PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

This experiment includes one preparation of a metal complex salt and two analyses of a provided sample of the same compound. The compound is a "classic" within inorganic photo chemistry.

Preparation of Potassium tris(oxalato)manganate(III) Hydrate, $K_3[Mn(C_2O_4)_3]\cdot xH_2O$

Note 1: The $[Mn(C_2O_4)_3]^{3-}$ ion is photosensitive and should therefore be protected from light as far as possible. Also, the thermal stability of the title compound is low.

Note 2: Before starting the synthesis, write down the thermometer reading in ice-water.

The synthesis comprises a reduction of manganese(VII) to manganese(II) with oxalic acid at 70 – 75 °C. After the addition of the suffi cient amount of potassium ions in form of potassium carbonate, manganese(III) is formed by the addition of manganese(VII) at a temperature below 2 °C.

$$2\ MnO_4^-(aq) + 8\ C_2O_4H_2(aq) \rightarrow 2\ Mn^{2+}(aq) + 10\ CO_2(g) + 3\ C_2O_4^{2-}(aq) + 8\ H_2O(l)$$

$$C_2O_4H_2(aq) + CO_3^{2-}(aq) \rightarrow C_2O_4^{2-}(aq) + CO_2(g) + H_2O(l)$$

$$4\ Mn^{2+}(aq) + MnO_4^-(aq) + 11\ C_2O_4^{2-}(aq) + 4\ C_2O_4H_2(aq) \rightarrow$$

$$\rightarrow 5\ [Mn(C_2O_4)_3]^{3-}(aq) + 4\ H_2O(l)$$

Dissolve 5.00 g of $C_2O_4H_2 \cdot 2\ H_2O$ in 35 cm^3 of water in a 150 cm^3 beaker by heating to 70 °C. Slowly add 1.00 g of $KMnO_4$ with magnetic stirring. The temperature must not exceed 70 - 75 °C. When the mixture is colourless, add 1.10 g of K_2CO_3 in small portions and cool the mixture in ice. When the temperature of the mixture has fallen to 25 - 30 °C, add 25 g of crushed ice. Meanwhile, cool the hotplate with a beaker containing ice.

Maintain the temperature of the reaction mixture not more than 2 ℃ above your reported temperature of ice-water while adding 0.24 g of $KMnO_4$ in small portions with vigorous stirring. Stir for another 10 min and filter off the white precipitate and unmelted ice, if any, using the 60 cm^3 filter syringe (see procedure A). Collect the filtrate in a 250 cm^3 beaker cooled in ice. Add 35 cm^3 of ice-cold ethanol to the cherry-red filtrate (just swirl the beaker; stirring will lead to the formation of tiny crystals), wrap the beaker in aluminium foil and cool it in ice for 2 h (swirl the beaker three or four times during this period).

Clean the filter - first with 4 M HCl, then with water. Collect the cherry-red crystals by filtration using a 60 cm^3 filter syringe, then wash them two times 5 cm3 of ethanol and then two times with 5 cm^3 of acetone, and dry the product in air and protect it from light for at least one hour. A brown vial with lid should be taken to be tared by the lab assistant. When dry, the product is placed in the vial. Write name and student code on the vial. Then close the vial and take it and your answer sheet to the lab. assistant who will weigh your sample. The theoretical yield is 7.6 mmol.

1.1 Record the yield in grams.

1.2 Suggest a molecular formula of the white precipitate which is removed in the first filtration.

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Analysis of the Provided Sample of $K_3[Mn(C_2O_4)_3] \cdot x\,H_2O$ for Oxidizing Ability

Note 3: The burette contains a cleanser and should therefore be rinsed 3 - 4 times with water before use.

Manganese(III) is reduced to manganese(II) by iodide ions and the triiodide ions formed are then titrated with thiosulfate.

$$2\,Mn^{III}(aq) + 3\,I^-(aq) \rightarrow 2\,Mn^{II}(aq) + I_3^-(aq)$$

$$I_3^-(aq) + 2\,S_2O_3^{2-}(aq) \rightarrow 3\,I^-(aq) + S_4O_6^{2-}(aq)$$

In a 250 cm^3 conical flask dissolve 1.0 g of KI in 25 cm^3 of demineralized water and add 10 cm^3 of 4 **M** HCl. Immediately after an accurately preweighed sample (approx. 200 mg) of the provided complex is transferred (as much as possible is poured directly into the

liquid in small portions before the residue is washed down) quantitatively with demineralized water to the flask. Titrate the I_3^- formed with the standardized, approx. 0.025 **M** $Na_2S_2O_3$ solution. When the brown colour has faded to light yellow, add 2 cm^3 of starch indicator solution and continue the titration until the colour changes from blue to colourless.

1.3 Calculate the molar mass of the analyzed compound from the titration data.

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Analysis of the Provided Sample of $K_3[Mn(C_2O_4)_3] \cdot x\ H_2O$ for Reducing Ability

Note 4: The burette should be rinsed 2 - 3 times with water before this titration.

Manganese(III) is reduced to manganese(II) by the oxalate ligands, and excess oxalate is titrated with permanganate.

$$2\ [Mn(C_2O_4)_3]^{3-}(aq) + 10\ H^+(aq) \rightarrow 2\ Mn^{2+}(aq) + 2\ CO_2(g) + 5\ C_2O_4H_2(aq)$$

$$5\ C_2O_4H_2(aq) + 2\ MnO_4^-(aq) + 6\ H^+(aq) \rightarrow 10\ CO_2(g) + 2\ Mn^{2+}(aq) + 8\ H_2O(l)$$

Transfer an accurately preweighed sample (approx. 200 mg) of the provided complex quantitatively with demineralized water to a 250 cm^3 conical flask. Add 25 cm^3 of 2 **M** sulphuric acid and heat the solution to 75 – 80 °C. Without further heating, titrate with the standardized, approx. 0.025 **M** $KMnO_4$ solution. Near the end of the titration add the titrant slowly, until one drop gives the solution a rose colour which does not fade on standing for 0.5 min.

1.4 Calculate the molar mass of the analyzed compound from the titration data.

The results of the two types of analysis may differ by up to 10 %. Use only the result from the titration with $KMnO_4$ for the following calculation.

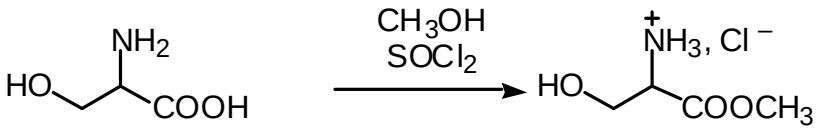
1.5 Calculate the value of x in the formula $K_3[Mn(C_2O_4)_3] \cdot x\ H_2O$ and the yield of your preparation in percent of the theoretical yield.

PROBLEM 2 (Practical)

Synthesis of Amino Acid Methyl Ester Hydrochloride

In the synthesis of peptides, one amino acid is reacted with another to form an amide bond between them. In order to ensure that the individual amino acids do not form amide bonds with themselves and that only one product is formed, the amino group in the first amino acid and the carboxyl group in the second amino acid are masked before the peptide synthesis.

The procedure described below can be used for masking the carboxylic acid groups in amino acids before peptide formation.



The experiment should be performed in a ventilated hood since thionyl chloride is an irritant and since irritating gases are evolved during the reaction.

Thionyl chloride is a corrosive acid chloride. Avoid contact with skin and eyes. Splashes in eyes or on skin should be flushed immediately with water. Thionyl chloride in larger amounts reacts violently with water.

Procedure

Absolute methanol (2.0 cm^3) is transferred quickly to a dry test tube which is then closed with a piece of aluminium foil. The foil is used as a lid throughout the subsequent manipulations with the tube. This protects the content from moisture from the air. The methanol is cooled in an ice-bath for 1 – 2 min. Thionyl chloride, handle with care, see above (0.52 cm^3) is drawn up into a 1 cm^3 graduated syringe with polyethylene tube tip, as described in separate procedure B, and is cautiously added to the methanol over a period of approximately 5 min.

The mixture is kept at 0 ℃ for approx. 2 min. (*S*)-Serine (0.210 g, weighed sample provided) is added and the mixture is kept at room temperature for approx. 2 min before gently heating to boiling (using a sand bath) for 10 min. All material should then have dissolved.

The mixture is cooled in an ice-bath for approx. 2 min. Dry *tert*.-butyl methyl ether (10 cm^3) is then added. The inside wall of the test tube is scratched at the surface region of the solution with a glass spatula for about 1 min. and the test tube is then left in the ice-bath for a further 5 –15 min for crystallization. The separated crystals are then isolated by filtration as described in separate procedure A. The filtrate is collected in a 100 cm^3 beaker.

The crystals are washed two times on the filter, each time with 1 cm^3 of *tert*.-butyl methyl ether. The filter cake is finally pressed with the piston, and the crystals are pre-dried by pumping air through the filter cake with the piston.

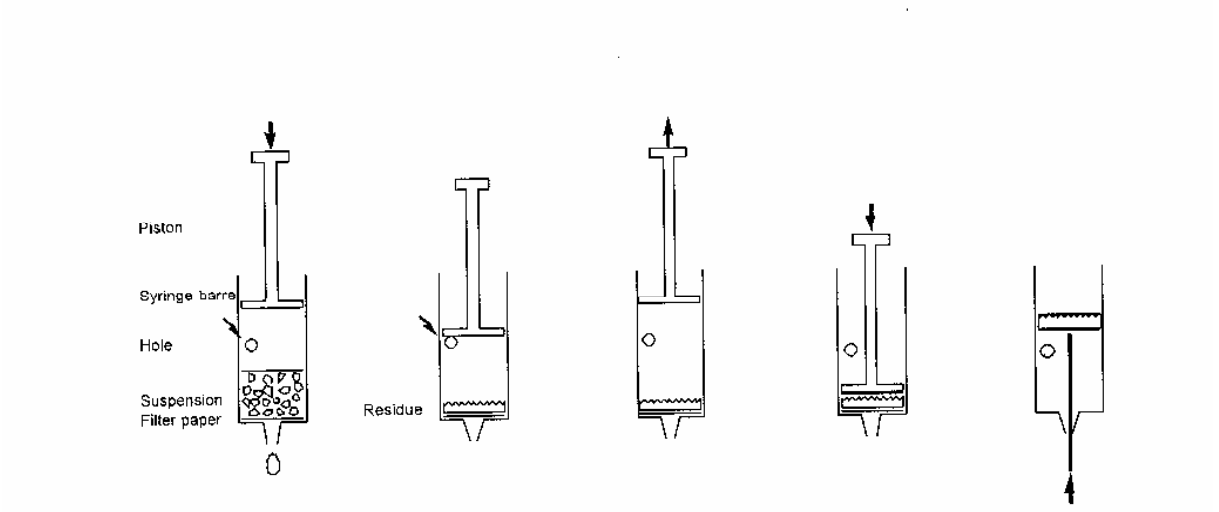
The solid is then collected on a piece of filter paper in order to absorb residual solvent. When dry, the residue is placed in a tarred plastic sample tube with lid (Eppendorf tube) found in the box. The sample tube is then closed and weighed.

PROCEDURE A

Filtration procedures

Modified syringes are used for filtration in the laboratory tasks. A 60 cm^3 syringe with a disc of porous polypropylene is used in task 1, while a 10 cm^3 syringe with a disc of filtration paper is used in task 2. The procedure is sketched on Fig. 1.

Fig. 1: Micro-scale filtration in plastic syringe



Procedure:

1. Fill the syringe from above with suspension to be filtered. The syringe can be filled to the level of the hole. Replace piston.
2. Close hole and press piston for filtration.
3. Stop before passing the hole.
4. Open hole and draw piston back.
5. Repeat steps 2-4 a couple of times.
6. Remove piston and place filter paper on top of the filter cake.
7. Press piston against filter cake.
8. Push filter cake out with straightened- out paper clip.

Filtration procedure for practical problem 1

The provided filter syringe to be used in this experiment is made from a 60 cm^3 standard medical polypropylene syringe from which the piston has been temporarily removed and a 3 mm hole drilled at the 35 cm^3 mark. With a plastic spatula a disc of porous polypropylene, which fits tightly inside the syringe, is pressed down to be positioned at the base of the syringe. The mixture to be filtered is applied without the piston inserted. Drops of solution may be moved downwards by tapping the syringe against a solid surface,

The piston is now placed in the syringe and gently pressed down while keeping the hole closed with a finger so to promote the passage of solvent through the filter. When the piston reaches just above the hole, the finger is removed from the hole, and the piston is drawn back again to the top position. This cycle can then be repeated a couple of times, until the filter cake looks dry. Remember to close the drilled hole, then the piston is moved downwards and to open the hole, when the piston is moved upwards. The filter cake can be washed and the washing solution pressed out using similar cycles.

Solvent remaining in the outlet can be sucked up with a small piece of tissue paper. The solid is then removed from the syringe and collected on a piece of weighing paper for drying.

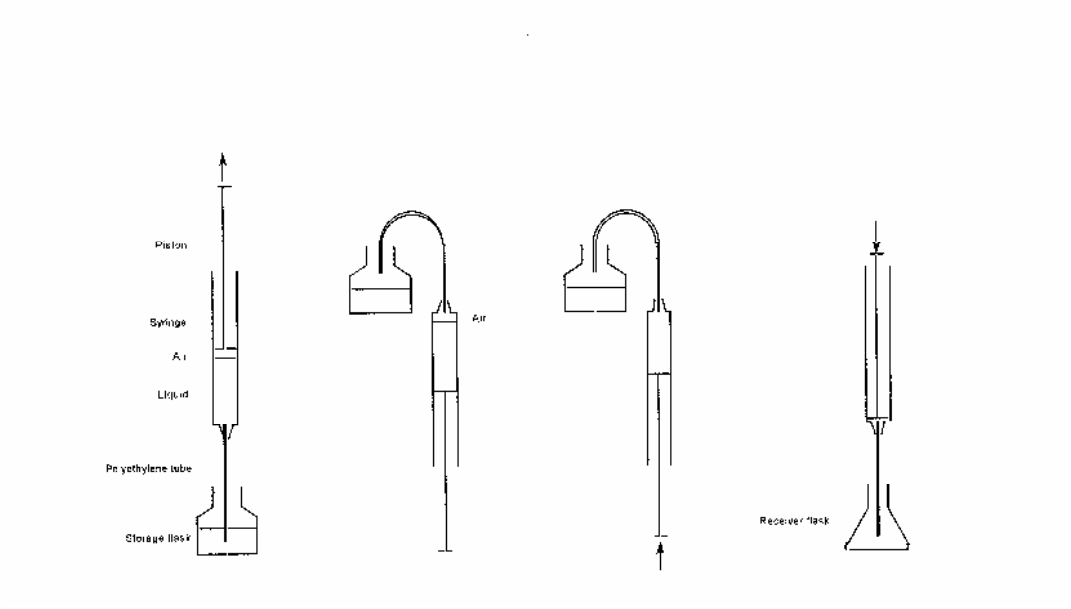
Filtration procedure for practical problem 2

The provided filter syringe to be used in this experiment is made from a 10 cm^3 standard medical polypropylene syringe from which the piston has been temporarily removed and a 3 mm hole drilled at the 5.5 cm^3 mark. A piece of filter paper which fits snugly in the syringe is pressed down to the bottom with the piston. Filtration and washing are then performed as described for task 1. Before removing the filter cake the piston is withdrawn. A piece of filter paper fitting the syringe is then pressed all the way down to the filter cake using the piston. The filter cake is pressed by means of the piston. Then the piston is then drawn back and out the syringe (slowly, until the hole is reached).
This leaves the filter cake between two pieces of filter paper. Solvent remaining in the outlet can be sucked up with a small piece of tissue paper.

The filter cake is cautiously pushed out of the syringe using an straightened-out metal paper clip introduced through the outlet of the syringe. The solid material is then removed from the syringe, if possible as a coherent plug. The residue is collected on a piece of filter paper for drying by using a small metal spatula. Filter paper from the filtration can be fixed with the paper clip tip while adhering solid is removed using the spatula.

PROCEDURE B

Fig. 2. Measuring volumes of liquids using a syringe



Procedure:

1. Suck up a slight excess of liquid in syringe.

2. Turn syringe upside down; the tip of the tube is kept in the storage nottle. Air in the syringe is accumulated at its top.
3. Air in the syringe is removed by pressing the piston. Press further until desired volume of liquid is left in the syringe. The tip of the tube is kept in the storage bottle.
4. Turn the syringe, place tip of the tube in the receiver flask and press piston until desired volume of liquid has left the syringe.