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**THE OPEN UNIVERSITY OF SRI LANKA**
**B.Sc. Degree Programme**
**Level 5 –Continuous Assessment Test 1– 2023/24**
**CYU 5302 – Analytical Chemistry**

Duration: One hour
Date: 23rd, July 2023
Time: 1.00 p.m. to 2.00 p.m.

Reg. No............................................

| Question number | Max. marks | marks |
|---|---|---|
| 1 | 30 | |
| 2 | 40 | |
| 3 | 30 | |
| Total | 100 | |

**Instructions to students**

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

1. A solution (100.0 $cm^3$) of $CO_3^{2-}$ (0.1M) and $S^{2-}$ was provided to determine the concentration of $S^{2-}$ using gravimetry. The analyst added 0.1 M $YCl_2$ solution and obtained the precipitate. The weight of the precipitate obtained was 0.4500 g. ($K_{sp}$ of $YCO_3 = 3.0 \times 10^{-10}$ $mol^2\ dm^{-6}$, $K_{sp}$ of $YS = 6.0 \times 10^{-12}$ $mol^2\ dm^{-6}$, Y= 45.0, S= 32.0, C= 6.0, O= 16.0)

   (a) One student stated that the precipitate obtained must be having $YCO_3$ also. Do you agree with the statement? Explain your answer with relevant calculations. (18 marks)

(b) The analyst added the $YCl_2$ solution dropwise while stirring. Explain briefly the theory behind these steps in relation to particle size. (12 marks)

2. A water sample (10.0 mL) containing metal ions $A^{2+}$ and $E^{+}$ (0.01 M) was buffered at pH 9 and titrated with 0.05 M EDTA solution. The endpoint obtained was 25.00 mL.
(At pH =9, $K_{AY}$= 3.2 x $10^8$ $mol^{-1}$ $dm^3$ and $K_{EY}$= 1.35 x $10^6$ $mol^{-1}$ $dm^3$)

(a) What may be the reason to have the pH of the solution at 9? (06 marks)

(b) Draw and label the expected titration curve. (12 marks)

(c) Calculate the concentration of $A^{2+}$ in the water sample. (12 marks)

(d) The buffer used here was made with a weak base and its salt. Briefly explain how the pH is maintained at 9 by the buffer with small additions of acid and base. (10 marks)

3. An effluent sample (25.0 mL) containing $D^{+}$ and $R^{3+}$ was titrated with 0.01M $Z^{3+}$ solution using an indicator.

$E^{0}_{Z3+/Z2+} = 3.24V$ $\quad$ $E^{0}_{D2+/D+} = 2.895V$ $\quad$ $E^{0}_{R3+/R2+} = 2.884V$

(a) Comment on the feasibility of the possible reaction/s taking place in the flask during the titration. (06 marks)

(b) How would you select a suitable redox indicator for this titration, considering the E° values? (10 marks)

(i) Comment on the potential changes that could have taken place in the flask before starting the titration, during the titration process up to the endpoint and after the endpoint giving reasons in brief. (14 marks)

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Name ................................................

Address ........................................

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**THE OPEN UNIVERSITY OF SRI LANKA**
**B.Sc. Degree Programme**
**Level 5 –Continuous Assessment Test 1– 2023/24**
**CYU 5302 – Analytical Chemistry-Answer guide**

1. A solution (100.0 $cm^3$) of $CO_3^{2-}$ (0.1M) and $S^{2-}$ was provided to determine the concentration of $S^{2-}$ using gravimetry. The analyst added 0.1 M $YCl_2$ solution and obtained the precipitate. Weight of the precipitate obtained was 0.450 g. ($K_{sp}$ of $YCO_3 = 3.0 \times 10^{-10}$ $mol^2\ dm^{-6}$, $K_{sp}$ of YS $= 6.0 \times 10^{-12}$ $mol^2\ dm^{-6}$, Y= 45.0, S= 32.0, C= 6.0, O= 16.0)

   (a) One student stated that the precipitate obtained must be having $YCO_3$ also. Do you agree with the statement? Explain your answer with relevant calculations. (18 marks)

   Answer

   YS precipitates first. If the concentration of $S^{2-}$ is very low ($<10^{-5}$M) at the time of $YCO_3$ starts precipitating, then the precipitate of YS can be obtained selectively in pure form. Otherwise, the precipitate will have both the precipitates.

   Ksp ($YCO_3$) $=[Y^{2+}]\ [CO_3^{2-}]$
   $3.0 \times 10^{-10}\ mol^2\ dm^{-6} = [Y^{2+}]\ [0.1\ mol\ dm^{-3}]$
   $[Y^{2+}]$ at the time of YS starts precipitating $= 3.0 \times 10^{-9}$ M
   Ksp (YS) $=[Y^{2+}]\ [S^{2-}]$
   $6.0 \times 10^{-12}\ mol^2\ dm^{-6} = [3.0 \times 10^{-9}\ mol\ dm^{-3}]\ [S^{2-}]$
   $[S^{2-}]$ at the time of $YCO_3$ starts precipitating $= 2.0 \times 10^{-3}$ M
   $2.0 \times 10^{-3}$ M $>10^{-5}$M (not very low)
   I agree with the statement. The precipitate had $YCO_3$ also.

   (b) The analyst added the Y solution dropwise while stirring. Explain briefly the theory behind these steps in relation to particle size. (12 marks)

   Answer

   These steps will decrease super saturation which in turn will reduce the rate of nucleation. This will result in large particles.

2. A water sample (10.0 mL) containing metal ions $A^{2+}$ and $E^+$ (0.01 M) was buffered at pH 9 and was titrated with 0.05 M EDTA solution. The end point obtained was 25.00 mL. (At pH =9, $K_{AY}= 3.2 \times 10^8\ mol^{-1}\ dm^3$ and $K_{EY}= 1.35 \times 10^6\ mol^{-1}\ dm^3$)

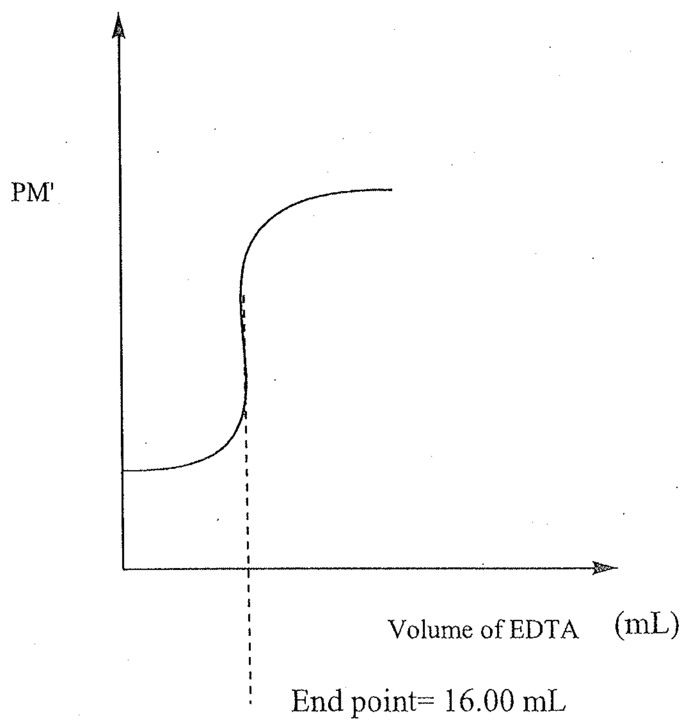
   (a) What may the reason to have the pH of the solution at 9? (06 marks)

   Answer

   To have an optimal conditional formation constant for AY complex.

(b) Draw and label the expected titration curve. (12 marks)

Answer




(c) Calculate the concentration of $A^{2+}$. (12 marks)

Answer

No. of moles of EDTA reacted with both ions = $25 \times 10^{-3} \times 0.05$

Stoichiometry- EDTA: $A^{2+}$ = 1:1 EDTA: $E^{+}$ = 1:1

$$[A^{2+}] + [E^{+}] = \frac{25 \times 10^{-3} \times 0.05}{10} \times 10^{3} = 0.125 \text{ M}$$

$[E^{+}]$ =0.01 M $[A^{2+}]$ = 0.125 M -0.01 M = 0.115 M

(d) The buffer used here was made with a weak base and its salt. Briefly explain how the pH is maintained at 9 by the buffer with small additions of acid and base. (10 marks)

Answer

When an acid ($H^{+}$) is added, the $OH^{-}$ resulted by partial dissociation of the weak base joins with $H^{+}$ and produces $H_2O$.

When a base ($OH^{-}$) is added, the cation resulted by partial dissociation of the weak base joins with $OH^{-}$ and produces the weak base.

3. An effluent sample (25.0 mL) containing $D^{+}$ and $R^{3+}$ was titrated with 0.01M $Z^{3+}$ solution using an indicator.

$E^{0}_{Z3+/Z2+} = 3.24$V $E^{0}_{D2+/D+} = 2.895$V $E^{0}_{R3+/R2+} = 2.884$V

(i) State the potential changes that could have taken place in the flask during the whole titration process giving reasons in brief. (20 marks)

Answer

1. $\Delta E^\circ$ of the reaction between $D^+$ and $R^{3+}$ is negative thus not feasible.
2. $\Delta E^\circ$ of the reaction between $D^+$ and $Z^{3+}$ is positive and high thus feasible.
3. Reaction between $R^{3+}$ and $Z^{3+}$ is not possible since both are in the oxidized form.
4. During the titration, the reaction between $D^+$ and $Z^{3+}$ is only possible.
5. The flask containing $D^+$ has a lower $E^\circ$ value at the beginning.
6. The $E_{cell}$ will be governed by the oxidation half-cell reaction of $D^+$ to $D^{2+}$ up to the end point since there is no $Z^{3+}$ in the flask.
7. During the titration, $E_{cell}$ will be increased with increasing $D^{2+}$ according to the Nernst equation.
8. At the half end point, $E_{cell} = E^0_{D2+/D+} = 2.895V$.
9. After the end point, there will be only a negligible amount of $D^+$ thus the $E_{cell}$ will be governed by the reduction half-cell reaction of $Z^{3+}$ to $Z^{2+}$.
10. After the end point, with the addition of $Z^{3+}$, $E_{cell}$ will be increased according to the Nernst equation.

(ii) How would you select a suitable redox indicator for this titration, considering the $E^\circ$ values? (10 marks)

Answer

The $E^0$ value of the half-cell reaction of the indicator should be in the range of 3.24V-2.895V.