PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Determination of Calcium by Precipitation with Oxalate Followed by Titration with Permanganate.

In this exercise, you must determine the amount of calcium ion in a solution that contains both calcium and magnesium, by selectively precipitating only the calcium as calcium oxalate, then quantitatively removing the precipitate from the solution by filtration.

$$Ca^{2+} + C_2O_4^{2-} \rightarrow CaC_2O_4\,(s)$$

The precipitate must then be re-dissolved in acid:

$$CaC_2O_4\,(s) + 2\,H^+ \rightarrow Ca^{2+} + H_2C_2O_4$$

The liberated oxalic acid is titrated with standard permanganate solution:

$$5\,H_2C_2O_4 + 2\,MnO_4^- + 6\,H^+ \rightarrow 10\,CO_2 + 2\,Mn^{2+} + 8\,H_2O$$

Formation of the calcium oxalate precipitate

1. Use a 25.00 cm^3 pipette and 250.0 cm^3 volumetric flask to accurately dilute (by a factor of 10), the calcium/magnesium solution that has been provided for you.
   Analyse two samples of the dilute calcium/magnesium solution. You have sufficient reagents for three analyses, but you must plan your time and use of equipment carefully. Take each of your samples through the following procedure:
2. Transfer a 25.00 cm^3 aliquot of the dilute calcium/magnesium solution into a 250 cm^3 beaker, add approximately 10 cm^3 of 3 M H_2SO_4 and about 50 cm^3 of water.

CARE! 3 M H_2SO_4 is very corrosive! The following steps involve hot (nearly boiling) solutions. Be careful and beware of steam!

3. Cover the beaker with a watch glass and gently heat on a hotplate until the solution is very hot, but not boiling.
4. Remove the beaker from the heat, then carefully add solid ammonium oxalate (1.5 g) and swirl the beaker until most of the ammonium oxalate dissolves.

CARE! Oxalate solutions are toxic. Do not wash solutions that contain oxalate down the sink. Place them in the “Permanganate/Oxalate residues” bottle at the end of your bench.

5. Add 5 –10 drops of methyl red indicator to the beaker, then while the solution is hot, increase the *pH* of the solution by slowly adding 1 : 1 ammonia solution with constant stirring, until the colour just changes from pink to orange. If you add too much ammonia, the solution will turn yellow. To correct this problem, add 1 drop of 3 M H_2SO_4 to lower the *pH* again, then repeat the pH adjustment with ammonia solution.

CARE! 1 : 1 ammonia solution is corrosive and has a very strong smell! Keep the bottle stoppered when not in use.

6. Allow the solution to stand for at least 60 minutes to quantitatively precipitate the calcium oxalate. Do not stir the solution during this time.

> You should complete Laboratory Task 2 during this waiting period.
> Do not proceed to the next step until you are confident that precipitation is complete**.**

Filtration of the calcium oxalate precipitate

7. Prepare a filter paper in a filter funnel supported in the neck of a 250 cm^3 conical flask. Rinse the paper with a few cm^3 of water then decant most of the supernatant solution from step 6. into the filter funnel. Collect the filtrate in the conical flask. Use a wash bottle to rinse the watch glass into the filter funnel.
8. Test the filtrate for the presence of calcium ion by adding a drop of ammonium oxalate test solution to a drop of the filtrate on a black plastic sheet. If a white precipitate (or cloudiness) is formed, the calcium oxalate precipitation in step 6 was unfortunately not complete. Perhaps the *pH* was not adjusted correctly or insufficient time was allowed for precipitation. Depending on the time you have left, you may start the analysis again or you may continue with the present experiment.
9. If there is no detectable calcium ion in the filtrate, use a wash bottle to carefully wash the calcium oxalate precipitate into the filter. Use the rubber “policeman” on the end of a glass rod to remove the last traces of precipitate from the beaker, and rinse these into the filter.
10. Wash the precipitate 4 times with approximately 10 cm^3 portions of water, collecting the washings in the conical flask.

11. Discard the combined filtrates from the previous steps into the residue bottle labeled "Permanganate/Oxalate residues" then carefully rinse the conical flask with water into the residue bottle.
12. Wash the precipitate one more time with 10 cm^3 of water. Collect this filtrate in the conical flask and test it for the presence of oxalate by adding a drop of saturated calcium nitrate solution to a drop of the filtrate on a black plastic sheet. If a white precipitate (or cloudiness) is formed, continue washing and testing until the washings are free from oxalate.
13. When the precipitate is free of oxalate, discard the washings and rinse and drain the conical flask.

NOTE! Show your demonstrator your precipitates. You must ask your demonstrator to sign your results sheet before proceeding to the next step.

14. Use a glass rod to break a small hole in the bottom of the filter paper and wash the precipitate through the hole into the conical flask with approximately 20 cm^3 water. Take care to rinse the rod and the creases of the filter paper.
15. Use a Pasteur pipette to dissolve any traces of calcium oxalate that remain in the paper with 25 cm^3 3 M sulphuric acid, collecting the acid in the conical flask. Finally, rinse the paper with ~ 20 cm^3 water.

Titration with permanganate

16. Make the volume up to about 100 cm^3 with water, heat the solution to about 60 ℃, then when all the calcium oxalate precipitate is dissolved, carefully titrate the hot solution with standard potassium permanganate solution.

    CARE! It is not necessary to measure the temperature of the solution with a thermometer. 60 ℃ is uncomfortably hot to touch.
17. Discard the titrated solution into the residue bottle labelled "**Permanganate/Oxalate residues**".

Calculate the average concentration of calcium ion in the original calcium/magnesium solution that was provided.

Molar masses in g mol^{-1}: Ca 40.08, Mg 24.31, Mn 54.94, C 12.01, O 16.00.

SOLUTION

Model solution

Analysis of calcium/magnesium solution

Permanganate titration

Concentration of standard $KMnO_4$ solution: 0.02039 mol dm^{-3}

Titration number	1	2	3
initial burette reading (cm^3)	0.90	0.80	3.00
final burette reading (cm^3)	28.55	28.45	30.80
volume of standard $KMnO_4$ (cm^3)	27.65	27.65	27.80
Average titre (cm^3)	27.70		

In a 25 cm^3 aliquot of dilute Ca/Mg solution:

$n(KMnO_4)$ required to titrate oxalate from dissolved calcium oxalate precipitate

$n(KMnO_4) = 0.0198 \text{ mol dm}^{-3} \times 0.0277 \text{ dm}^3 = 5.485\times10^{-4} \text{ mol}$

n(oxalate) from dissolved calcium oxalate precipitate:

$n(\text{oxalate}) = 5/2 \times 5.485\times10^{-4} \text{ mol} = 1.371\times10^{-3} \text{ mol}$

$n(Ca^{2+})$ from dissolved calcium oxalate precipitate = n(oxalate) = 1.371×10^{-3} mol

$c(\text{Ca}) = 1.371\times10^{-3} \text{ mol} / 0.02500 \text{ dm}^3 = 0.0548 \text{ mol dm}^{-3}$

In original Ca/Mg solution:

$c(\text{Ca}) = 0.0548 \text{ mol dm}^{-3}$

PROBLEM 2 (Practical)

Analysis of a Mixture of Cobalt(III) Complexes

When the complex $[Co(NH_3)_5NO_2]Cl_2$ is prepared in the laboratory, it often contains a considerable amount of $[Co(NH_3)_6]Cl_3$ by-product.

In this exercise, you must determine the amount of $[Co(NH_3)_5NO_2]Cl_2$ in a sample that also contains only $[Co(NH_3)_6]Cl_3$ as a by-product, using a cation-exchange procedure. The cation exchange resin used in this exercise is a cross-linked polystyrene resin of the strong acid type. It contains $-SO_3H$ groups from which the H^+ can be exchanged. When a solution containing 1 mol of M^{n+} is allowed to react with the resin this liberates n mol of H^+. In this exercise, the solution resulting from ion exchange of the mixture of the two different complex cations is used to titrate a standardised NaOH solution.

Preparation of the cation exchange resin

You are provided with about 10 g of wet resin in the H^+ form. Wash the resin using the following procedure to remove all traces of free acid:

1. Transfer your resin to a 250 cm^3 beaker, washing it from the container with about 50 cm^3 of water, then let the resin settle. This will take a few minutes.
2. Carefully pour off (decant) as much of the acidic solution as possible into a 'waste' beaker. Try to minimise loss of any of the resin in this process. Wash the resin with ~20 cm^3 portions of distilled water and test a drop of washing solution using a glass rod and pH paper until the excess acid is completely removed (*pH* ~5). You should not need to use more than 200 cm^3 of water to do this.
3. Drain off all but enough water to leave the resin just covered with water.
   Be sure to put all your acidic wash solutions into a waste bottle labelled "acid waste" - not down the sink! Do not allow the resin to dry out.

Preparation and standardisation of approximately 0.0125 M NaOH

4. Prepare 250.0 cm^3 of approximately 0.0125 M NaOH by accurately diluting your ~0.125 M NaOH with distilled water in a volumetric flask.
5. With the standard 0.01253 M HCl that is provided, titrate 25.00 cm^3 aliquots of the diluted NaOH solution, using phenolphthalein indicator.

Analysis Procedure

You are provided with approximately 40 cm^3 of a 0.00500 M solution of HCl that contains 0.2000 g of a mixture of the cobalt(III) complexes $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_6]Cl_3$ in 40.00 cm^3.

6. Use a pipette to transfer a 25.00 cm^3 aliquot of the cobalt complex solution into a 250 cm^3 beaker (beaker No 1) and add ~25 cm^3 water.
7. Use a plastic spoon to add about half (~5 g) of your wet resin to the cobalt(III) solution and allow to stand for at least 5 minutes for ion-exchange to take place, liberating H^+. You should occasionally gently swirl the mixture to hasten the ion-exchange process.
8. Carefully wash the acidic solution into a second 250 cm^3 beaker (beaker No 2) with about 20 cm^3 of distilled water. Try to leave as much as possible of the resin behind. Notice that the solution is now much lighter in colour, indicating that most, but not all of the cobalt complex mixture is stuck to the resin. You must now remove the last traces of cobalt(III) from solution (liberating more acid in the process), with a second batch of resin.
9. Add most of the remainder of your resin (~4 g) to the solution in beaker No 2 and again allow to stand for at least 5 minutes to allow the cation exchange to take place, liberating more H^+.

   At the end of this process, the solution should be colourless - if not, (perhaps you did not wait long enough for ion-exchange to take place) repeat the ion-exchange and washing steps with the last portion (~1 g) of your ion-exchange resin.
10. Filter the two resin samples through a carefully washed filter paper, and collect the acidic filtrate in a 100 cm^3 volumetric flask. Carefully wash the resin with small portions of water into the volumetric flask and make up to the mark with water.
11. With this acid solution titrate 25.00 cm^3 aliquots of your standardized NaOH solution.

Calculate the number of moles of H^+ liberated by the 25 cm^3 aliquot of your mixture of cobalt(III) complexes and report the percentage of $[Co(NH_3)_5NO_2]Cl_2$ that is present in your sample.

Molar masses in g mol^{-1}: Co 58.93; N 14.01; H 1.01; Cl 35.45; O 16.00.

SOLUTION

Model solution

Standardization of 0.0125 M NaOH

Concentration of standard HCl in bottle: 0.01253... mol dm^{-3}

Titration number	1	2	3
aliquot of NaOH	25.00	25.00	25.00
initial burette reading (cm^3)	13.60	17.40	10.35
final burette reading (cm^3)	37.75	41.50	34.45
volume of standard $KMnO_4$ (cm^3)	24.15	24.10	24.10
Average titre (cm^3)		24.12	

c(NaOH) = 0.01250 mo! $dm^{-3} \times 0.02412\ dm^3 = 0.01206$ mol dm^{-3}

Aliquot of cobalt complex solution used for ion-exchange: 25 cm^3

Titration number	1	2	3
initial burette reading (cm^3)	26.25	16.10	3.80
final burette reading (cm^3)	48.50	38.40	26.20
volume of standard $KMnO_4$ (cm^3)	22.25	22.30	22.40
Average titre (cm^3)		22.32	

Calculations

$c(H^+)$ collected in 100 cm^3 flask:

$c(H^+) = 0.01206$ mol $dm^{-3} \times (25.00\ cm^3) / (22.32\ cm^3) = 0.01351$ mol dm^{-3}

total $n(H^+)$ collected from column:

$n(H^+) = 0.01351$ mol $dm^{-3} \times 0.100\ dm^3 = 1.351 \times 10^{-3}$ mol

$n(H^+)$ from aliquot put onto column:

$n(H^+) = 0.00500$ mol $dm^{-3} \times 0.02500\ dm^3 = 1.250 \times 10^{-4}$ mol

$n(H^+)$ ion-exchanged from complexes in aliquot put onto column:

$n(H^+) = 1.351 \times 10^{-3}$ mol $- 1.250 \times 10^{-4}$ mol $= 1.226 \times 10^{-3}$ mol

let y = mass $[Co(NH_3)_5NO_2]Cl_2$ in 25.00 cm^3 aliquot of mixture added to column mass of mixture added to column = $(25.00\ cm^3 / 40\ cm^3) \times 0.2000$ g = 0.1250 g

then mass $[Co(NH_3)_6]Cl_3$ in aliquot = (0.1250 - y) g

$n(H^+)$ ion-exchanged from $[Co(NH_3)_5NO_2]Cl_2$:

$n(H^+) = 2\ y\ /\ 261.00\ g\ mol^{-1} = 0.007663x$ mol

$n(H^+)$ ion-exchanged from $[Co(NH_3)_6]Cl_3$:

$n(H^+) = 3\ (0.1250 - y)\ g\ /\ 267.50\ g\ mol^{-1} = (0.001402 - 0.011214\ y)$ mol

Thus, $0.007663\ y + (0.001402 - 0.011214\ y) = 0.001226$ or y = 0.04956 g

% $[Co(NH_3)_5NO_2]Cl_2 = 100\ (0.04956\ g\ /\ 0.1250\ g) = 39.6$ %