



THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 –Continuous Assessment Test– 2013 / 2014

CMU 3123/CME 5123 – Analytical Chemistry

Duration: One hour

Date and time: 02nd March, 2014 from 8.45 a.m. to 9.45 a.m.

Reg. No.....

Question number	Max. marks	marks
1	48	
2	52	
Total		

Instructions to students

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

- (1). A 0.1 M Na_2CO_3 solution (500.0 cm^3) was contaminated with S^{2-} ions. In order to remove all S^{2-} ions from the solution, a student added 0.1 M CaCl_2 solution. Weight of the CaS precipitate obtained was 0.1250 g.
(K_{sp} of $\text{CaCO}_3 = 3.8 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$, K_{sp} of $\text{CaS} = 3.6 \times 10^{-29} \text{ mol}^2 \text{ dm}^{-6}$, Ca= 40.0, S= 32.0, C= 6.0, O= 16.0)

- (a) Assuming that sulfide ions have been precipitated completely as CaS, calculate the concentration of sulfide ions in the solution.

(10 marks)

- (b) (i) State two techniques that the student should have followed in order to get large particles

- (ii) Explain briefly the theory behind each above technique in relation to particle size.

(18 marks)

- (c) Will the student be able to obtain CaS precipitate selectively? Explain your answer with relevant calculations.

(20 marks)

- (2) A 25.0 cm³ of an industrial effluent having only Zn²⁺ as metal ions was titrated with 0.01 M EDTA solution at pH= 7 in order to determine the concentration of Zn²⁺. The end point reading was obtained at 25.00 cm³.

- (a) Draw the relevant titration curve.

(08 marks)

- (b) Derive an expression for the conditional formation constant K'_{ZnY} in terms of K_{ZnY} , $\alpha_{Y^{4-}}$ and α_{Zn} . Identify all the symbols used.

(18 marks)

- (c) Calculate the concentration of Zn^{2+} at equilibrium at the end point.

$$K_{ZnY} = 1.2 \times 10^{15} \text{ mol}^{-1} \text{ dm}^3, \alpha_{Y^{4-}} = 3.54 \times 10^{-9} \text{ and } \alpha_{Zn} = 1$$

(10 marks)

- (d) What are the factors affecting the feasibility of acid-base titrations and redox titrations? (You can write relevant equations to show the factors but with all the symbols identified)

(16 marks)

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Answers for CAT I – CMU 3123 [2013/2014]

1. a)	Molecular weight of CaS	=	72g
	No. of moles of CaS in 0.125g	=	0.125g/72g
	No. of moles of S ²⁻ in 500ml	=	0.125g/72g
	[S ²⁻]	=	0.125 x 1000ml
			<hr/>
			72g x 500ml
		=	0.00347 M

b) (i) slow addition , Stirring while adding , Use dilute solutions

(ii) Particle size $\propto 1 /$ Rate of nucleation (V_n)

Rate of nucleation \propto Relative supersaturation

Relative supersturation \propto Absolute supersturation

All the above techniques reduce the absolute supersturation making the rate of nucleation low. As a result particle size will be high.

c) .1.Since CaS has a low K_{sp} value CaS precipitates first. We have to find out whether all S²⁻ is precipitated as CaS by the time CaCO₃ starts precipitating. If so, we can precipitate CaS selectively.

2.[Ca²⁺] required to start precipitating CaCO₃

3. In another words if $[S^{2-}]$ is very low at that time possibility of forming CaS will be negligible.

4.

$$\begin{aligned} K_{sp} \text{ of CaCO}_3 &= [Ca^{2+}][CO_3^{2-}] = 3.8 \times 10^{-29} = [Ca^{2+}][0.1M] \\ [Ca^{2+}] &= 3.8 \times 10^{-8} \end{aligned}$$

We have to find out whether the $[S^{2-}]$ concentration is low.

$[S^{2-}]$ at the time when $CaCO_3$ starts precipitating –

$$\begin{aligned} K_{sp} \text{ of CaS} &= [Ca^{2+}][S^{2-}] \\ 3.6 \times 10^{-29} &= \frac{(3.8 \times 10^{-8}) [S^{2-}]}{[S^{2-}]} \\ [S^{2-}] &= \frac{3.6 \times 10^{-29}}{3.8 \times 10^{-8}} \\ &= 9.5 \times 10^{-22} \text{ M} \end{aligned}$$

$[S^{2-}]$ in the solution at the time $CaCO_3$ starts precipitating is very much less , compared to the initial $[S^{2-}]$.

Initial

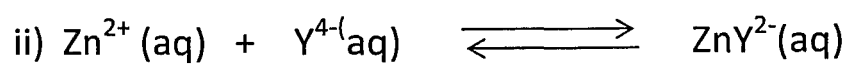
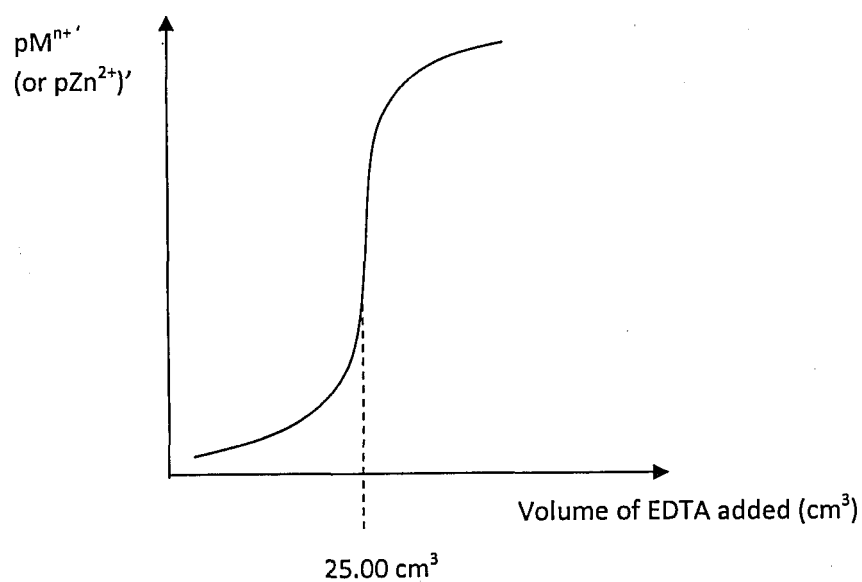
Now

$$3.47 \times 10^{-3} \text{ M} \gggg 9.5 \times 10^{-22}$$

Therefore we can say that almost all S^{2-} is precipitated as CaS.
Therefore selective precipitation of CaS is possible.

2.

(I).



$$\text{Formation constant} = \frac{[\text{ZnY}^{2-}]}{[\text{Zn}^{2+}][\text{Y}^{2-}]} \quad \text{--- [1]}$$

Since there will be other side reactions for both the Zn^{2+} and Y^{4-} ,

$$\alpha_{\text{Zn}^{2+}} = \frac{[\text{Zn}^{2+}]}{[\text{Zn}]'} \quad \text{--- [2]} \quad \alpha_{\text{Y}^{4-}} = \frac{[\text{Y}^{4-}]}{[\text{Y}]'} \quad \text{--- [3]}$$

$\alpha_{Zn^{2+}}$ = Fraction of Zn in equilibrium

$[Zn]'$ = Concentration of all forms of Zn that is not coordinated with Y^{4-}

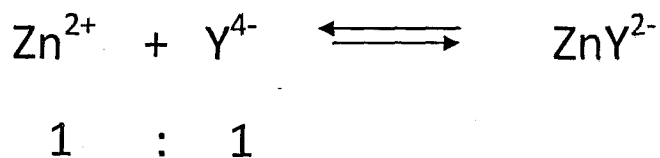
$\alpha_{Y^{4-}}$ = Fraction of Y^{4-} in equilibrium

$[Y]'$ = Concentration of all forms of EDTA that is not coordinated with Zn^{2+}

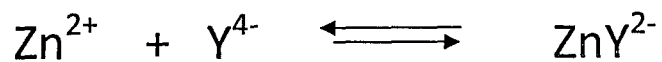
By substituting equation (1) with (2) and (3)

$$\alpha_Y^{4-} \cdot \alpha_{Zn^{2+}} \cdot K_{ZnY^{2-}} = \frac{[ZnY^{2-}]}{[Zn]' [Y]'} = K'_{Zn'Y'}$$

$$\text{iii) } K_{MY} = \frac{[ZnY^{2-}]}{\alpha_{Y^{4-}} [Y]' \alpha_{Zn^{2+}} [Zn]'}$$



$$[ZnY^{2-}] = \frac{0.01 \times 25 \times 10^3}{10^3 \times 50} = 0.005M$$



$$x \quad \quad x \quad \quad 0.005\text{M}-x$$



(0.005-x \approx 0.005M) since x is very small compared to 0.005M

$$K_{MY} = \frac{(0.005\text{M})}{3.54 \times 10^{-9} \times (x)(1)(x)}$$

$$1.2 \times 10^{15} = \frac{(0.005\text{M})}{3.54 \times 10^{-9} \times x^2}$$

$$x = \sqrt{\frac{0.005}{1.2 \times 10^{15} \times 3.5 \times 10^{-9}}} \text{ M} = 1.09 \times 10^{-4} \text{ M}$$

iv) For any titration, ΔG should be of a high (-) value in order to make the titration feasible.

$$\Delta G = -RT \ln K_{eq}$$

K_{eq} = Equilibrium constant

R = Universal Gas Constant

T = Temperature

In acid- base titrations, ($K_{eq} = K_{f''}$)

$$\Delta G = -RT \ln K_{f''}$$

$K_{f''}$ = Conditional formation constant of water

$$K_{f''} = K_a K_b K_f$$

K_a = Dissociation constant of the weak acid

K_b = Dissociation constant of the weak base

K_f = Formation constant of water

Therefore feasibility depends on T, K_a , K_b & K_f values.

In redox titrations,

$$\Delta G = -nFE_{cell}^{0'}$$

$E_{cell}^{0'}$ = Conditional formal potential of the cell reaction

E^0 should be high and positive. Feasibility will depend on the E^0 value.

In both titrations conditional formation constants will depend on the concentration of the reactants and the products too.