ce^{3+}]}{[Ce^{4+}]}$

$$3\ E_{eq} = 3E^0_{UO_2^{2+}/U^{4+}} + E^0_{Ce^{4+}/Ce^{3+}} - 0.059\ ln\frac{1}{[H^+]^4}$$

(iv) molar ratio, $U^{4+} : Ce^{4+} = 1:2$

$2x\ 25.00 \times 0.01x\ 10^{-3} = 22.50 \times [Ce^{4+}] \times 10^{-3}$

$[Ce^{4+}] = 0.02\ mol\ dm^{-3}$

(v) Changing the color very close to the equivalence point.

Act as a second oxidant or reductant.

Should be weaker than the analyte.(Should react with the indicator after almost completing the reaction).

(b) Occlusion – Impurities trapped inside the ppt

(b) (i) Rapid addition of reagent

- Direct addition may cause contamination due to to occlusion.
- Large number of smaller particle size of the ppt gives porosity ($\downarrow$Quality)
- Purity is low

(ii) Precipitation from homogeneous solution (PFHS)

- Slow in- situ precipitation gives rise to good crystalline ppt.
- Super saturation is very low and precipitates are homogeneous.
- Precipitate size is higher, therefore purity is high.

(c) $$\underset{S}{AgCl_{(s)}} \rightleftharpoons \underset{S+0.01}{Ag^{+}_{(aq)}} + Cl^{-}_{(aq)}$$

$K_{sp} = [Ag^{+}]_{(aq)}\ [Cl^{-}]_{(aq)}$

1.8 x 10-10 = S X (S + 0.01)

S << 0.01, S+ 0.01 = 0.01

$1.8 \times 10^{-10} = S \times 0.01$

$S = 1.8 \times 10^{-8}$ mol dm^{-3}

$S < 4.4 \times 10^{-6}$

Here , Cl^{-} is acting as a common ion.

ie. Solubility is decreasing when washing with 0.01 M Cl^{-} solution . precipitate is not soluble.

3. (a) In acid base titrations, a measured volume of the base in the burette is added to the acid (until $H^{+} = OH^{-}$) , neutralization reaction taking place.

In an redox titration, the equivalence point is reached when the number of moles of oxidizing agent and the number of moles of reducing agent are in the correct stoichiometric ratio.

Etc.

(b) (i) B undergoes reduction ,where B has a higher reduction potential.

(ii) $E^{o}_{Cell} = E^{o}_{cathode} - E^{o}_{anode} = 0.076\ V - (-0.325) = 0.401\ V$

(c) (i) $E^{o}_{Cell} = E^{o}_{cathode} - E^{o}_{anode} = 1.440\ V - 0.334\ V = +\ 1.106\ V$

(ii) E^{o}_{Cell} value is positive according to $\Delta G = -nFE$: E^{o}_{Cell}, n,and F are