PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Analysis of Chloride Mixtures

Introduction

Composition of a solution containing only $MgCl_2$ and NaCl can be determined by an indirect titration method by performing a precipitation titration to determine the total amount of chloride present, followed by a complex formation titration to determine the amount of magnesium ions. A common precipitation titration technique used to determine the amount of chloride ions present in a solution is the Fajans method. In this argentometric procedure, silver nitrate is used as the titrant to precipitate the chloride ions present in the solution. The end point is detected through the use of an adsorption indicator, typically dichlorofluorescein, a weak organic acid. Prior to the end point, silver chloride particles are negatively charged because of the adsorption of excess chloride ions present in solution. The indicator anions are repelled by the negatively charged surface of the silver chloride particles imparting a yellow-green colour to the solution. Beyond the equivalence point, however, silver chloride particles adsorb silver ions. Thus a positively charged layer is formed and it attracts the dichlorofluoresceinate ions displaying a pink-red colour. Dextrin is used to stabilize the silver chloride particles against the coagulation.

On the other hand, the amount of magnesium ions present in a solution can be determined by complexometric titration with ethylenediaminetetraacetic acid, EDTA. As a hexadentate ligand, EDTA forms chelates with all metal ions, except alkali metal ions, in a 1 : 1 mole ratio regardless of the charge of the cation. Eriochrome Black T (EBT) is a common indicator used for EDTA titrations. When pH > 7.00 EBT imparts a blue colour to the solution in the absence of metal ions and forms a red colour when coordinated to metal ions.

In this experiment the chloride content of the solution containing $MgCl_2$ and NaCl will be determined by Fajans method. Magnesium ion concentration will be determined by EDTA titration.

A 100 cm^3 solution prepared by dissolving $MgCl_2$ and NaCl in water is given as the unknown sample. The task is to determine the mass concentration (in g/100 cm^3) of both $MgCl_2$ and NaCl in the unknown solution.

Reagents

- Unknown solution, 100 cm^3
- Dextrin in Eppendorf tubes (3) in a zipper bag
- Dichlorofluorescein, indicator
- $AgNO_3$ solution, c = 0.1 mol dm^{-3} *), 100 cm^3
- EDTA solution, c = 0.01 mol dm^{-3} *), 100 cm^3
- pH 10 buffer (NH_3/NH_4Cl), 5 cm^3
- Eriochrome Black T, indicator

*) The exact value of the concentration is given on the label.

A. Determination of total chloride concentration by Fajans method

1. Using a 10 cm^3 pipette, transfer 10.0 cm^3 aliquot from the bottle labelled as unknown solution into a 250 cm^3 Erlenmeyer flask. Complete the volume to approximately 100 cm^3 by adding distilled water.
2. Take one of the Eppendorf tubes given in the zipper bag labelled as “dextrin” and transfer all its content into the Erlenmeyer flask.
3. Add 5 drops of dichlorofluorescein indicator solution.
4. Record the exact concentration of $AgNO_3$ in standard solution.
5. Fill one of the burettes with the standard $AgNO_3$ solution.
6. Titrate the unknown solution until the whole solution has pink-red colour.
7. Record the volume of $AgNO_3$ used in cm^3.
8. Use the same Erlenmeyer flask when repeating the titration. Before doing this, pour the content of Erlenmeyer flask into the “Aqueous Waste” container and rinse it twice with distilled water.

B. Determination of Mg^{2+} by direct titration with EDTA

1. Fill the second burette with the standard EDTA solution.
2. Record the exact concentration of EDTA in standard solution.

3. Using a 25 cm^3 pipette, transfer a 25.0 cm^3 aliquot of the unknown solution into a 250 cm^3 Erlenmeyer flask. Complete the volume to approximately 100 cm^3 by adding distilled water.
4. Using a 1 cm^3 pipette, add 1.0 cm^3 of pH 10 buffer.
5. Add 3 – 4 drops of EBT indicator solution.

6. Titrate the unknown solution with standard EDTA solution until the colour changes from red to blue.
7. Record the volume of EDTA solution used, in cm^3.
8. Use the same Erlenmeyer flask when repeating the titration. Before doing this, pour the content of Erlenmeyer flask into the "Aqueous Waste" container and rinse it twice with water.

Treatment of Data

1.1 Determine the amount of Cl^- ions (in mmol) in 100 cm^3 of the unknown solution.

1.2 Determine the amount of Mg^{2+} ions (in mmol) in 100 cm^3 of the unknown solution.

1.3 Calculate the concentration of both $MgCl_2$ and NaCl in g/100 cm^3 in the unknown solution.

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SOLUTION

1.1 – 1.3

- Some distribution graphs were proposed by the organizer and approved by the International Jury that could be applied for evaluating of accuracy of the titrations and, consequently, for awarding points.
- For determinations of amounts of substance of Cl^- and Mg^{2+} ions, as well concentrations of both $MgCl_2$ and NaCl in the unknown solution, simple stoichiometric calculations can be applied.

PROBLEM 2 (practical)

Hydrogen generation from ammonia borane

Hydrogen has been considered as a clean and environmentally benign new energy carrier in the way towards a sustainable energy future. An effective and safe storage of hydrogen is one of the key issues of the hydrogen economy. Among the chemical hydrides, considered as potent solid hydrogen storage materials, ammonia-borane ($H_3N{\cdot}BH_3$) has been attracting a great deal of attention due to its high hydrogen content and stability under fuel cell operating conditions. Ammonia borane can release hydrogen upon hydrolysis, (Equation 1):

$$H_3N.BH_3(aq) + 2\ H_2O(l) \rightarrow NH_4BO_2(aq) + 3\ H_2(g) \qquad (1)$$

Aqueous solution of ammonia borane is stable and its hydrolysis occurs only in the presence of a suitable catalyst. Recent studies have shown that palladium(0) nanoclusters stabilized by water soluble polymers are highly active catalyst in the hydrolysis of ammonia borane. Palladium(0) nanoclusters are generated in situ by the reduction of potassium tetrachloropalladate(II) with ammonia borane in the presence of poly(4-styrenesulfonic acid-co-maleic acid).

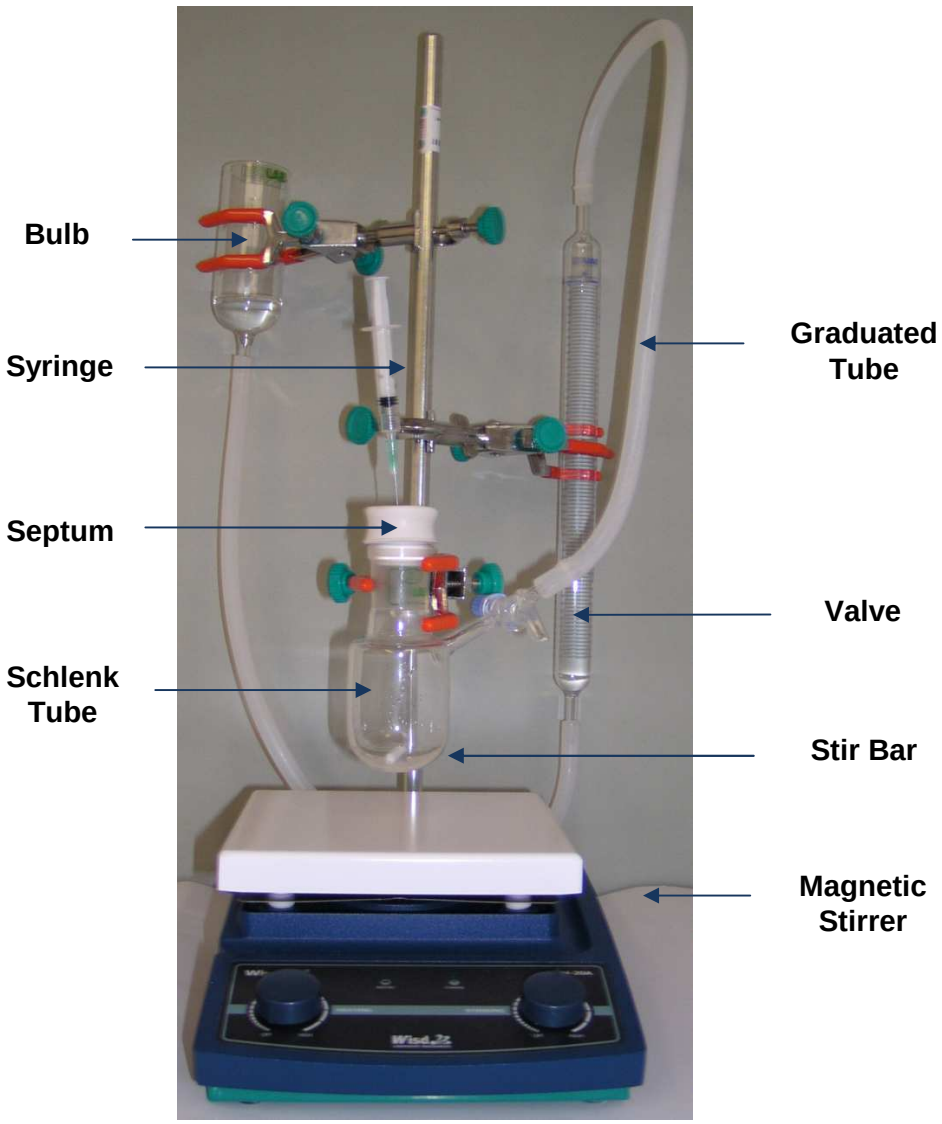
In this experiment, the catalytic hydrolysis of ammonia borane will be carried out starting with potassium tetrachloropalladate(II) in a solution containing poly(4-styrenesulfonic acid-co-maleic acid). Potassium tetrachloropalladate(II) will be used as precatalyst, which will be reduced by ammonia borane and palladium(0) nanoclusters will be formed and stabilized by poly(4-styrenesulfonic acid-co-maleic acid). These nanoclusters will catalyze the hydrolysis of ammonia borane.

Chemicals

- Solution A: H_3NBH_3 , 29.5 mg dissolved in 10 cm^3 H_2O,
- Solution B: poly(4-styrenesulfonic acid-co-maleic acid), 137.7 mg in 9 cm^3 H_2O,
- Solution C: Potassium tetrachloropalladate(II), $K_2[PdCl_4]$, 6.7 mg in 1 cm^3 H_2O.

I. Preparation of the Experimental Set-up

1. Check that the experimental setup, shown below, is held on a support, the graduated tube is connected to the Schlenk tube by Tygon tubing, and a stir bar is in the Schlenk tube.
2. Make sure that the septum is off and the valve is open.
3. By changing the bulb height adjust the water level in the graduated tube to zero.
4. Close the valve on the Schlenk tube.



Experimental Set-up

II. Hydrolysis of ammonia borane

A. In the absence of catalyst

1. Transfer all of the ammonia-borane solution (Solution A) from the glass vial to the Schlenk tube through the funnel,
2. Add the polymer solution (Solution B) from the glass vial to the Schlenk tube through the funnel.
3. Close the Schlenk tube with the septum, turn the stirring on at 600 rpm (as marked on the stirrer), and open the valve connecting to the graduated tube. Record the water level as V_0 at time zero. Start the timer.
4. Every minute read the total volume of gas produced and write in the Table given on the answer sheet. Do this for 10 minutes. Stop the timer.

B. In the presence of catalyst

1. While stirring, transfer all of the potassium tetrachloropalladate(II) solution (Solution C) from the glass vial to the Schlenk tube by injecting through the septum using a 2.0 cm^3 syringe. Keep the syringe inserted in the septum throughout the experiment. Start the timer.
2. Every minute read the total volume of gas produced and write in the Table given on the answer sheet. Do this for 10 minutes. Stop the timer.

Treatment of Data

A. Reaction of ammonia-borane without catalyst

2.1 Plot the volume of gas recorded versus time in Graph 2.1.

2.2 Report the volume of gas evolved as $V_{\text{uncatalyzed}}$.

B. Reaction of ammonia-borane with catalyst

2.3 Plot the volume of the gas generated versus time in Graph 2.2.

2.4 Calculate the maximum amount of substance (mol) and the maximum volume (cm^3) of hydrogen gas which will be evolved theoretically from the hydrolysis of 29.5 mg ammonia borane with a purity of 97 % w/w at 25 ℃. The atmospheric pressure is 690 torr.

2.5 Calculate the rate of hydrogen generation in your experiment

i) in cm^3 H_2/ min.

ii) in mmol H_2/min by assuming that the temperature is 25 ℃. The atmospheric pressure is 690 torr.

2.6 Based on your experiment calculate the rate of hydrogen production per mole of palladium in (mol H_2)×(mol Pd)$^{-1}$×(min)$^{-1}$. The purity of potassium tetrachloro-palladate(II) is 98 % w/w.

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SOLUTION

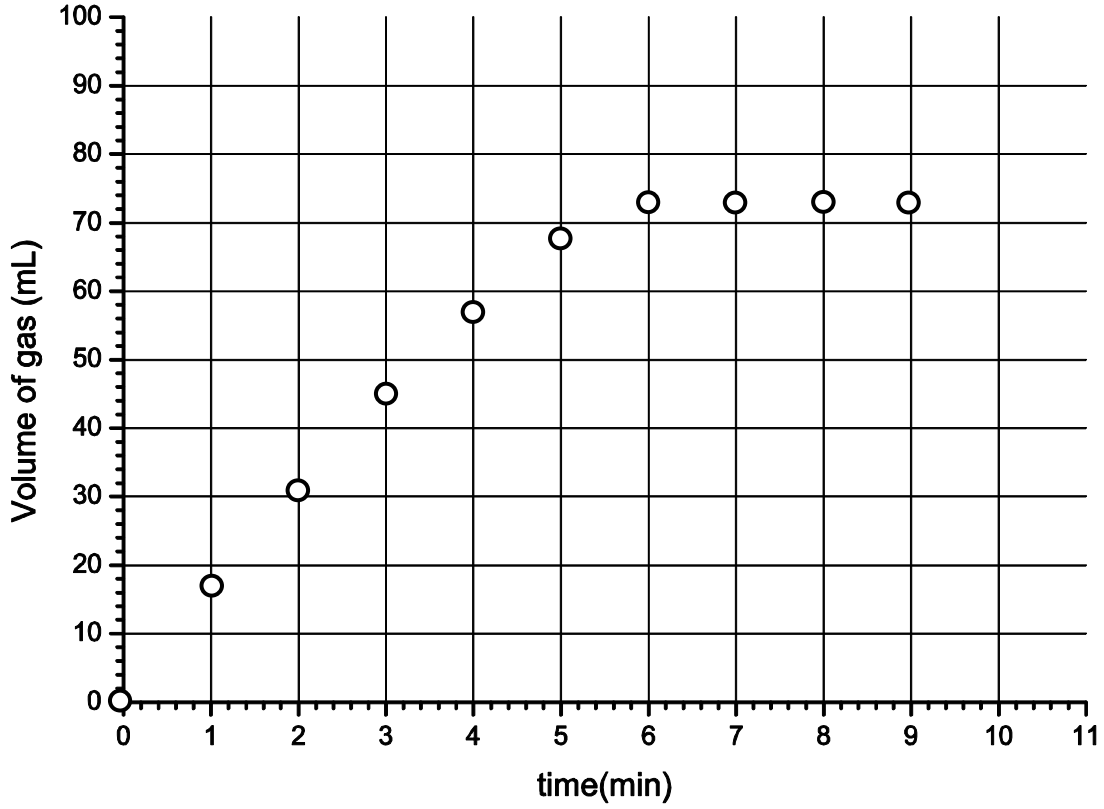
2.1 **Part A.** The volume of the gas evolved stays within a range of 0 – 2 cm^3 (maximum).

2.2 $V(H_2)_{uncatalyzed} = 0\ cm^3$

2.3 **Part B.** The gas volume versus time data for the reaction of ammonia borane in the presence of catalyst, are given in the table below.

Time (min)	0	1	2	3	4	5	6	7	8	9
Volume (cm^3)	0	17	31	45	57	68	73	73	73	73

Graph of gas volume versus time in the presence of catalyst:



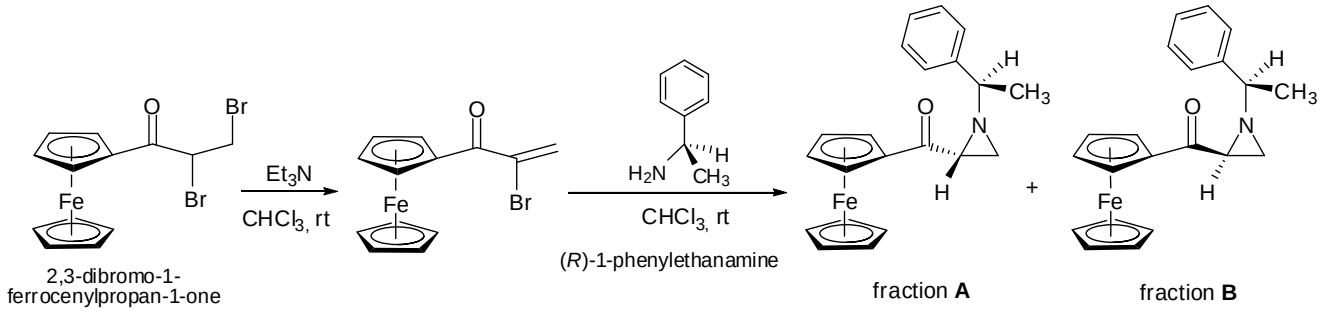
2.4 – 2.6

The required calculations are based on the experimental data obtained in practical problem 2. The well known relations between the mass, molar mass, amount of substance, and the volume of a gaseous substance at a certain pressure and temperature, as well as the experimental volume data in dependence on time (part 2.3) should be used to solve the tasks 2.4 – 2.6.

PROBLEM 3 (practical)

Synthesis, purification and separation of a diastereomeric mixture

Nature has many compounds in the form of a single enantiomer or diastereomer such as sugars, amino acids, steroids, etc. Some of these compounds are biologically active and used as drugs. Therefore, the asymmetric synthesis of organic compounds is important. One of the methods for the asymmetric synthesis of organic compounds employes a metal-catalyst, in which the metal is coordinated to a chiral organic molecule named as chiral ligand. In this experiment two chiral ligands will be synthesized.



2,3-dibromo-1-ferrocenylpropan-1-one

(*R*)-1-phenylethanamine

fraction **A**

fraction **B**

Chemicals

- 2,3-dibromo-1-ferrocenylpropan-1-one, 0.50 mmol, labelled as "Rxn RB"
- Triethylamine, 1.0 mmol in 1.0 cm^3 of $CHCl_3$, label: "V 1"
- (*R*)-1-phenylethanamine, 1.0 mmol in 0.5 cm^3 of $CHCl_3$, label: "V 2"
- 2,3-dibromo-1-ferrocenylpropan-1-one, reference starting material for TLC, label: "SM"
- Heptane : ethyl acetate mixture in a volume ration 3 : 2, 500 cm^3, label: "ELUENT",

A. Synthesis

1. Using a syringe, transfer through the septum the triethylamine solution in vial 1 (V 1) to the 10 cm^3 round bottom reaction flask (Rxn RB) containing 0.50 mmol 2,3-dibromo-1-ferrocenylpropan-1-one.
2. Stir the mixture at room temperature for 30 minutes using the magnetic stirrer at 600 rpm (as marked on the stirrer).
3. After 30 minutes, transfer through the septum the (*R*)-1-phenylethanamine solution in vial 2 (V2) to the reaction flask using the same syringe.
4. Stir the mixture for additional 60 minutes at room temperature.

5. After 60 minutes turn off the magnetic stirrer and perform a thin layer chromatography, TLC, analysis as follows:
   i) Check your TLC plates before use. Damaged plates will be replaced upon request without penalty.
   ii) Draw a start line on the lower portion of TLC plate with a pencil (Fig. 3.1).
   iii) Apply starting material from the vial labelled as SM two times to the spot on the left and then two times to the spot in the middle of plate. To the same plate, apply the reaction mixture (RM) taken from the reaction flask once to the spot on the right and then once to the spot in the middle as shown in Figure 3.1 (use a different capillary tube for each sample).
   iv) Develop TLC plate in the TLC chamber with the eluent. Mark the solvent front with the pencil (Fig. 3.2).
   v) When the TLC plate is dry, place it in a zipper storage bag marked as TLC1.

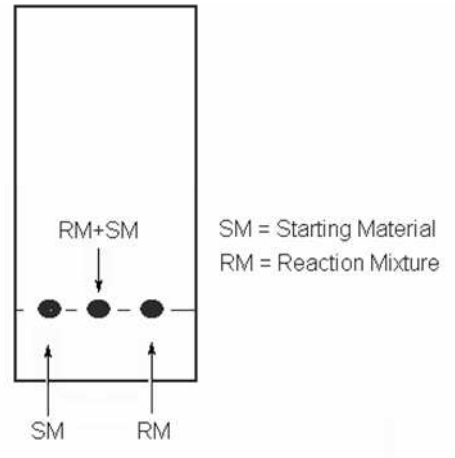


Figure 3.1. TLC plate

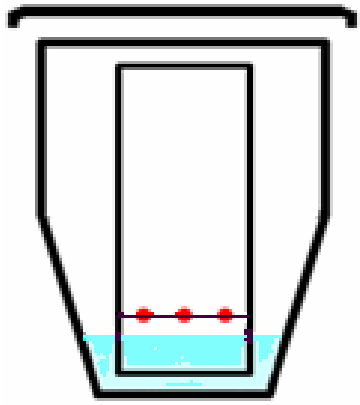


Fig. 3.2 TLC plate placed in the TLC developing chamber.

B. Flash Column Chromatography

1. Remove the stopper, open the valve, and bring the eluent level at top of column to the upper level of silica gel. (Fig. 3.3).
2. Close the valve and load the content of reaction flask on the top of flash column using a Pasteur pipette.
3. Rinse the reaction flask with 0.5 cm^3 eluent taken from the bottle labelled as ELUENT using a clean syringe. Using the same Pasteur pipette, load the washings also on the top of column.
4. Open the valve of the column and let the solvent run down to the upper level of silica gel.

5. Close the valve and add 1.0 cm^3 eluent by a Pasteur pipette. Open the valve. When the eluent is at the upper level of silica gel, add 2 - 3 cm^3 eluent slowly without closing the valve.
6. Fill the column by adding more eluent.
   CAUTION: Be careful during the addition of eluent; do not disturb silica gel.

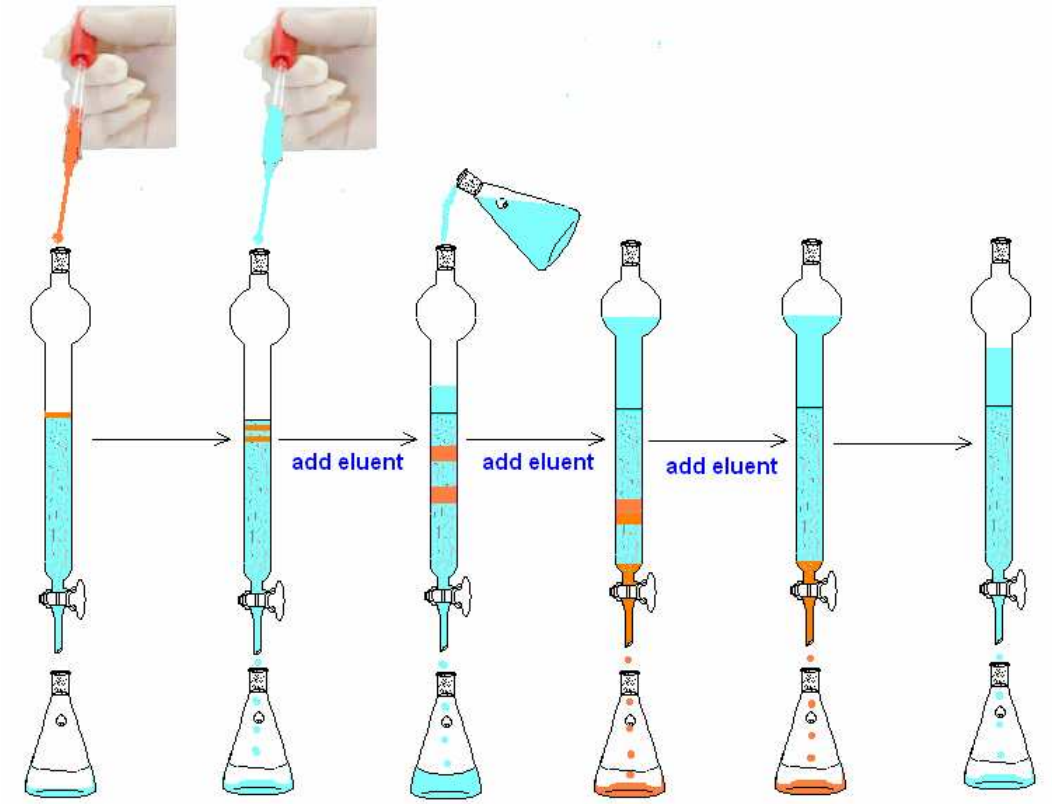


Figure 3.3. Flash Column Chromatography

7. In order to speed up the purification, apply little pressure by connecting the pressure applying bulb with an adapter on top of the column.
   CAUTION: Be careful not to apply too much pressure. Add eluent time to time to avoid silica gel run dry.
8. You are expected to collect two major fractions **A** and **B**. Discard any material which elutes before major fraction **A** and between **A** and **B** into the container labeled as Organic Waste.

9. Collect the first major fraction into a 100 cm^3 Erlenmeyer flask and label it as fraction **A**.
10. Collect the second major fraction into a 250 cm^3 Erlenmeyer flask and label it as fraction **B**.
11. After collecting fraction **B** stop the elution by closing the valve.

C. Analysis. Perform

1 Perform another TLC by applying the starting material (**SM**) two times to the spot on the left, apply fraction **A** two times to the spot in the middle, and then fraction **B** five times to the spot on the right. After development, when the TLC plate is dry, place it in a zipper storage bag marked **TLC2**.

2. Measure the volume of fraction **A** using 50 cm^3 graduated cylinder and record the volume to your answer sheet.
3. Measure the volume of fraction **B** using 250 cm^3 graduated cylinder and record the volume to your answer sheet.
4. Using a 2 cm^3 pipette transfer 2.0 cm^3 of fraction **A** into the 10 cm^3 volumetric flask and complete the volume to 10 cm^3 by adding eluent. After shaking the flask, fill out the UV-visible cell (at least ¾ of its volume) by using a Pasteur pipette. Ask the assistant to measure the absorbance at 450 nm using the spectrophotometer and record the result to your answer sheet.
5. Using fraction **B**, fill out (at least ¾ of its volume) the other UV-visible cell by a Pasteur pipette (no need for dilution). Ask the assistant to measure the absorbance at 450 nm using the spectrophotometer and record the result to your answer sheet.

Treatment of Data

3.1 Copy (sketch) the TLC1 plate on your answer sheet.

3.2 Copy (sketch) the TLC2 plate on your answer sheet.

3.3 Calculate and record the R_f values of the spots (fraction **A**, fraction **B**, and starting material **SM**) using the TLC2 plate.

3.4 The molar extinction coefficient, molar absorptivity, ε, is 404 $M^{-1}cm^{-1}$ for **A** and 400 $M^{-1}cm^{-1}$ for **B** at 450 nm (M = mol dm^{-3}). Calculate in percent:

i) the yield of fraction **A** based on the starting material.

ii) the yield of fraction **B** based on the starting material.

SOLUTION

3.1 – 3.2

Maximum points are given:

- for the appearance of three spots loaded on the base line,
- for the well developed and separated spots on the TLC,
- for the solvent front line and the base line,
- for the accurate presentation of the sketch of the TLC,
- in part 3.2, moreover, for the absence of fraction **B** in fraction **A** and vice versa.

3.3 Maximum points if calculated and recorded R_f values fall within those given in the following table:

Spots	R_f value
Fraction **A**	0.40 – 0.50
Fraction **B**	0.20 – 0.30
Starting material **SM**	0.65 – 0.75

3.4 Points were awarded in accordance with some distribution graphs proposed by the organizer and approved by the International Jury. The graphs were applied for fraction **A** and **B**, when evaluating their volumes, absorbance and yields.