Problemi pratici

Analisi qualitativa

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

There are ten test tubes in the rack at your disposal (1 – 10) and each test tube contains one of aqueous solutions of the following salts: Na_2SO_4, $AgNO_3$, KI, $Ba(OH)_2$, NH_4Cl, Ag_2SO_4, $Pb(NO_3)_2$, NaOH, NH_4I, KCl.

For identification of the particular test tubes you can use mutual reactions of the solutions in the test tubes only.

Determine in which order the solutions of the salts in your rack are and write chemical equations of the reactions you used for identification of the salts.

PROBLEM 2 (Practical)

Each of the six test tubes (A – F) in the rack contains one of the following substances:

benzoic acid, salicylic acid, citric acid, tartaric acid, oxalic acid and glucose.

Determine the order in which the substances in the test tubes are placed in your rack and give chemical reactions you used for identification of the substances.

For identification of the substances the following aqueous solutions are at your disposal: HCl, H_2SO_4, NaOH, NH_4OH, $CuSO_4$, $KMnO_4$, $FeCl_3$, KCl, and distilled water.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

a) Three numbered test-tubes (1-3) contain mixtures of two substances from the following pairs (4 variants):

1.	$ZnSO_4$ - NaBr	NaCl - $Ca(NO_3)_2$	$MgSO_4$ - NH_4Cl
2.	$AlCl_3$ - KBr	$CaCl_2$ - $NaNO_3$	$ZnCl_2$ - $(NH_4)_2SO_4$
3.	KNO_3 - Na_2CO_3	KCl - $MgSO_4$	NH_4Cl - $Ba(NO_3)_2$
4.	$MgCl_2$ - KNO_3	K_2CO_3 - $ZnSO_4$	$Al(NO_3)_3$ - NaCl

b) Each of the test-tubes numbered 4 and 5 contains one of the following substances: glucose, saccharose, urea, sodium acetate, oxalic acid.

Problem:

By means of reagents that are available on the laboratory desk determine the content of the individual test-tubes. Give reasons for both the tests performed and your answers and write the chemical equations of the corresponding reactions.

Note:

For the identification of substances given in the above task, the following reagents were available to competing pupils: 1 N HCl, 3 N HCl, 1 N H_2SO_4, concentrated H_2SO_4, $FeSO_4$, 2 N NaOH, 20 % NaOH, 2 N NH_4Cl, 2 N $CuSO_4$, 2 N $BaCl_2$, 0,1 N $AgNO_3$, 0,1 % $KMnO_4$, distilled water, phenolphtalein, methyl orange. In addition, further laboratory facilities, such as platinum wire, cobalt glass, etc., were available.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

An unknown sample is a mixture of 1.2-molar H_2SO_4 and 1.47-molar HCl. By means of available solutions and facilities determine:

1. the total amount of substance (in val) of the acid being present in 1 dm^3 of the solution,
2. the mass of sulphuric acid as well as hydrochloric acid present in 1 dm^3 of the sample.

PROBLEM 2 (Practical)

By means of available reagents and facilities perform a qualitative analysis of the substances given in numbered test tubes and write down their chemical formulas.

Give 10 equations of the chemical reactions by which the substances were proved:
5 equations for reactions of precipitation,
2 equations for reactions connected with release of a gas,
3 equations for redox reactions.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Determine unknown samples in ten numbered test tubes using reagents and facilities available on the laboratory desk. Write chemical equations for the most important reactions that were used to identify each substance. In case that the reactions take place in solutions, write equations in a short ionic form.

PROBLEM 2 (Practical)

On June 10th, a mixture of formic acid with an excess of ethanol was prepared. This mixture was kept in a closed vessel for approximately one month. Determine quantitatively the composition of the mixture on the day of the competition, using only reagents and facilities available on the laboratory desk. Calculate the amounts of the acid and ethanol in per cent by mass which were initially mixed together.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

The following solutions of salts are available in twelve numbered test-tubes: $AgNO_3$, $BaCl_2$, $(NH_4)_2CO_3$, NaCl, KI, $ZnCl_2$, NH_4Cl, $Pb(NO_3)_2$, $Al(NO_3)_3$, $CrCl_3$, $Cr(NO_3)_3$, $Hg(NO_3)_2$.

The numbering of the test tubes does not correspond to the order of the salts given above. Prove the content of the test tubes by means of the least number of operations. In your answer align the proper salt with each number of the test tube. Write chemical equations for the reactions.

PROBLEM 2 (Practical)

Six test tubes contain the following compounds:

Na_2CO_3 or $NaHCO_3$ $\qquad$ $NiCl_2$ or $CuCl_2$
$AgNO_3$ or $Pb(NO_3)_2$ $\qquad$ $ZnCl_2$ or $Al(NO_3)_3$
$ZnSO_4$ or KI $\qquad$ NH_4NO_3 or $Ba(NO_3)_2$

The numbers of the test tubes do not correspond to the order of the compounds. Prove the content of each test tube by available reagents. Describe the reactions by chemical equations.

PROBLEM 3 (Practical)

There are three test tubes marked by numbers 1, 2, and 3. Prove the content of each test-tube by means of available reagents and write the proper formula of the compound to each number. Write chemical equations for the reactions.

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Test tubes with unknown samples contain:

- a salt of carboxylic acid,
- a phenol,
- a carbohydrate,
- an amide.

Determine the content of each test tube using reagents that are available on the laboratory desk.

PROBLEM 2 (practical)

Determine cations in solutions No 5, 6, 8 and 9 using the solution in test tube 7.

Without using any indicator find out whether the solution in test tube 7 is an acid or a hydroxide.

SOLUTION

Test tube: No 5 - NH_4^+; No 6 - Hg^{2+}; No 7 - OH^-; No 8 – Fe^{3+} ; No 9 – Cu^{2+}

PROBLEM 3 (practical)

The solution in test tube No 10 contains two cations and two anions.

Prove those ions by means of reagents that are available on the laboratory desk.

SOLUTION

The solution in test tube No 10 contained: Ba^{2+}, Al^{3+}, Cl^-, CO_3^{2-}

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Aqueous solutions of the following compounds: $AgNO_3$, HCl, Ag_2SO_4, $Pb(NO_3)_2$, NH_3 and NaOH are available in numbered bottles. Allow to react each of them with others and align the numbers of the bottles with formulas of the compounds.

Attention! The use of any other reagent is not permitted. In performing the reactions do not use the whole volume of the solutions. A few cm^3 of the solution should remain in each bottle after your work is finished. It is advisable to make a draft at first but only those solutions will be evaluated by the jury that will be written in the Table.

Write your observations into the squares of the Table bellow the diagonal using the following uniform symbols:

white precipitate : ↓

coloured precipitate: ↓↓

formation of a complex soluble in water: [ ]

evolution of a gas: ↑

Write into the corresponding squares above the diagonal the chemical formulas of the precipitate, the complex ion or gas which are formed by the corresponding reactions.

Write into the last line of the Table the final results obtained on the basis of your experiments.

Number of sample	1	2	3	4	5	6
1	▨					
2		▨				
3			▨			
4				▨		
5					▨	
6						▨
Formula of compounds						

PROBLEM 2 (practical)

A solid compound is in each of the numbered test-tubes. It might be chloride, iodide, oxide, hydroxide, sulphide, sulphate or carbonate, each combined with one of the following cations: Ag^+, Pb^{2+}, Cu^{2+}, Cd^{2+}, Sb(V), Sn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, Al^{3+}, Zn^{2+}, Ba^{2+}.

Problem:

Write the chemical formula for each solid compound given as a sample. You can use only reagents that are available on your laboratory desk.

Attention! In carrying out reactions do not use the whole quantity of the sample. A small portion of the sample is to remain in each test tube. Only those results will be evaluated that will be written in the Table below.

Table:

Compound			
Number of sample	Formula	Number of sample	Formula
1		6	
2		7	
3		8	
4		9	
5			

PROBLEM 3 (practical)

Three samples are found in sealed ampoules. All of them are aromatic compounds: a hydrocarbon, a phenol, and an aldehyde.

Determine the group of compounds to which your numbered samples belong, using only the reagents which are at your disposal.

Attention! Be careful when opening the ampoules. The identification of the samples based upon physical characteristics only (colour, smell), is not sufficient. Only those results will be taken into account that will be written in the Table below.

Table:

No of sample	Reagent	Observation	Type of compound
1			
2			
3			

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

A sample contains two of the following cations: Ag^+, Pb^{2+}, Fe^{2+}, Cr^{3+}, Co^{2+}, Al^{3+}, Mn^{2+}, and one of the following anions: SO_4^{2-}, Cl^-, NO_3^-.

Prove the cations and anions in the sample by means of the following reagents:
2 N-HCl, concentrated H_2SO_4, 2 N-H_2SO_4, 2 N-HNO_3, 2 N-CH_3COOH, NaOH, NH_4OH, H_2O_2, Na_2CO_3, KNO_3/Na_2CO_3, NH_4SCN, $Na_2B_4O_7$, NaF, C_2H_5OH, $BaCl_2$, $AgNO_3$, NH_4Cl, $(NH_4)_2Fe(SO_4)_2$, alizarin B.

Write the results into the attached table in the following way:

a) into the column "Reagent" write the formula of the reagent which was needed to prove whether the cation or anion is present or absent in the sample;

b) into the column "+/–" mark the presence or absence of an ion, proved in the sample, by the sign "+" and "–" , respectively.

PROBLEM 2 (practical)

A solution contains sodium oxalate and oxalic acid.

Determine how many milligrams of sodium oxalate and oxalic acid are contained in the solution under investigation.

The following solutions are at your disposal: $KMnO_4$ (c = 0.01972 mol dm^{-3}), NaOH (c = 0.1019 mol dm^{-3}), concentrated H_2SO_4, and a solution of phenolphthalein.

PROBLEM 3 (practical)

Four unknown organic aliphatic compounds of a general formula A–CH_2–B are numbered from 1 to 4, and given as samples. Some of them may be in an aqueous solution.

Perform the following experiments:

1. Determine the pH value of the solution.
2. Allow the sample to react with hydrochloric acid.
3. Reaction with alkali hydroxide (basic hydrolysis – 5 minutes boiling under a reverse cooler) and a subsequent proof of halides.

Moreover, the following data are at your disposal:

a) One of the compounds under investigation forms an intra-molecular anhydride.

b) The content of carbon and hydrogen (in mass %) as well as the relative molecular mass are known for the same compound, the data being given, however, in an arbitrary order which does not correspond to the numbering of samples.

Determine the functional groups A and B for each substance using results of your experiments as well as the available data.

Write your results into the attached table; mark positive results with sign "+" whereas the negative ones with sign "–".

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

10 numbered test tubes, 20 cm^3 each, contain 0.1 M solutions of the following substances: barium chloride, sodium sulphate, potassium chloride, magnesium nitrate, sodium orthophosphate, barium hydroxide, lead nitrate, potassium hydroxide, aluminium sulphate, sodium carbonate. Using only these solutions as reagents, determine in which of the numbered test tubes each of the above given substances, is found.

Draw up a plan of the analysis and write equations of the reactions to be carried out. Do not forget to leave at least 2 cm^3 of the solutions in each test tube for checking. If in the course of the analysis an additional quantity of a solution is needed, you may ask the teacher to give it to you but in such case you will lose some points.

SOLUTION

Table:

	$BaCl_2$	Na_2SO_4	KCl	$Mg(NO_3)_2$	Na_3PO_4	$Ba(OH)_2$	$Pb(NO_3)_2$	KOH	$Al_2(SO_4)_3$	Na_2CO_3
$BaCl_2$	▨	↓	—	—	↓	—	↓	—	↓	↓
Na_2SO_4	↓	▨	—	—	—	↓	↓	—	—	—
KCl	—	—	▨	—	—	—	↓	—	—	—
$Mg(NO_3)_2$	—	—	—	▨	↓	↓	—	↓	—	↓
Na_3PO_4	↓	—	—	↓	▨	↓	↓	—	↓	—
$Ba(OH)_2$	—	↓	—	↓	↓	▨	↓	—	↓	↓
$Pb(NO_3)_2$	↓	↓	↓	—	↓	↓	▨	↓	↓	↓
KOH	—	—	—	↓	—	—	↓	▨	↓	—
$Al_2(SO_4)_3$	↓	—	—	—	↓	↓	↓	↓	▨	↓
Na_2CO_3	↓	—	—	↓	—	↓	↓	—	↓	▨

Using the table, the entire problem cannot be solved at once: all the precipitates are white and there are substances that form the same number of precipitates. From the number of precipitates only KCl (1), $Mg(NO_3)_2$ (4), and $Pb(NO_3)_2$ (8) can be determined immediately.

Furthermore, Na_2SO_4 and KOH (giving three precipitates each) can be differentiated via the reaction with $Mg(NO_3)_2$ ($Mg(OH)_2$).

$Ba(OH)_2$ and $Al_2(SO_4)_3$ (giving 6 precipitates each): through the reaction with KOH ($Al(OH)_3$).

$BaCl_2$, Na_3PO_4 and Na_2CO_3 (giving 5 precipitates each): first the reaction with Na_2SO_4 indicates $BaCl_2$. Then the reaction with $BaCl_2$: $Al_2(SO_4)_3$ yields $AlCl_3$ ($BaSO_4$ precipitate is flittered off). Evolution of CO_2 and formation of $Al(OH)_3$ in the reaction with $AlCl_3$ solution indicates Na_2CO_3.

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Qualitative organic analysis

Four different substances that all occur in the nature, are present in 4 test tubes. Find two substances that form basic components of fodders and human foodstuff. Only these two substances are to be identified. Propose the names and structural formulae for those two substances on the basis of combustion tests, solubility experiments, identification of the functional groups and the determination of the melting point.

As an aid the following can be used:

A table of melting points, the Thiele apparatus for melting point determination, a solubility scheme and the following reagents:

diethyl ether, $NaHCO_3$ (5 %), NaOH (2 M), HCl (2 M), H_2SO_4 conc., H_3PO_4 conc., ethanol, Tollens' reagents, (an ammoniac Ag solution), Fehling's solution I and II, phenylhydrazine hydrochloride, β-naphthol, $NaNO_2$ (solid) $Ca(OH)_2$ sat., $FeCl_3$ (5 %), ice, 2,4-dinitrophenylhydrazine, ninhydrine solution (1 % alk.), Seliwanoff's reagent (resorcinol/HCl), phloroglucine.

The requirements: An exact description of the experiments, reaction equations (or reaction schemes where the equation cannot be given) for the reaction required for the identification, the names and the structural formulae of the two test substances.

APPENDIX 1

Determination of the melting point by the Thiele apparatus

A finely pulverized sample is placed in a capillary that is sealed at one side, to a height of 2 – 4 mm. To fill the capillary, it is immersed in the sample. The sample is cautiously wiped off the capillary walls and the content of the capillary is brought to the bottom by cautious tapping. Then the capillary is placed in the opening so that the sample is at the height of the mercury bead of the thermometer. As the heat transmitter, suitable high-boiling silicone oil is used in this apparatus.

To determine the melting point of an unknown organic substance, an approximate melting range is sought first. Thus the heating is carried out according to the figure at about 5 °C/min. For an exact determination another sample is brought about 10 °C below the determined melting range at about 5 °C/min and then the temperature is very slowly, 1 – 2 °C/min., brought to complete melting. The temperature, at which the substance is clearly melted, is taken as the melting point.

APPENDIX 2

Tables of melting points (MP, in °C) and boiling points (BP, in °C)

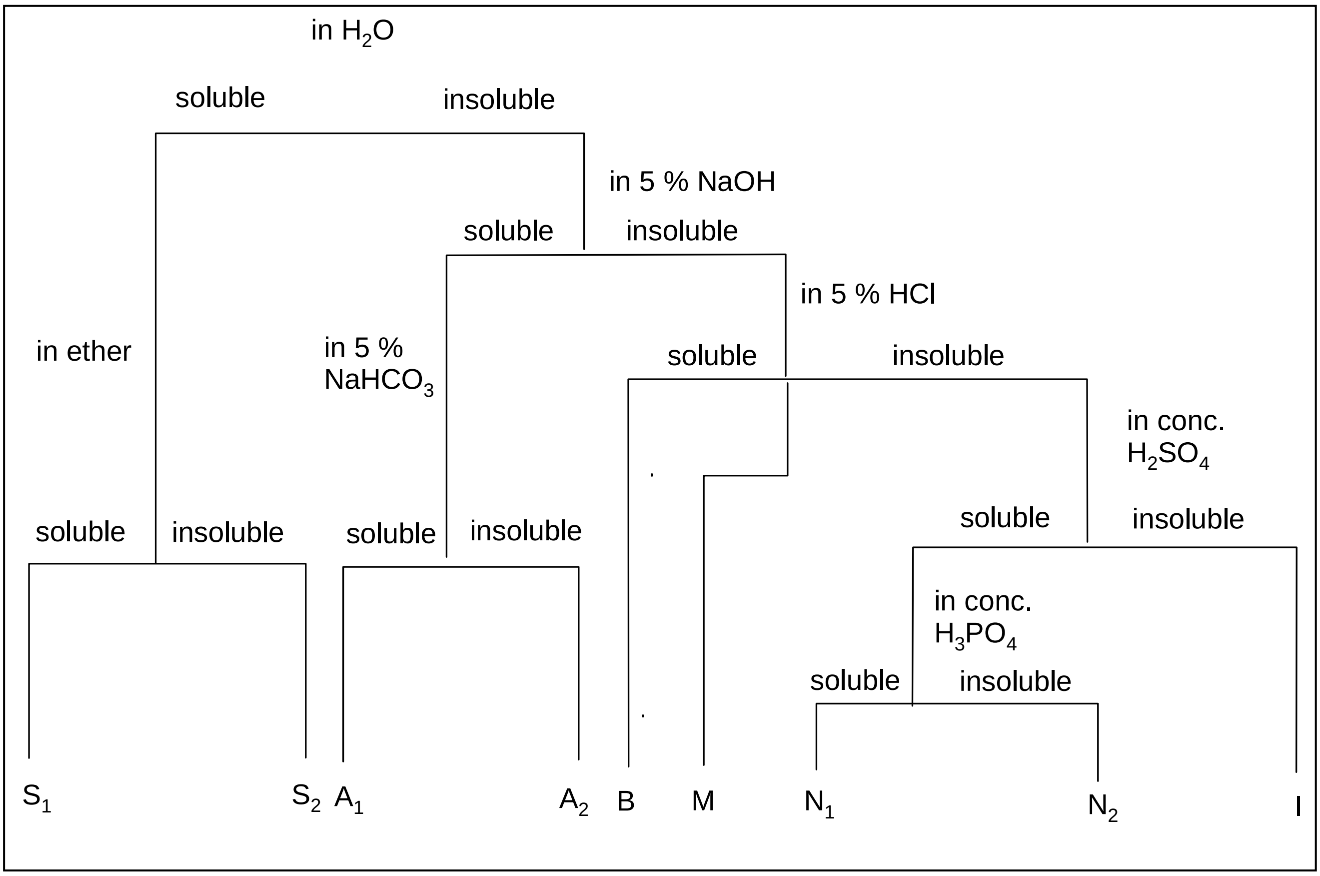
Compound	MP	BP	Compound	MP	BP
ALDEHYDES					
Pentanal	-	103	Acrolein	-	52
Benzaldehyde	-	179	Furfurol	-	161
Salicylaldehyde	-	196	o-Chlorobenzaldehyde	11	214
o-Nitrobenzaldehyde	44	-	α-Naphthaldehyde	34	-
p-Dimetylamino-bemzaldehyde	74	-	Vanillin	81	-
ALCOHOLS					
terc.-Butanol	25	82	Propanol-1	-	97
n-Pentanol	-	136	Ethyleneglycol	-	197
Cyclohexylalcohol	-	160	Butanediol-1,4	-	230
Triphenylcarbinol	165	-	Glycerine	-	290
AMINES					
Diethylamide	-	56	Morpholine	-	130
Cyclohexylamine	-	134	α-Naphthylamine	50	300
Aniline	-	184	p-Bromoaniline	66	-
Diphenylamine	54	-	m-Nitraniline	114	-
o-Phenylenediamine	102	-	p-Aminophenol	186 D	-
ACIDS					
Palmitic acid	63	-	n-Valeric acid	-	186
Stearic acid	70	-	Oleic acid	14	222
Oxalic acid (. 2 H_2O)	101	-	Mandelic acid	118	-
Acetylsalicylic acid	135	-	Benzoic acid	122	-
Phthalic acid	203	-	Malonic acid	135	-
Anthranilic acid	146	-	S-Naphthoic acid	185	-
Glycine	232 D	-	p-Hydroxybenzoic acid	215	-

HALOGENDERIVATIVES					
n-Butyl bromide	-	100	p-Dichlorobenzene	53	-
Cyclohexyl iodide	-	179	p-Bromotoluene	28	185
Trichloroethylene	-	67	Hexachlorobenzene	230	-
KETONES					
Diethyl ketone	-	102	Methylisobutyl ketone	-	118
Cyclohexanone	-	156	Acetophenone	20	202
Benzophenone	49	-	p-Bromoacetophenone	51	-
Benzil	95	-	dl-Camphor	178	-
CARBOHYDRATES					
d-Ribose	95 D	-	β-Maltose	165	-
α-d-Glucose	146	D	β-d-Fructose		
Saccharose	180	-	α-Lactose		
HYDROCARBONS					
n-Heptane	-	99	Pentene-2	-	36
cis-Decaline	-	194	Cyclohexene	-	84
Cumol	-	216	Diphenyl	70	-
Anthracene	216	-	Styrene	-	146
MERCAPTANS – THIOPHENOLS					
n-Amylmercaptan	-	126	p-Thiocresol	-	200
Thiophenol	-	169	p-Bromothiophenol	74	-
PHENOLS					
p-Cresol	36	200	o-Nitrophenol	45	-
α-Naphthol	94	-	Resorcinol	110	-
Pyrocatechol	105	-	β-Naphthol	123	-
Picric acid	122	-	Phloroglucine	218	-
ACID DERIVATIVES					
Acetyl bromide	-	77	Acetamide	82	-
Butyric acid chloride	-	102	N-Methylacetanilide	102	-
4-Nitrobenzoylchloride	73	-	Urea	132	-
Butyric acid ethylester	-	121	Sodium formate	255	-
Malonic acid diethylester	-	199	Al-Acetate	200 – 320 D	-
Palmitic acid cetylester	54	-	Ba-Propionate	ca. 300	-

D after the number denotes decomposition.

APPENDIX 3

Solubility scheme



S_1: Substances with higher volatility;
All low molecular alcohols, aldehydes, ketones, acids, amines, nitriles and acid chlorides.

S_2: Substances with low volatility, often distillable without decomposition: polyols, salts, hydroxyaldehydes and hydroxyketones, carbohydrates, amino- and hydroxyl acids.

A_1: Substances with low volatility: higher molecular acids, nitrophenols.

A_2: Substances with high boiling points: Phenols, primary and secondary nitro compounds, sulfonamides, weak acids.

B: Substances with high boiling points, distillable with water vapour: Basic compounds, amines (with maximum of a few aryl groups), hydrazine.

M: Low volatility substances:
Neutral compounds, tertiary nitro compounds, nitroaniline, azo- and azoxy compounds, nitrito-, nitrato-, sulphuric-, and phosphoric acid esters.

N_1: Substances with small volatility:
Alcohols, aldehydes, methyl ketones and esters with less than 9 C atoms, neutral compounds, ethers, olephins.

N_2: Substances with a very low volatility:
Alcohols, aldehydes, ketones, esters and thioalcohols with more than 9 C atoms, neutral compounds, ethers, olephins.

I: Substances with low boiling point:
Inert compounds, hydrocarbons, halogenoalkanes.

APPENDIX 4

Preparation of the reagents

Tollen's reagent

Mix 0.5 cm^3 2 M NaOH + 1 cm^3 0.1 M $AgNO_3$ in 2 M NH_3.

Fehling's reagent

I: 1.73 g $CuSO_4 . 5 H_2O$ in 25 cm^3 of water

II: 8.5 g Seignette salt + 2.5 g NaOH in 25 cm^3 H_2O

Seliwanoff's reagent

125 g resorcinol is dissolved in 250 cm^3 of diluted HCl (83 cm^3 conc. HCl + 167 cm^3 H_2O), preparing only a necessary amount.

Phenylhydrazine solution

0.5 g of phenylhydrazine hydrochloride + 0.5 cm^3 glacial acetic acid in 2 cm^3 H_2O are shaken until a clear solution is obtained.

2,4-dinitrophenylhydrazine solution,

2 cm^3 of conc. H_2SO_4 are added to 0.4 g of 2,4-dinitrophenylhydrazine and then, with stirring and shaking, 3 cm^3 of H_2O are added. To the warm solution, 10 cm^3 of 95 % ethanol are added.

SOLUTION

In the four test tubes, pure sodium chloride, D-fructose, palmitic acid (hexadecanoic acid), and vanillin were present. D-fructose, as a building block of cane sugar, and palmitic acid, as the building block of most animal and plant fats, were identified.

a) *Fructose*

Melting range: 102 – 105 ℃

Combustion test: Carbonizes during combustion with caramel smell.

Solubility: Readily soluble in water, insoluble in diethyl ether.

Identification of the functional groups:

Aldehydic group:

1. With Fehling's reagent

   The oxidation of the carbonyl group with simultaneous reduction of Cu(II) to Cu(I).

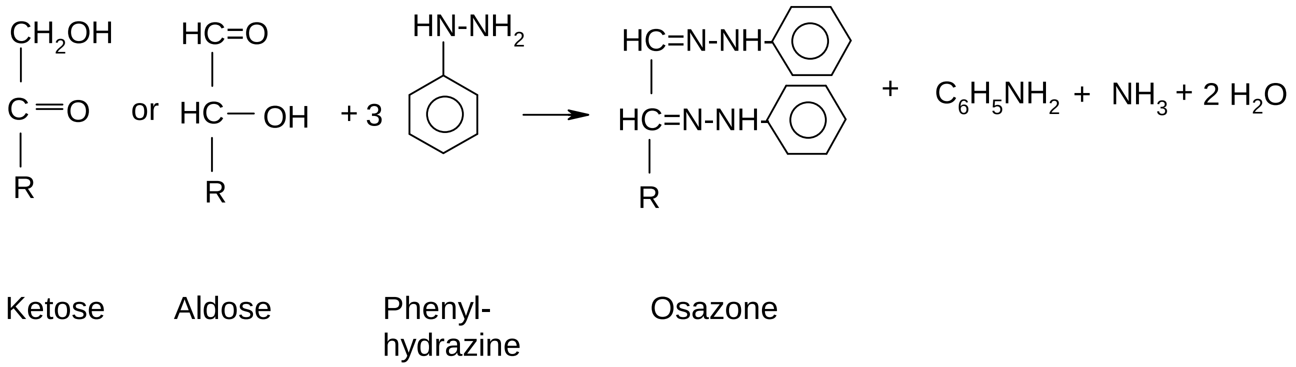
   $$–CHO + 2\,[Cu(C_4H_4O_6)_2]^{2-} + 5\,OH^- \rightarrow –COOH + Cu_2O\downarrow + 3\,H_2O + 4\,C_4H_4O_6^{2-}$$

2. With Tollen's reagent

   The oxidation to the carboxyl group with simultaneous reduction of Ag(I) to Ag.

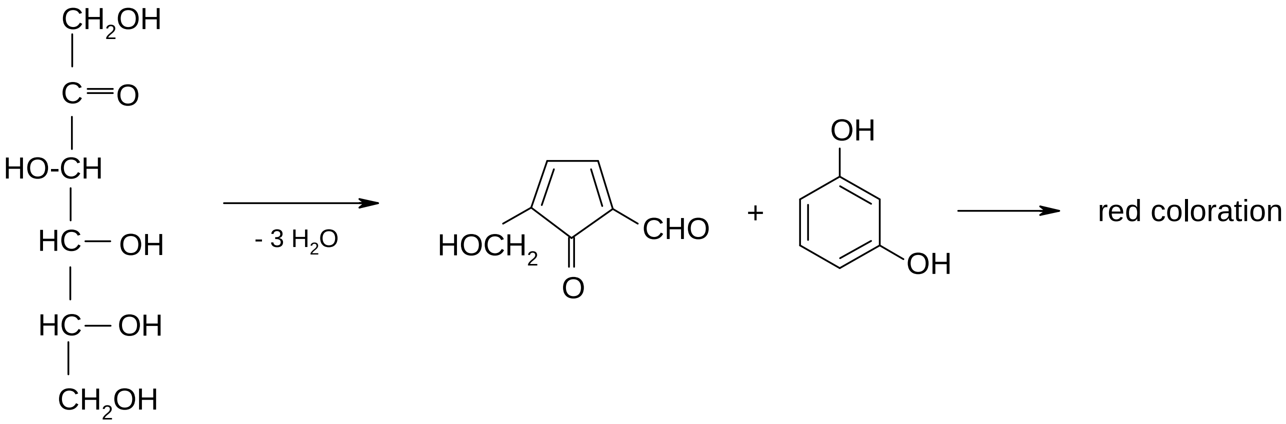
   $$–CHO + 2\,[Ag(NH_3)_2]^+ + 2\,OH^- \rightarrow –COOH + 2\,Ag + 4\,NH_3 + H_2O$$

Osazone formation (indication of monoses)



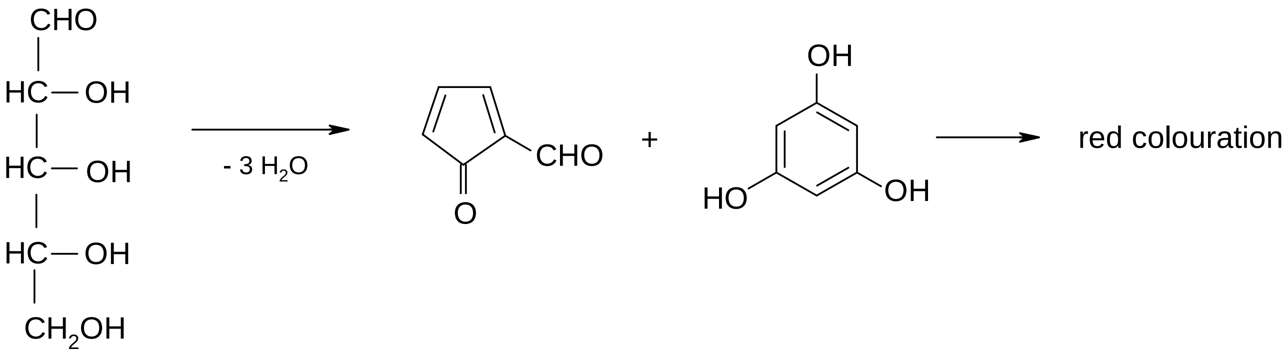
Test for ketohexoses (Saliwanoff's reaction)

Ketohexoses form, with heating in acidic solution, 5-hydroxy-methylfurfural that condenses with resorcinol to red-coloured substances.

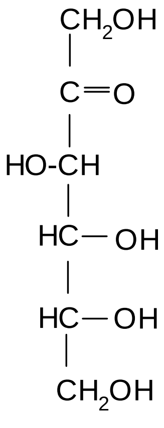


Test for pentoses (Tollens test)

Pentoses, in contrast to hexoses, form furfural in acidic solution that condenses with phloroglucine to give red coloured substances.



Name: The above reactions, the solubility behaviour and the melting range indicate that this substance is D-fructose, a building block of cane sugar.



When giving the configuration, use the Fischer projection.

b) *Palmitic acid*

Melting range: 60 – 63 °C

Combustion test: Burns with yellowish, slightly smoking flame.

Solubility: Insoluble in water, very well soluble in 2 M NaOH, less soluble in 5 % $NaHCO_3$.

Identification of the functional groups:

From alkaline solution a colourless substance is precipitated by Ca^{2+}:

$2\ R\text{-}COO^- + Ca^{2+} \rightarrow (R\text{-}COO)_2Ca$

On the basis of flammability the solubility behaviour and the precipitation of the calcium salt from alkaline solution one can conclude that the substance is an organic carboxyl acid. The melting range indicates palmitic acid = hexadecanoic acid.

$CH_3\text{-}(CH_2)_{14}\text{-}COOH$

PROBLEM 2 (practical)

In 10 reagent bottles are 10 different pure metal samples. By evaluating the solubility and by the following identification, only the six following elements are to be specified by their sample numbers:

calcium, iron, aluminium, zinc, magnesium, tin.

It is expected to specify:

a) the symbol of the identified metal and the corresponding bottle number,

b) a reaction equation for dissolution of each of the six metals,

c) an unambiguous verbal proof or a proof in the form of a chemical equation.

The following chemicals are at disposal:

HCl conc., HCl (2 M), H_2SO_4 (2 M), CH_3COOH (2 M), NaOH (2 M), NH_3 (2 M), NH_4SCN (0.2 M), CH_3COONa (conc.), 3 % H_2O_2, Na_2CO_3 (0.2 M), H_2S (0.1 M), Na_2HPO_4 (0.2 M), $K_4Fe(CN)_6$ (0.2 M), $K_3Fe(CN)_6$ (0.2 M), morin (in CH_3OH), quinalizarine (in C_2H_5OH), urotropine (20 %), dithizone (in CCl_4), $(NH_4)_2C_2O_4$ (0.2 M), distilled water.

SOLUTION

a) See the list at the end.

b) $Ca + 2\ H_2O \rightarrow Ca(OH)_2 + H_2$

$Ca + 2\ H_3O^+ \rightarrow Ca^{2+} + H_2 + 2\ H_2O$

$Fe + 2\ H_3O^+ \rightarrow Fe^{2+} + H_2 + 2\ H_2O$

$Al + 3\ H_3O^+ \rightarrow Al^{3+} + 3/2\ H_2 + 3\ H_2O$

$Al + NaOH + 3\ H_2O \rightarrow Na^+ + [Al(OH)_4]^- + 3/2\ H_2$

$Zn + 2\ H_3O^+ \rightarrow Zn^{2+} + H_2 + 2\ H_2O$

$Zn + 2\ NaOH + 2\ H_2O \rightarrow 2\ Na^+ + [Zn(OH)_4]^{2-} + H_2$

$Mg + 2\ H_2O \rightarrow Mg(OH)_2 + H_2$

$Mg + 2\ H_3O^+ \rightarrow Mg^{2+} + H_2 + 2\ H_2O$

$Sn + 2 H_3O^+ \rightarrow Sn^{2+} + H_2 + 2 H_2O$

$Sn + 2 NaOH + 2 H_2O \rightarrow 2 Na^+ + [Sn(OH)_4]^{2-} + H_2$

---

c) Ca^{2+}: white precipitate with $(NH_4)_2C_2O_4$;

Fe^{2+}: blue with $K_3[Fe(CN)_6]$
or after oxidation with H_2O_2: blue with $K_4[Fe(CN)_6]$ or red with NH_4SCN, or brown precipitate with NaOH;

Al^{3+}: green fluorescence with morine (in dilute acetic acid);

Zn^{2+}: white precipitate with H_2S (in acetic acid),
with dithizone red coloration of the organic phase;

Mg^{2+}: with quinalizarine light blue lacquer (alkali solution);

Sn^{2+}: with H_2S deep brown precipitate (weakly acidic solution),
blue fluorescence of the outer wall of a glass bottle filled with cold water that was immersed in an Sn^{2+} solution (acidified with HCl),
in the flame of a Bunsen burner ("light test").

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Fourteen numbered test tubes contain solutions of pure inorganic substances. Each test tube contains only one substance. The samples contain the following ions:

cations K^+, Na^+, Hg_2^{2+}, Ag^+, NH_4^+, Ba^{2+}, Sr^{2+}, Fe^{3+};

anions $OH^–$, NO_3^-, $Cl^–$, $SCN^–$, $I^–$, CO_3^{2-}, $Cr_2O_7^{2-}$, CrO_4^{2-}, $Fe(CN)_6^{4-}$, $Co(NO_2)_6^{3-}$.

Determine the contents of the test tubes. In addition to reactions between samples, the only other possible reagent is a solution of hydrochloric acid with a concentration of 2 mol dm^{-3}.

Fill in the following information on the sheet provided:

1. The chemical formulae of the individual samples and the numbers of the corresponding test tubes.
2. The chemical formulae in ionic form on the basis of which you demonstrated the presence of individual cations present in the samples.

PROBLEM 2 (practical)

Determine the samples in the test tubes using the following reagents:
$FeCl_3$ (2.5 % aqueous solution), water, 2,4-dinitrophenylhydrazine, Lucas' reagent ($ZnCl_2$ – HCl), NaOH (5 % aqueous solution), $NaHCO_3$ (5 % aqueous solution), HCl (conc.), Fehling's solution (an alkaline aqueous solution containing Cu^{2+} ions; this is prepared immediately prior to use by mixing identical volumes of Fehling's solutions I and II), Tollen's reagent (prepared immediately prior to use by mixing identical volumes of 10 % solution of $AgNO_3$ and an NaOH solution with a concentration 2 mol dm^{-3}. Finally, ammonia is added dropwise to complete dissolution of silver dioxide.

Write the results of your observations during testing the unknown substances with the reagents into the table provided.

Write the (IUPAC) names and structural formulae for the substances in the test tubes.

Write the chemical equations for the reactions on the basis of which the individual substances were identified. Write only a reaction scheme where this not possible.

PROBLEM 2 (practical)

Each of 8 numbered test tubes contains a solution of one salt. In the solutions the following positive ions can be found (a maximum of one in each test tube):

Ag^+, Al^{3+}, Cu^{2+}, Na^+, NH_4^+, and Zn^{2+}

and the following negative ions (at most one in each test tube)

$Br^–$, $Cl^–$, $I^–$, NO_3^-, $OH^–$, and $S_3O_3^{2-}$.

A test plate, test tubes in a rack, dropping pipettes, indicator paper, and a gas burner are also provided.

Determine by means of mutual reactions which salt is dissolved in each test tube. Confirm your conclusions by carrying out as many reactions as possible. It may be necessary to use combinations of solutions and reagents.

Give a list of numbers and corresponding formulae of the substances, indicate the formation of a precipitate by a downward arrow, and gas evolution by an upward arrow in the square array provided for reporting the reactions.

Write chemical equations for all the reactions observed.

SOLUTION

Numbers of solutions mixed	Chemical equation for the observed reaction
1 + 2	$NH_4^+ + OH^– \rightarrow NH_3(g) + H_2O$
2 + 3	$2\ OH^– + 2\ Ag^+ \rightarrow Ag_2O(s) + H_2O$
2 + 3 + 1	$Ag_2O(s) + 4\ NH_4^+ + 2\ OH^– \rightarrow 2\ Ag(NH_3)_2^+ + 3\ H_2O$
2 + 4	$Zn^{2+} + 2\ OH^– \rightarrow Zn(OH)_2(s) \leftrightarrow Zn(OH)_2(s) + 2\ OH^– \rightarrow Zn(OH)_4^{2-}$
2 + 5	$Al^{3+} + 3\ OH^– \rightarrow Al(OH)_3(s) \leftrightarrow Al(OH)_3(s) + OH^– \rightarrow Al(OH)_4^-$

Reactions to distinguish Zn^{2+} from Al^{3+}:

Numbers of solutions mixed	Chemical equation for the observed reaction
2 + 4 + 1	$Zn(OH)_4^{2-} + 4\ NH_4^+ \rightarrow Zn(NH_3)_4^{2+} + 4\ H_2O$
2 + 5 + 1	$Al(OH)_4^- + 2\ NH_4^+ \rightarrow Al(OH)_3(s) + NH_3 + H_2O$
2 + 6	$Cu^{2+} + 2\ OH^– \rightarrow Cu(OH)_2(s)$

2 + 6 + 1	$Cu(OH)_2(s) + 4\ NH_4^+ + 2\ OH^- \rightarrow Cu(NH_3)_4^{2+} + 4\ H_2O$
3 + 4	$Ag^+ + Cl^- \rightarrow AgCl(s)$
3 + 6	$Ag^+ + Br^- \rightarrow AgBr(s)$
3 + 7	$Ag^+ + I^- \rightarrow AgI(s)$
3 + 8	$2\ Ag+ + S_2O_3^{2-} \rightarrow Ag_2S_2O_3(s) \leftrightarrow Ag_2S_2O_3(s) + 3\,S_2O_3^{2-} \rightarrow$ $\rightarrow 2\,Ag(S_2O_3)_2^{3-}$

Reactions to distinguish Cl^- from Br^- and from I^-

3 + 4 + 1 + 2	$AgCl(s) + 2\ NH_4^+ + 2\ OH^- \rightarrow Ag(NH_3)_2^+ + Cl^- + H_2O$
3 + 4 + 8	$AgCl(s) + 2\ S_2O_3^{2-} \rightarrow Ag(S_2O_3)_2^{3-} + Cl^-$
3 + 6 + 1 + 2	AgBr(s) does not dissolve
3 + 6 + 8	$AgBr(s) + 2\ S_2O_3^{2-} \rightarrow Ag(S_2O_3)_2^{3-} + Br^-$
3 + 7 + 8	AgI(s) does not dissolve
6 + 7	$2\ Cu^{2+} + 4\ I^- \rightarrow 2\ CuI(s) + I_2$
6 + 7 + 8	$I_2(s) + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

	1	2	3	4	5	6	7	8
1		↑						
2	↑		↓	↓	↓	↓		
3		↓		↓		↓	↓	↓
4		↓	↓					
5		↓						
6		↓	↓				↓	
7			↓			↓		
8			↓					

List of numbers and corresponding formulae for the substances:

1. NH_4NO_3
2. $NaOH$
3. $AgNO_3$
4. $ZnCl_2$
5. $Al(NO_3)_3$
6. $CuBr_2$
7. NaI
8. $Na_2S_2O_3$

PRACTICAL PROBLEMS

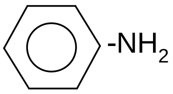
PROBLEM 1 (practical)

In test tubes **A**, **B**, **C**, and **D** there are four benzene derivatives containing one or two functional groups of three distinct types. Identify the functional groups of compounds **A**, **B**, **C**, and **D** using the available reagents.

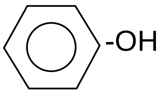
- Justify your choice by writing down the identification reactions.
- Using as reagents the four compounds **A**, **B**, **C**, and **D** synthesize four organic dyes and write the equations for the reactions performed.

SOLUTION

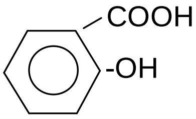
The four compounds are as follows:



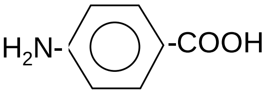
A



B



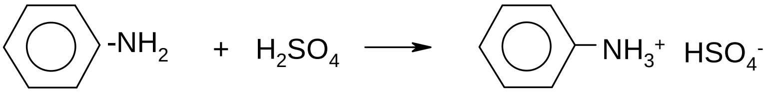
C

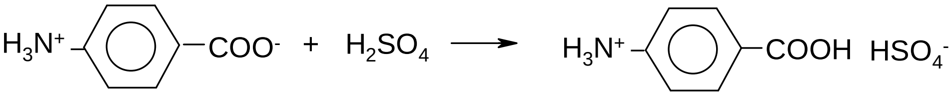


D

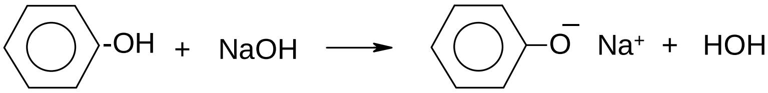
The identification reactions:

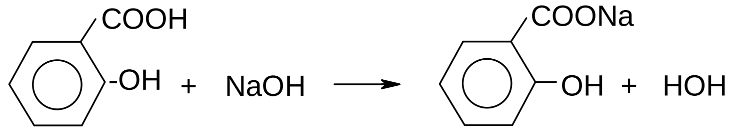
a) With H_2SO_4:

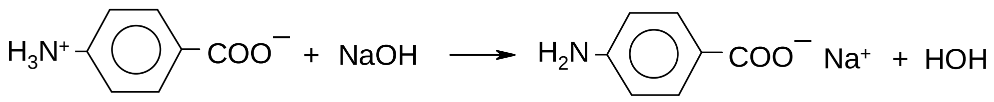




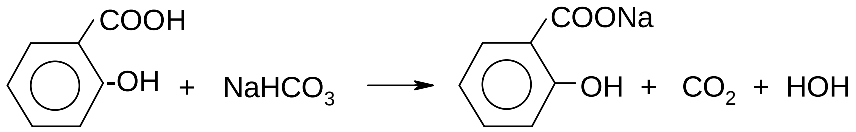
b) With NaOH:

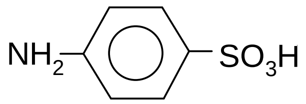


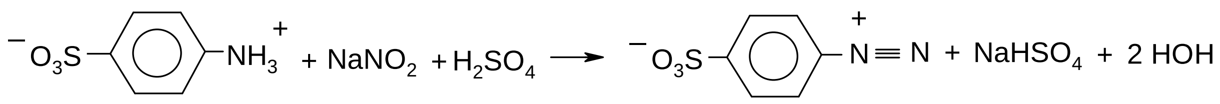


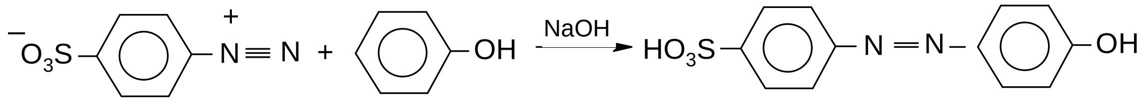


c) With $NaHCO_3$:

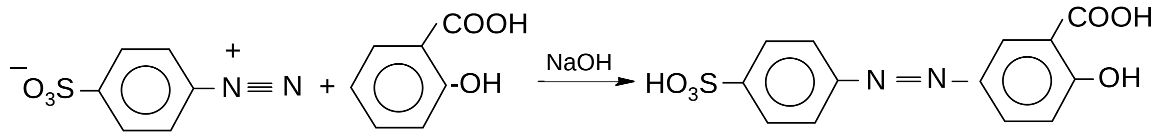


d) With 

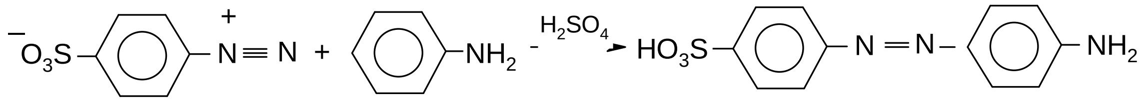




(orange)

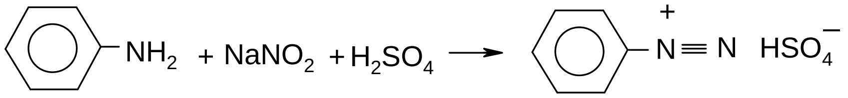


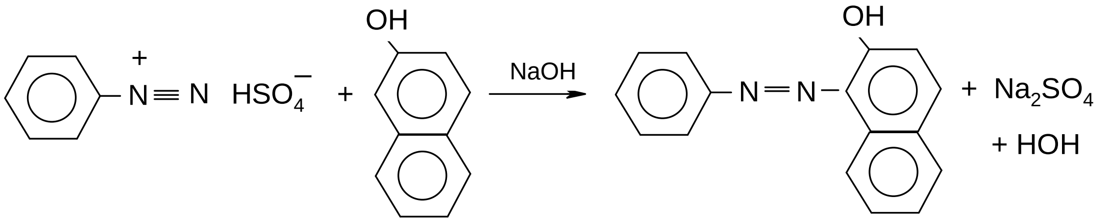
(orange)



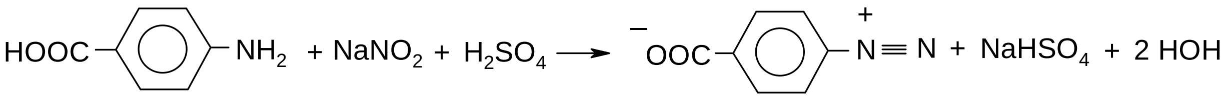
(orange)

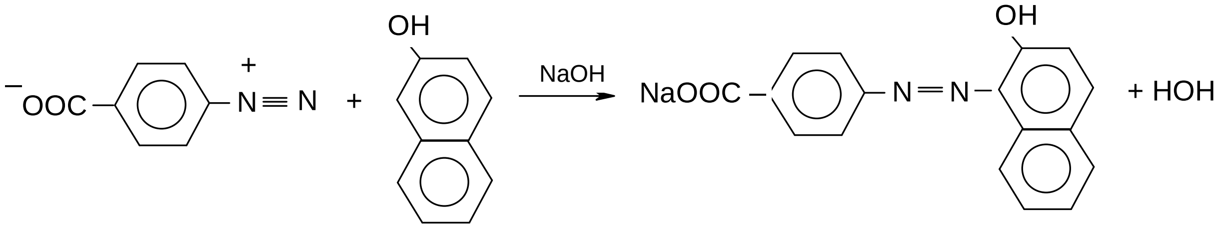
II. e) With β-naphthol:





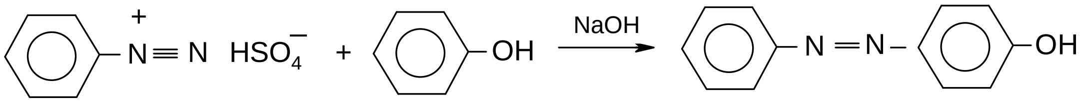
yellow - orange



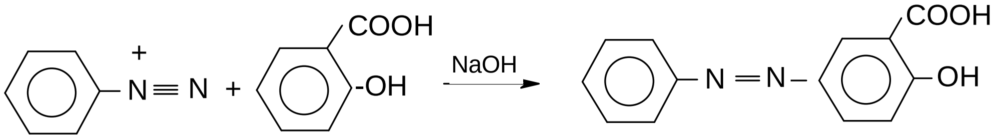


red

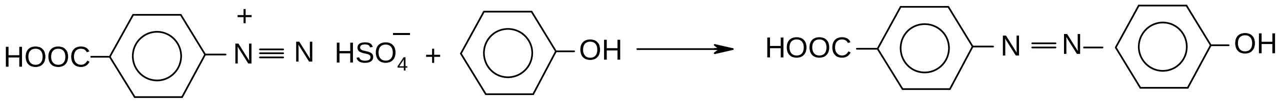
The following dyes can be obtained:



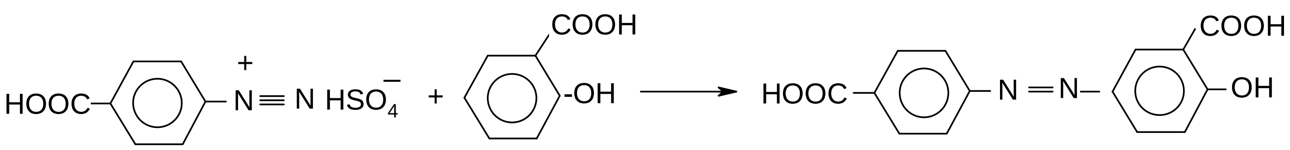
(red - orange)



(red - orange)



(red - orange)



(red - orange)

PROBLEM 3 (practical)

Six test-tubes contain aqueous solutions of $FeSO_4$, H_2SO_4, $Mn(NO_3)_2$, H_2O_2, $Pb(NO_3)_2$, NaOH.

a) Identify the content of each test-tube without using other reagents. Write the results in tabular form. Write the equations for the chemical reactions used for the identification.

b) After identification, perform four reactions each time using three of the identified compounds and write the equations.

SOLUTION

	$FeSO_4$	H_2SO_4	$Mn(NO_3)_2$	H_2O_2	$Pb(NO_3)_2$	NaOH
1) $FeSO_4$		–	–	$Fe(OH)SO_4$ yellowish	$PbSO_4\downarrow$ white	Fe(OH)2 $\downarrow$ white-greenish $\downarrow$ Fe(OH)3 $\downarrow$ brown-redish
2) H_2SO_4	–		–	–	$PbSO_4\downarrow$ white	–
3) $Mn(NO_3)_2$	–	–		–	–	$Mn(OH)_2\downarrow$ white $\downarrow$ $MnMnO_3\downarrow$ brown black
4) H2O2	$Fe(OH)SO_4$ yellowish	–	–		–	–
5) $Pb(NO_3)_2$	$PbSO_4\downarrow$ white	$PbSO_4\downarrow$ white	–	–		–
6) NaOH	$Fe(OH)_2\downarrow$ white-greenish $\downarrow$ $Fe(OH)_3\downarrow$ brown-redish	–	$Mn(OH)_2\downarrow$ white $\downarrow$ $MnMnO_3\downarrow$ brown black	–	$Pb(OH)_2\downarrow$ white $\downarrow$ $Pb(OH)_4^{2-}$	

	Reactions	Observation
(1) + (4)	$FeSO_4 + H_2O_2 \rightarrow 2\ Fe(OH)SO_4$	Colour change - yellowish (Fe^{3+})
(1) + (5)	$FeSO_4 + Pb(NO_3)_2 \rightarrow PbSO_4\downarrow + Fe(NO_3)_2$	Appearance of a white precipitate.
(1) + (6)	$FeSO_4 + 2\ NaOH \rightarrow Fe(OH)_2\downarrow + Na_2SO_4$ $Fe(OH)_2 + ½\ O_2 + H_2O \rightarrow Fe(OH)_3$	Appearance of a greenish white precipitate $Fe(OH)_2$ which after oxidation by air turns into a reddish brown precipitate $Fe(OH)_3$.
(2) + (5)	$H_2SO_4 + Pb(NO_3)_2 \rightarrow PbSO_4\downarrow + 2\ HNO_3$	Appearance of a white precipitate $PbSO_4$.
(3) + (6)	$Mn(NO_3)_2 + 2\ NaOH \rightarrow Mn(OH)_2 + 2\ NaNO_3$ $2\ Mn(OH)_2 + ½\ O_2 \rightarrow MnMnO_3 + 2\ H_2O$ $Mn(OH)_2 + ½\ O_2 \rightarrow MnO_2 + H_2O$	Appearance of a white precipitate $Mn(OH)_2$ which after oxidation by air coverts into a brown-black precipitate $MnMnO_3$ which eventually changes into MnO_2 – a black-brown precipitate.
(5) + (6)	$Pb(NO_3)_2 + 2\ NaOH \rightarrow Pb(OH)_2 + 2\ NaNO_3$ $Pb(OH)_2 + 2\ NaOH \rightarrow Na_2Pb(OH)_4$	Appearance of a white precipitate $Pb(OH)_2$ which dissolves in excess reagent.
b)		
(1) + (2) + (4)	$2\ FeSO_4 + H_2O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2\ H_2O$	Colour change → yellowish (Fe^{3+})
(1) + (4) + (6)	$2\ FeSO_4 + H_2O_2 + 4\ NaOH \rightarrow Fe(OH)_3 + 2\ Na_2SO_4$	Appearance of a brown-reddish precipitate $Fe(OH)_3$
(3) + (4) + (6)	$Mn(NO_3)_2 + H_2O_2 + 2\ NaOH \rightarrow MnO_2 + 2\ NaNO_3 + 2\ H_2O$	Appearance of a brown precipitate MnO_2
(5) + (4) + (6)	$Pb(NO_3)_2 + H_2O_2 + 2\ NaOH \rightarrow PbO_2 + 2\ NaNO_3 + 2\ H_2O$	Appearance of a brown precipitate PbO_2.

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

You are required to investigate seven inorganic compounds.

Your test-tube rack is numbered 1 to 9. Two of the positions are empty. Each of the seven test-tubes provided contains only one compound in aqueous solution. Using only these solutions, pH indicator paper, and test-tubes, you are to identify as many of the ions present as you are able.

For your information, record in the table the observations you make on mixing the solutions. Use the following symbols:

elimination reactions: $\downarrow$ precipitate; $\uparrow$ gaseous product;

$\downarrow_s$ precipitate soluble in the excess of a precipitating agent.

colours: w - white or colourless, b - blue, g - green, y - yellow, p - pink, r - red, br - brown.

pH: a - acidic, b - alkaline, n - neutral.

Equipment:

A home-made rack contained 9 test-tubes with the unknown solutions, 30 empty Wassermann-tubes and one small beaker containing the pH indicator paper. Into each solution a dropper was inserted, and thus, the test-tubes need not to be removed from the rack while handling them. According to the original plan the following nine unknown solutions were expected to be given to the participants: $CoCl_2$, $Fe(SCN)_3$, NH_4OH, KI, $AgNO_3$, Na_2HAsO_4, $HgCl_2$, $NiCl_2$, $CuCl_2$.

During the discussion of the International Jury it became known that in some countries the corresponding laws forbid the pupils in secondary schools to handle mercury and arsenic compounds. For this reason these two compounds were removed from the rack and consequently the number of ions to be detected - and the marks available - were reduced to 12 (from the original 15). (Under these conditions the alkali and nitrate ions cannot be detected.)

The order of the test-tubes varied individually, but the first two contained invariably red solutions ($CoCl_2$ and $Fe(SCN)_3$), while the last two were the green $NiCl_2$ and $CuCl_2$ symbolizing the Hungarian national colours, red-white-green.

SOLUTION

The ions of the remaining seven solutions can easily be identified by mutual reactions. Out of the 21 possible reactions, 12 are common positive reactions. Additional information is available from the colour of 4, and the smell of one solution.

$AgNO_3$:	reacts with all the six compounds;
NH_3:	with the exception of iodide it gives a characteristic reaction with all the others salts;
$Fe(SCN)_3$:	its colour and reaction with NH_3, I^-, Ag^+ are characteristic;
$CoCl_2$:	can be detected from its colour and by adding NH_3 or Ag^+;
KI:	can be identified by its reaction with Ag^+ and from the evolution of I_2 due to an addition of Fe^{3+} or Cu^{2+};
$CuCl_2$:	can be detected from its colour and reaction with NH_3, I^- and Ag^+;
$NiCl_2$:	has a characteristic colour and reacts with NH_3 and Ag^+.

PROBLEM 2 (Practical)

Qualitative Analysis

Equipment:

Five flasks are labelled 2.1 through 2.5. Each contains an aqueous solution of a colourless metal nitrate. Except for silver nitrate, the concentrations of the nitrates used to prepare these solutions, are all 0.1 mol dm^{-3}.

The solutions are: aluminium(III) nitrate
calcium(II) nitrate
lead(II) nitrate
silver(I) nitrate
zinc(II) nitrate

Moreover, available are pH indicator paper and the following three reagents of a concentration of about 5 mol dm^{-3}, contained in flasks labelled 2.6 through 2.8.

2.6 : hydrochloric acid,
2.7 : aqueous ammonia solution,
2.8 : sodium hydroxide solution.

Beware: these solutions are all concentrated and corrosive.

Tasks:

2.1 Carry out reactions between each reagent and each solution. For each of the solutions 2.1 through 2.5, record your observations for each reaction observed.

2.2 Write the name of the cation contained in each of the solutions 2.1 through 2.5 in the corresponding space on the answer sheet.

2.3 For each cation identified, write the equation for each reaction observed.

SOLUTION

2.1 Aluminium(III) nitrate

- $Al^{3+} + HCl \rightarrow$ no reaction
- $Al^{3+} + 3\,NH_3 + 3\,H_2O \rightarrow Al(OH)_3\downarrow + 3\,NH_4^+$
- $Al^{3+} + 3\,OH^- \rightarrow Al(OH)_3\downarrow$

- $Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$ (aq)

calcium(II) nitrate

- $Ca^{2+} + HCl \rightarrow$ no reaction
- $Ca^{2+} + 2\ OH^- \rightarrow Ca(OH)_2\downarrow$

lead(II) nitrate

- $Pb^{2+} + 2\ Cl^- \rightarrow PbCl_2\downarrow$ (in cold solutions)
- $Pb^{2+} + 2\ NH_3 + 2\ H_2O \rightarrow Pb(OH)_2\downarrow + 2\ NH_4^+$
- $Pb^{2+} + 2\ OH^- \rightarrow Pb(OH)_2\downarrow$

  $Pb(OH)_2 + 2\ OH^- \rightarrow [Pb(OH)_4]^{2-}$ (aq)

silver(I) nitrate

- $Ag^+ + Cl^- \rightarrow AgCl\downarrow$
- $Ag^+ + NH_3 + H_2O \rightarrow AgOH\downarrow + NH_4^+$ (or Ag_2O)

  $AgOH + 2\ NH_3 \rightarrow [Ag(NH_3)_2]^+$ (aq) $+ OH^-$
- $Ag^+ + OH^- \rightarrow AgOH\downarrow$

  $2\ AgOH \rightarrow Ag_2O + H_2O$

zinc(II) nitrate

- $Zn^{2+} + HCl \rightarrow$ no reaction
- $Zn^{2+} + 2\ NH_3 + 2\ H_2O \rightarrow Zn(OH)_2\downarrow + 2\ NH_4^+$

  $Zn(OH)_2 + 4\ NH_3 \rightarrow [Zn(NH_3)_4]^{2+}$(aq) $+ 2\ OH^-$
- $Zn^{2+} + 2\ OH^- \rightarrow Zn(OH)_2\downarrow$

  $Zn(OH)_2 + 2\ OH^- \rightarrow [Zn(OH)_4]^-$ (aq)

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Identification of Unknown Solutions

You are supplied with five different solutions contained in five test tubes labelled as A, B, C, D and E, respectively. The solution in each test tube contains one of the following compounds:

NH_4Cl $(NH_4)_2SO_4$ $NaNO_3$ $MgCl_2$ Na_2SO_4

Identify these solutions.

Reagents

H_2SO_4 (conc.)
HNO_3 (conc.)
HCl (conc.)
$Ba(OH)_2$ (satd.)
$BaCl_2$ (0.5 mol dm^{-3})
H_2SO_4 (6 mol dm^{-3})
HNO_3 (6 mol dm^{-3})
HCl (6 mol dm^{-3})
NaOH (6 mol dm^{-3})
$Ba(NO_3)_2$ (0.5 mol dm^{-3})

NOTES:

(1) You can only select the provided reagents and use a procedure as simple as possible to complete your task. You are getting a mark not only according to the correct identification, but also to the number of steps you have taken.

(2) You have to carry out the whole analysis by using the provided amount of these unknown solutions. Supplement of them will be available, but it will reduce the mark you obtain.

PROBLEM 2 (Practical)

Organic qualitative analysis

You have six bottles containing six different organic compounds. From the list of eight compounds given below, identify the contents of each bottle using the reagents available.

Many of these compounds have strong odours. To prevent the laboratory from becoming too odorous, you must keep each bottle tightly capped when it is not in use. Dispose of any waste produced in the bottle labelled "ORGANIC WASTE" at your station. Also place used litmus paper in this bottle. Keep the waste bottle capped when not in use.

Chemicals Available
litmus paper, red and blue
aqueous ceric ammonium nitrate
aqueous chromic-sulfuric acid
aqueous 2,4-dinitrophenylhydrazine
aqueous 0.2% KMnO4
acetone (2-propanone)

Possible Unknowns*
2-butanone
1-decene
2,3-diamino-2,3-dimethylbutane
hexane
3-methyl-1-butanol
2-methyl-2-butanol
nonanal
propanoic acid

*Several of the unknowns are present as dilute aqueous solutions.
This will not interfere with the test results.

PROBLEM 2 (Practical)

Isolation and Identification of an Essential Oil from Natural Source

In this experiment, you will steam distil and determine the structures of the main essential oil (**S**) from a given natural source and a product from its chemical conversion (unknown **Y**).

To determine the structures, you have to use organic qualitative analysis to identify any functional groups present in the compounds by using the reagents at your station. NMR data will be given only after the functional group test is completed.

Chemicals Available:

Sample (1 g in a vial)

Unknown **Y** (in a vial)

Anhydrous Na_2SO_4 (in a plastic vial), dichloromethane, ceric ammonium nitrate solution, 2,4-Dinitrophenylhydrazine (labelled as 2,4-DNP), 2 % aq. NH_3, 5 % aq. $AgNO_3$, 5 % aq. HCl, 5 % aq. NaOH, 5 % aq. $NaHCO_3$, 1 % $FeCl_3$ in EtOH, 0.2 % aq. $KMnO_4$, decolourised with easily oxidised functional groups, acetone (for washing).

Procedure:

1. Apparatus: Assemble a distillation apparatus using a 25 cm^3 round bottomed flask for distillation and a 10 cm^3 round bottomed flask to collect the distillate. Heat the sand bath to approximately 150 °C before proceeding the next step.

Simplified Steam Distillation: Mix 1 g of ground sample with 15 cm^3 of water in the 25 cm^3 round bottomed flask and allow the sample to soak in the water for about 10 minutes before distillation. Do not forget to put in a magnetic bar, turn on the water in the condenser and stirring motor, heat the mixture (the temperature of the sand bath should not be below 170 °C) to provide a steady rate of distillation. At least 5 cm^3 of distillate must be collected. Hot plate must be turned off after distillation is finished. Disassemble the apparatus and rinse the condenser with acetone. Be sure that the condenser is dry before using in the next step

Extraction of the Essential Oil: Transfer the distillate to a 15 cm^3 capped centrifuge tube and add 1 cm^3 of dichloromethane to extract the distillate. Cap the tube securely and shake vigorously, cool in ice. Allow the layers to separate.

Using a Pasteur pipette, transfer the dichloromethane layer to a 10 cm^3 test tube. Repeat this extraction with fresh 1 cm^3 dichloromethane twice and combine with the first extract.

Drying: Dry the dichloromethane extract by adding anhydrous Na_2SO_4 and stir occasionally for 10 minutes.

Evaporation: With a clean, dry cotton plugged Pasteur pipette transfer the organic layer to a dry 5 cm^3 conical vial. Use approximately 1 cm^3 of clean dichloromethane to wash Na_2SO_4 using the dry cotton plugged Pasteur pipette, then transfer into the vial. Be careful not to transfer any of the Na_2SO_4 into the vial. Use Hickman still head and dry condenser to distil the dichloromethane from the solution until the volume is reduced to 1 cm^3. Discard the distilled dichloromethane from the Hickman still head with a Pasteur pipette or a syringe to a vial (for recovered dichloromethane) and keep the residue for functional group analysis.

Functional Group Analysis: Carry out the functional group analysis of the residue solution (1 cm^3) by using the appropriate reagents at your station. (Note: dichloromethane is immiscible with water.)

Tollen's Reagent: add 1 drop of 5 % aq. $AgNO_3$ in a small test tube followed by 1 drop of 5 % aq. NaOH, brown precipitate will appear. Add 2 % aq NH_3 to the tube until all the precipitate dissolved. The solution is ready for the test.

2. Structure elucidation of the main essential oil (S)

Reaction of the main essential oil (**S**) with CH_3I in the presence of K_2CO_3 gives compound **X** ($C_{11}H_{14}O_2$). Oxidation of **X** gives unknown **Y** ($C_{10}H_{12}O_4$) as the main product and CO_2.

3. Structure elucidation of the unknown Y:

Identify the functional groups of unknown Y (provided in a conical vial) by using the reagents at your station and fill in your results in the answer sheet. Indicate the functional group(s) present or not present.

Hand in your copy of answer sheet PART I (Demonstrator copy) of functional group analysis and ask for ^{1}H NMR spectra. ^{1}H NMR spectra will be given only when the functional group analysis is completed.

4. Draw the structure which represents the main component in the essential oil (S) that was distilled from the sample. Assign each proton from the provided ^{1}H NMR spectra by labelling the peak number on the proton in the structure in the answer sheet.

5. Draw the structures of compound X and unknown Y. Assign each proton of unknown **Y** from the provided ^{1}H NMR spectra in the same manner as in (4).

SOLUTION

1. It was expected to obtain at least 5 cm^3 of distillate.
2. Functional group analysis of the distilled essential oil:

Reagents	Positive test	Negative test
0.2 % $KMnO_4$	✓	
1 % $FeCl_3$	✓	
2,4-DNP		✓
Ceric ammonium nitrate	✓	
Tollen's Reagent		✓

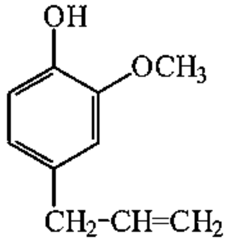
Functional groups in S	Present	Not present
-C=C-	✓	
-OH (alcoholic)		✓
-OH (phenolic)	✓	
-CHO		✓
-CO-		✓
-COOH		✓

3. Funcional group analysis of the unknown compound Y:

Reagents	Positive test	Negative test
5 % HCl		✓
5 % NaOH	✓	
5 % $NaHCO_3$	✓	
0.2 % $KMnO_4$		✓
1 % $FeCl_3$		✓
2,4-DNP		✓
Ceric ammonium nitrate		✓
Tollen's Reagent		✓

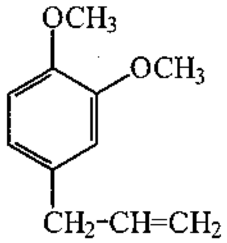
Functional groups in **Unknown Y**	Present	Not present
-C=C-		✓
-OH (alcoholic)		✓
-OH (phenolic)		✓
-CHO		✓
-CO-		✓
-COOH	✓	

4. The structure which represents the main essential oil (S):

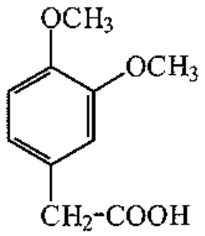


5. The structure of compound **X** and unknown **Y**:

Compound **X**



Compound **Y**

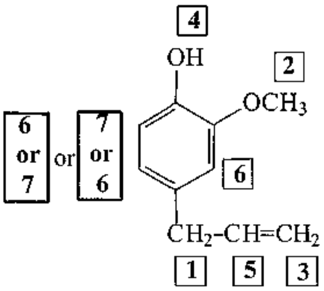


NMR spectrum of the main essential oil (S):

(See peak number in the given 'H NMR spectrum)

Peak No.	Chemical shift (δ, ppm)	No. of proton(s)	Multiplicity
1	3.31	2H	d
2	3.84	3H	S
3 4	5.0 – 5.1	2H	m
5	5.6	1H	S
	5.9 – 6.0	1H	m
6	6.7	2H	S d or m
7	6.87	1H	d

NMR assignment of the main essential oil (S):

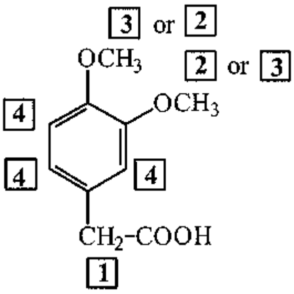


NMR spectrum of the unknown **Y**:

(See peak number in the given 'H NMR spectrum. Labile proton does not appear in the spectrum.)

Peak No.	Chemical shift (δ, ppm)	No. of proton(s)	Multiplicity
1	3.59	2H	s
2	3.86	3H	s
3	3.88	3H	s
4	6.81	3H	s

NMR assignment of the main essential oil (S):



PROBLEM 2 (Practical)

Qualitative and Quantitative Analysis of a Superconductor

Introduction

Superconductors based on lanthanum cuprate (La_2CuO_4) have the general composition of $La_xM_{(2-x)}CuO_4$ (M = Ca, Sr, Ba).

This problem consists of two parts:

- the qualitative determination of the alkaline earth metal(s)
- the quantitative determination of lanthanum and copper.

Read the burette as accurately as possible. Report your results on the answer sheets.
Answer the additional questions and write the results with adequate accuracy.
The qualitative and quantitative parts of this experiment may be done in any order.

Procedures

2.1 *Qualitative determination of the alkaline earth metal(s)*

(If the hood is occupied start with the titration 2.2)

In this experiment you have to use the superconductor as a solid ($La_xM_{(2-x)}CuO_4$; No. **14**).
At the beginning, lanthanum has to be separated as an insoluble residue.
All steps must be carried out in the hood!
Dissolve the complete sample in a beaker in about 5 cm^3 of perchloric acid (No. **22**) by heating the mixture. Add 5 cm^3 of demineralized water afterwards.
Cool down the solution until it is lukewarm.

Add about 5 cm^3 of demineralized water and then ammonia solution (No. **17**), until the reaction mixture shows a basic reaction. Lanthanum precipitates as hydroxide and copper forms an intense blue-coloured tetraammine complex. The precipitate is filtered off and washed with a small amount of demineralized water.

An excess of ammonium-carbonate solution (No. **18**) is added to the filtrate and the mixture is being boiled for some minutes. The alkaline earth metal(s) will precipitate as carbonate(s). The precipitate is filtered off and washed a few times with a small amount of demineralized water.

Then, the precipitate is dissolved in acetic acid (No. **16**). Add sodium acetate (No. **9**) and an excess of potassium-dichromate solution (No. **23**). In the presence of barium, yellow $BaCrO_4$ precipitates. After boiling the mixture for one minute barium chromate is filtered off and washed with demineralized water.

(If there is no barium chromate precipitation, proceed in a way as if there were precipitation.)

Ammonia solution (No. **17**) is added to the clear filtrate until it is basic. Add an excess of ammonium-carbonate solution (No. **18**) and boil the mixture for some minutes. In the presence of strontium and/or calcium, white carbonate(s) precipitate(s).

The precipitate is filtered off and washed a few times with demineralized water.

Then it is dissolved in a mixture of about 2 cm^3 of demineralized water and a few drops of hydrochloric acid (No. **3**). This solution is devided between two test tubes:

- Saturated calcium-sulfate solution (No. **21**) is added to one of the test tubes. In the presence of strontium a small amount of white strontium sulfate precipitates. To accelerate the precipitation, you can grind the inner surface of the test tube with a glass rod for a few minutes.
- Ammonium-sulfate solution (No. **20**) is added to the second test tube. In the presence of strontium and/or calcium, white sulfate(s) precipitate(s). The precipitate is filtered off and washed with a very small amount of demineralized water.

  1 cm^3 of ammonium-oxalate solution (No. **19**) is added to the filtrate. In the presence of calcium, white calcium oxalate precipitates after a few minutes.

Preparation of the superconductor parent solution

There is a superconductor solution ($La_xM_{(2-x)}CuO_4$ in perchloric acid; No. 13) in a volumetric flask.

Fill it up with demineralized water to a volume of 250.0 cm^3. From now on this solution is called “parent solution”.

2.2 *Quantitative determination of the total content of lanthanum and copper*

Transfer 25.00 cm^3 of the parent solution into an Erlenmeyer flask. Add about 5-6 piled spatula of sodium acetate (CH_3COONa; No. **8**) and 2 micro spatula of xylenol orange indicator (No. **15**) to this solution and make up with demineralized water to a volume of

about 75 cm^3. The *pH*-value has to be about ***pH* 6** before the determination, otherwise add more sodium acetate.

Titrate the solution with Na_2-EDTA solution (No. **7**). The color of the solution changes from light violet to intensely light-green. (In between, the color changes a few times.)

Repeat this procedure as many times as necessary.

2.3 *Quantitative determination of the copper content*

Transfer 25.00 cm^3 of your parent solution (No. **13**) into the 100 cm^3 volumetric flask and fill up with demineralized water to a volume of 100.0 cm^3. For each titration, transfer 25.00 cm^3 of this solution into an Erlenmeyer flask and add sodium hydroxide solution (No. **6**), until the solution shows an alkaline reaction. During this procedure, a blue precipitate forms. Add sulfuric acid (No. **12**) until the blue precipitate dissolves. The solution has to be acidic (**pH 1-2**) and will contain a small amount of a white precipitate.

Add 10 cm^3 of sodium-iodide solution (No. **9**), and swirl the Erlenmeyer flask for about 1 minute. Titrate the solution with sodium-thiosulfate solution (No. **10**). Add some starch solution (No. **11**) as an indicator just before the end of the titration. At the end, the solution has to be colourless for at least 60 seconds.

Repeat this procedure as many times as necessary.

SOLUTION

2.1 Which alkaline earth metal(s) can be found in the superconductor? Mark only one box!

Ca ☐ Sr ☐ Ba ☒

Ca and Sr ☐ Ca and Ba ☐ Sr and Ba ☐

Ca and Sr and Ba ☐

Complete the following reaction equations:

$$Ca^{2+} + C_2O_4^{2-} \rightleftharpoons CaC_2O_4$$

$$Sr^{2+} + CO_3^{2-} \rightleftharpoons SrCO_3$$

$2\ Ba^{2+} + Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\ BaCrO_4 + 2\ H^+$

2.2 Quantitative determination of the total content of lanthanum and copper.

Appropriate consumption of 0.1000 mol dm^{-3} EDTA solution: $V = 11.60$ cm^3

(accoding to 100 cm^3 of superconductor solution)

2.3 Quantitative determination of the copper content.

Appropriate consumption of 0.01000 mol dm^{-3} $Na_2S_2O_3$ solution: $V = 10.50$ cm^3

(according to 100 cm^3 of superconductor solution)

Complete the following reaction equations:

$2\ Cu^{2+} + 4\ I^- \rightleftharpoons I_2 + 2\ CuI$

$I_2 + 2\ S_2O_3^{2-} \rightleftharpoons 2\ I^- + S_4O_6^{2-}$

2.4 Mass (in mg) of copper in your parent solution,
mass (in mg) of lanthanum in your parent solution.

[M(Cu) = 63.55 g mol^{-1}; M(La) = 138.91 g mol^{-1}]

Amount of copper:

10,50 cm^3 × 0.01 mol dm^{-3} × 4 × 10 × 63.55 g mol^{-1} = 266.9 mg

Amount of lanthanum:

[11.60 – (10.50 / 10 × 4)] cm^3 × 0.1 mol dm^{-3} × 10 × 138.91 g mol^{-1} = 1028 mg

Mass Cu: m(Cu) = 266.9 mg
Mass La: m(La) = 1028 mg

2.5 Assume a fictive consumption of 39.90 cm^3 of 0.1000 mol dm^{-3} EDTA solution and 35.00 cm^3 of 0.01000 mol dm^{-3} $Na_2S_2O_3$ solution. Calculate the coefficient x in the formula $La_xM_{(2-x)}CuO_4$ (M = Ca and/or Sr and/or Ba) and give the exact formula of the superconductor

Consumption for lanthanum = [39.90 – (35.00/10 × 4)] cm^3 = 25.90 cm^3

Consumption for copper = (39.90 – 25.90) cm^3 = 14.00 cm^3

n(La) : n(Cu) = 25.90 : 14.00 = 1.85 : 1

coefficient x: 1.85 formula: $La_{1.85}Ba_{0.15}CuO_4$

PROBLEM 2 (Practical)

Identification of Unknown Inorganic Samples

Note

(1) This practical exercise is a kind of “spot test”. You can do it on the pallet or on a sheet of black film (for white precipitate).

(2) Please check all items written in the equipment and reagent list.

(3) Please check carefully the code number of the unknown sample with the Check List accompanied with your unknown samples.

(4) The volume of each unknown solution is about 1.5 cm^3 (about 30 drops). No more reagents or samples will be provided.

(5) Be sure to confirm your results before writing your answers in the blanks of the Answer Sheet.

(6) Make sure the switch on the battery box is closed.

(7) You will get 8 points for each correct identification.

Introduction

There are 12 unknown samples in your plastic bag□9 unknown solutions are in droppers and 3 unknown solids are in vials. All unknown samples are numbered with a 3 digit code. Please check the number with the List of Unknown Inorganic Samples carefully, then write your student code, and name on the list. (The list is accompanied with your unknown samples) Each vial contains about 20 mg of crystals or powder of one pure compound. Each dropper contains about 1.5 cm^3 solution of one pure compound dissolved in distilled water. The concentration of unknown solutions is in the range of 0.05 to 0.5 M (mol dm^{-3}).

The unknown samples are as follows:

HCl H_2O_2 H_2SO_4 $ZnCl_2$ NH_4SCN
$NaOH$ Na_2CO_3 Na_2SO_3 $BaCl_2$ $K_4Fe(CN)_6$

Note

1) Two unknown samples are duplicates.

2) The crystal water (. H_2O) is omitted in the formulas listed above.

2.1 Use the four reagents provided and mutual reactions among the unknown samples, and the simple electrolysis apparatus to identify each unknown sample, and write your answer (3 digit code) in the blanks of your answer sheet.

2.2 In this practical work, you have performed a series of tests to identify (or confirm) the unknowns. Show the reactions involved by way of chemical equations.

A. Write the electrolysis equation that would help you confirm that an unknown sample is $ZnCl_2$.

B. Write one equation that shows how to clean the deposit of Zn on the electrode (limited to the items provided in this task).

SOLUTION

2.2A $Zn^{2+}(aq) + 2\ Cl^{-}(aq) \rightarrow Cl_2(g)$ (anode) + $Zn(s)$ (deposit on cathode)

2.2B $Zn(s) + 2\ H^{+}(aq) \rightarrow H_2(g) + Zn^{2+}(aq)$

or

$Zn(s) + 2\ OH^{-}(aq) + 2\ H_2O(l) \rightarrow H_2(g) + [Zn(OH)_4]^{2-}(aq)$

PROBLEM 3 (Practical)

Qualitative Analysis of Organic Compounds

In this experiment your task is to identify seven solid unknowns from the list of compounds on page 7 that are common drugs in everyday life and valuable agents in organic chemistry. To achieve this, perform chemical tests on unknowns according to the following procedures and analyze your results.

Procedure

Helpful Comments

a) The weight of a spatula tip-full of a solid is about 15~20 mg.
b) Wipe spatula cleanly with Kimwipe between uses.
c) After adding any reagent described below to a solution of an unknown sample, mix the contents thoroughly and observe the resulting mixture carefully.
d) To get full marks, you should perform all the tests and fill out the table.

Test 1: Solubility test

To a test tube, add a spatula tip-full (15~20 mg) of an unknown sample and 1 cm^3 of CH_3CN. Shake the test tube and report the solubility. Repeat the test with 1M HCl, water, and 1M NaOH.

Test 2: 2,4-DNPH test

Place about 15~20 mg of an unknown sample in a test tube and dissolve with 2 cm^3 of 95 % EtOH. (For the water soluble unknowns, dissolve about 15~20 mg of an unknown in 1 cm^3 of water.) Add five drops of the 2,4-dinitrophenylhydrazine solution in concentrated sulphuric acid and 95% ethanol (labelled as 2,4-DNPH).

Test 3: CAN test

Mix 3 cm^3 of the cerium(IV) ammonium nitrate solution in dilute HNO_3 (labelled as CAN) with 3 cm^3 of CH_3CN in a test tube. In another test tube add about 15~20 mg of an unknown sample in 1 cm^3 of the mixed solution. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown sample in 1 cm^3 of water first, and then add 1 cm^3 of CAN.) If there is a colour change in the solution, the solution may contain alcohol, phenol or aldehyde.

Test 4: Bayer test

In a test tube, dissolve about 15~20 mg of an unknown sample in 2 cm^3 of CH_3CN. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown in 1 cm^3 of water.) To the solution, slowly add five drops of the 0.5 % $KMnO_4$ solution, drop by drop while shaking.

Test 5: *pH* test

In a test tube, dissolve about 15~20 mg of an unknown sample in 2 cm^3 of 95 % EtOH. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown sample in 1 cm^3 of water). Measure the pH of the solution with pH paper.

Test 6: Iron(III) chloride test

Take the solution from Test 5 and add five drops of a 2.5 % $FeCl_3$ solution.

Results

1. Record your test results in the answer sheet. Write *O* if soluble and *X* if insoluble for the solubility tests. Write (+) for the positive reactions and (–) for the negative reactions for tests 2 ~ 4 and 6. Write *a*, *b* and *n* for acidic, basic or neutral, respectively, for pH test 5.
2. Based on your test results, identify the most plausible structures for the unknown compounds from the provided list of compounds. Write the compound initial in appropriate box.

Possible Unknown Compounds (next page):

PROBLEM 3 (Practical)

Caution:

Handle all unknown solutions as if they were toxic and corrosive. Discard them only in the appropriate waste container.

The heat gun heats the expelled air up to 500 ℃. Do not direct the stream towards combustible materials or body parts. Be careful with the hot nozzle.

Always place a single piece of pumice into liquids before heating to avoid bumping. Never point the mouth of a heated test tube towards a person.

You have eight unknown aqueous solutions. Each solution contains only one compound. The same ion may appear in more than one solution. Every compound formally consists of one type of cation and one type of anion from the following list:

Cations: H^+, NH_4^+, Li^+, Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Sr^{2+}, Ag^+, Sn^{2+}, Sn^{4+}, Sb^{3+}, Ba^{2+}, Pb^{2+}, Bi^{3+}

Anions: OH^-, CO_3^{2-}, HCO_3^-, CH_3COO^-, $C_2O_4^{2-}$, NO_2^-, NO_3^-, F^-, HPO_4^{2-}, $H_2PO_4^-$, SO_4^{2-}, HSO_4^-, S^{2-}, HS^-, Cl^-, ClO_4^-, MnO_4^-, Br^-, I^-

You have test tubes and heating at your disposal but no additional reagents apart from distilled water and *pH* paper.

Identify the compounds in the solutions **1-8**. You can use the solubility table for some of the anions on the next page. If you are unable to identify an ion exactly, give the narrowest selection possible.

Remarks: The unknown solutions may contain minor impurities arising from their exposure to air. The concentration of all solutions is around 5 % by mass so you can expect clearly observable precipitates from the main components. In some cases, precipitation does not occur instantaneously; some substances may remain in an oversaturated solution for a while. Don’t draw negative conclusions too hastily, wait 1-2 minutes where necessary. Always look carefully for all signs of a reaction.

Keep in mind that heating accelerates all processes, increases the solubility of most substances, and may start reactions that do not take place at room temperature.

SOLUTION

The solutions received by the students contain the following compounds in eight test-tubes: $AgNO_3$, BaI_2, $KHCO_3$, $MgSO_4$, NaHS, NaOH, NH_4ClO_4, $Pb(CH_3COO^-)_2$ ($Pb(OAc)_2$). There were eight sets of samples differing in order of the compounds in particular test tubes.

The problem can be approached in many ways. A systematic solution is given here for one of the sets of test tubes with the following order of the compounds:

Test tube No	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Compound	$AgNO_3$	$KHCO_3$	NH_4ClO_4	NaOH	NaHS	$Pb(OAc)_2$	BaI_2	$MgSO_4$

All solutions are colourless (NaHS may be slightly yellowish because of polysulfide impurity). Solutions **1**, **3**, **6**, **7**, and **8** are practically neutral (*pH* paper reading about 5-6). Solution **2** is basic (*pH* = 9) while solutions **4** and **5** are very strongly basic (*pH* > 11).

We can exclude all ions that only form coloured compounds in aqueous solutions: Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and MnO_4^-. (In principle we should also exclude Mn^{2+} but its solutions have a very light pink colour that might be mistaken for colourless. The yellowish solution is strongly basic hence its colour cannot be attributed to iron.) The compounds of H^+, Sn^{2+}, Sn^{4+}, Sb^{3+}, Bi^{3+}, and HSO_4^- with the possible counter-ions could only exist in markedly acidic solutions; therefore they can also be safely excluded.

Thus the list of possible ions is:

Cations: NH_4^+, Li^+, Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Mn^{2+}, Zn^{2+}, Sr^{2+}, Ag^+, Ba^{2+}, Pb^{2+}.

Anions: OH^-, CO_3^{2-}, HCO_3^-, CH_3COO^-, $C_2O_4^{2-}$, NO_2^-, NO_3^-, F^-, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, SO_4^{2-}, S^{2-}, HS^-, Cl^-, ClO_4^-, Br^-, I^-.

The unknown solutions react with each other as follows (↓ = precipitate; ↑ = volatile product; “no change” means even when boiled, unless indicated otherwise):

	1 $AgNO_3$	**2** $KHCO_3$	**3** NH_4ClO_4	**4** NaOH	**5** NaHS	**6** $Pb(OAc)_2$	**7** BaI_2	**8** $MgSO_4$
1 $AgNO_3$	—	—	—	—	—	—	—	—
2 $KHCO_3$	↓ light yellow ↑ neutral, odourles	—	—	—	—	—	—	—
3 NH_4ClO_4	no change	↓ white crystals (*)	—	—	—	—	—	—
4 NaOH	↓ brown-black	no change	boiling: ↑ basic, odour of ammonia	—	—	—	—	—
5 NaHS	↓ black solution turns acidic	no change	boiling: ↑ basic, odour of NH_3, H_2S	no change	—	—	—	—
6 $Pb(OAc)_2$	↓ white crystals	↓ white ↑ neutral, odourles	no change	↓ white	↓ black	—	—	—
7 BaI_2	↓ yellow	↓ white ↑ (**)	no change	no change	no change	↓ yellow	—	—
8 $MgSO_4$	↓ white crystals	no change (***)	no change	↓ white	no change (****)	↓ white	↓ white	—

(*): upon boiling, the formation of NH_3 is detectable by its odour and by *pH* paper.

(**): gas bubbles are usually not observed when **2** is in excess.

(***): upon boiling, an odourless gas evolves and a white precipitate forms.

(****): upon boiling, a white precipitate forms and the odour of H_2S appears.

$2\ Ag^+ + 2\ HCO_3^- = Ag_2CO_3 + CO_2 + H_2O$

$Pb^{2+} + 2\ HCO_3^- = PbCO_3 + CO_2 + H_2O$

$Ba^{2+} + 2\ HCO_3^- = BaCO_3 + CO_2 + H_2O$

$Mg^{2+} + 2\ HCO_3^- = MgCO_3 + CO_2 + H_2O$ (more accurately, basic carbonates of variable composition are formed)

$Ag^+ + I^- = AgI$; $2\ Ag^+ + SO_4^{2-} = Ag_2SO_4$; $Ag^+ + CH_3COO^- = CH_3COOAg$

$Pb^{2+} + 2\ OH^- = Pb(OH)_2$; $Pb^{2+} + 2\ I^- = PbI_2$; $Pb^{2+} + SO_4^{2-} = PbSO_4$

$K^+ + ClO_4^- = KClO_4$; $Ba^{2+} + SO_4^{2-} = BaSO_4$; $Mg^{2+} + 2\ OH^- = Mg(OH)_2$

$2\ Ag^+ + 2\ OH^- = Ag_2O + H_2O$

$2\ Ag^+ + HS^- = Ag_2S + H^+$; $Pb^{2+} + HS^- = PbS + H^+$; $CH_3COO^- + H^+ = CH_3COOH$

$NH_4^+ + OH^- = NH_3 + H_2O$

$NH_4^+ + HCO_3^- = NH_3 + CO_2 + H_2O$

Two groups of the observed phenomena give instant clues to the identification of some of the ions.

First, the reactions of **2** are often accompanied with the formation of a colourless and odourless gas that can only be CO_2. Thus **2** contains CO_3^{2-} or HCO_3^-.

Second, there are only 3 dark precipitates that can be formed from the given ions: Ag_2O, Ag_2S, and PbS. This fact, together with the *pH* of the solutions, instantly identifies the cation of **1** as $\mathbf{Ag^+}$, the cation of **6** as $\mathbf{Pb^{2+}}$, the anion of **4** as $\mathbf{OH^-}$, and the anion of **5** as sulfide or hydrosulfide (confirmed by the distinct smell of the solution).

The choice between the latter two can be made by measuring the *pH* of the solution formed in the reaction of **5** with an excess of **1** or **6**. In the case of **1**, the reaction mixture is strongly acidic. Thus the anion of **5** is $\mathbf{HS^-}$.

The evolution of CO_2 in the reaction with Ag^+ and Pb^{2+} also identifies the anion of **2** as $\mathbf{HCO_3^-}$. (in accord with the moderately basic *pH*)

The reaction of **3** and **4** yields ammonia. **4** is obviously not a solution of NH_3 itself. Thus the cation of **3** is $\mathbf{NH_4^+}$.

2+**4** form either a precipitate or ammonia. The cations of **2** and **4** are Na^+ or K^+.

2+**5** do not form either a precipitate or ammonia. The cation of **5** is an alkali metal.

3 is the only solution that does not give a precipitate with Ag^+. Accordingly, it can be ammonium nitrate, fluoride, or perchlorate. But it does give a precipitate with **2**, a hydrocarbonate of Na^+ or K^+. Thus the anion of **3** is $\mathbf{ClO_4^-}$ and the cation of **2** is $\mathbf{K^+}$. **4** does not give a precipitate with NH_4ClO_4. The cation of **4** is $\mathbf{Na^+}$.

5 does not give a precipitate either with NH_4ClO_4 (K^+) or with a mixture of $KHCO_3$ and NaOH (Li^+). The cation of **5** is **Na^+**.

7 forms no precipitate or ammonia with NaOH but gives a precipitate with $KHCO_3$. **7** cannot be an alkali metal perchlorate because it forms yellow precipitates with **1** and **6**. Thus the cation of **7** is **Ba^{2+}** and the anion of **7** is **$I^–$**.

At room temperature **8** gives a precipitate with $OH^–$ but not with $HS^–$ which means it can only be a salt of a Group 2A metal. Thus the reaction of **8** with BaI_2 is obviously one between Ba^{2+} and the anion of **8**. The latter is very likely $SO_4^{2–}$ but $HCO_3^–$ and $H_2PO_4^–$ are also theoretically possible. The solution of **8** is unchanged upon boiling and gives a white precipitate with Ag^+. This excludes both $HCO_3^–$ and $H_2PO_4^–$. Thus the anion of **8** is **$SO_4^{2–}$**. This instantly identifies the cation of **8** as **Mg^{2+}**.

6 is a soluble compound of lead. The anion could be $CH_3COO^–$, $NO_2^–$, $NO_3^–$, or $ClO_4^–$. The slight odour of acetic acid might give a clue. Unlike **1**, the reaction of an excess of **6** with $HS^–$ does not yield a markedly acidic solution which shows that **6** is a salt of a weak acid. If **6** were a nitrite, it would give a yellowish precipitate with Ag^+. It would also react with NH_4ClO_4 upon heating with the evolution of N_2 (and nitrogen oxides from the reaction with $HS^–$ would also be noticeable). The absence of these reactions indicates that the anion of **6** is **$CH_3COO^–$**.

Soluble salts of silver are even less numerous, the only choices are $NO_3^–$, $F^–$, and $ClO_4^–$. The anion can be examined if one removes the silver ions from the solution of **1** with an excess of NaOH. The Ag_2O precipitate quickly separates from the solution which can be easily poured off. This solution, containing the anion of **1**, does not give a precipitate with BaI_2 which rules out $F^–$. The solubility of $KClO_4$ is quite significant;
therefore the absence of a precipitate with $KHCO_3$ is inconclusive. The anion of **1** is therefore either **$NO_3^–$** or **$ClO_4^–$**.

Labware

Item	Quantity
All tasks, on the table of common use	
Latex gloves of different sizes, choose your size	-
General equipment for all tasks, for each student, on the table	
Test tube rack (60 holes)	1
Paper tissue (can ask for extra)	5
Permanent marker	1
Glass stirring rod, 20 cm	1
Polypropylene funnel, diam. 3.5 cm	1
Soft plastic cup	3
Strong plastic cup	1
All tasks, for each student in the soft plastic cup	
Caps for polystyrene test tubes	22
Task 1, for each student, on the table	
Rack for centrifuge tubes (21 holes)	1
Container with a screw cap for waste,1 dm^3, labeled “Liquid Waste, Test 1”	1
Paper filters in zip-bag	5
Task 1, for each student, in the strong plastic cup	
Pasteur pipettes	20
Task 1, for each student, in the 60-hole rack	
Polystyrene test tubes, 10 cm^3	35

Chemicals

Name	**State**	**Conc.**	**Q-ty**	**Placed in**	**Labeled**
All tasks, for each student, on the table					
Distilled water	Liquid	-	1 dm^3	Wash bottle, 1 dm^3	H_2O dist.
Task 1, for each student, on the table					
Hexane	Liquid	-	25 cm^3	Glass bottle with screw cap, 50 cm^3	Hexane
Sodium hydroxide	Aqueous solution	1 M	80 cm^3	Amber plastic bottle with screw cap, 125 cm^3	NaOH
Nitric acid*	Aqueous solution	2 M	150 cm^3	Glass bottle with dropper cap, 250 cm^3	HNO_3
Task 1, for each student, in the 21-hole rack					
5 unknowns	Aqueous solution	-	45 cm^3	Centrifuge tubes, 50 cm^3	Unknown No ___
Silver nitrate	Aqueous solution	0.1 M	25 cm^3	Centrifuge tube, 50 cm^3	$AgNO_3$
Aluminium sulfate	Aqueous solution	0.3 M	25 cm^3	Centrifuge tube, 50 cm^3	$Al_2(SO_4)_3$
Barium nitrate	Aqueous solution	0.25 M	25 cm^3	Centrifuge tube, 50 cm^3	$Ba(NO_3)_2$
Iron(III) nitrate	Aqueous acidic (HNO_3) solution	0.2 M	25 cm^3	Centrifuge tube, 50 cm^3	$Fe(NO_3)_3$
Potassium iodide	Aqueous solution	0.1 M	25 cm^3	Centrifuge tube, 50 cm^3	KI
Potassium iodate	Aqueous solution	0.1 M	25 cm^3	Centrifuge tube, 50 cm^3	KIO_3
Magnesium chloride	Aqueous solution	0.2 M	25 cm^3	Centrifuge tube, 50 cm^3	$MgCl_2$
Sodium carbonate	Aqueous solution	0.2 M	25 cm^3	Centrifuge tube, 50 cm^3	Na_2CO_3
Sodium sulfite	Aqueous solution	0.2 M	25 cm^3	Centrifuge tube, 50 cm^3	Na_2SO_3
Ammonia*	Aqueous solution	1 M	25 cm^3	Centrifuge tube, 50 cm^3	$NH_3(aq)$

* Nitric acid and ammonia solutions are needed in a subsequent task.

Task 1

You have 10 different compounds dissolved in water in 5 unknown solutions. Each numbered container contains two of the following compounds in aqueous solution (every compound is used, and each compound is used only once):

$AgNO_3$, $Al_2(SO_4)_3$, $Ba(NO_3)_2$, $Fe(NO_3)_3$, KI, KIO_3, Na_2CO_3, Na_2SO_3, $MgCl_2$, NH_3

You are given HNO_3 solution, NaOH solution, hexane and the aqueous solutions of the 10 pure compounds listed above.

You can use empty test tubes and any of the liquids provided (including the unknowns) to identify the unknown samples. A funnel and filter paper can be used for separation.

Identify the compounds in the solutions **1**-**5**. Give the number of the solution that contains the individual compounds on the answer sheet. Indicate two observations caused by a chemical reaction for each compound in your unknown mixtures by giving the letter code of the appropriate observation (choose one or more from the list), and write appropriate balanced ionic equation(s) that explain the observation. At least one of the reactions has to be specific for clearly identifying the compound from this selection of unknowns.

Note: After the STOP signal close all the centrifuge test tubes containing the unknown mixtures with the blue caps labeled with the student code and leave these in the rack.

Task 1 13% of the total

7	7	7	7	7	7	7	7	7	7	Sum: 70

Only fill out this table when you are ready with all your assignments. Use the following observation codes:

A - Formation of white precipitate
B - Formation of colored precipitate (red, brown, yellow, black etc.)
C - Dissolution of precipitate
D - Color change in the solution
E - Formation of colored solution

F - Brown color in the organic phase
G - Purple color in the organic phase

H - Formation of colored gas
I - Formation of colorless and odorless gas
J - Formation of colorless and odorous gas
K – Change in the color of precipitate

Compound	No. of unknown	Formula of reaction partner(s)	Observation code(s)	Balanced net ionic equation(s)
NH_3				
$Fe(NO_3)_3$				
$Al_2(SO_4)_3$				
$AgNO_3$				
KIO_3				

Compound	No. of unknown	Formula of reaction partner(s)	Observation code(s)	Balanced net ionic equation(s)
Na_2CO_3				
$MgCl_2$				
Na_2SO_3				
$Ba(NO_3)_2$				
KI				

Replacements:

Item	Quantity	Lab assistant's signature	Student's signature

5p for locating each compound, 1 p for each relevant equation. Altogether 10x7p.

Subpoints for 1p: 0.4p for correct observation with appropriate reagent(s); 0.6p for the relevant balanced ionic equation (-0.1p for minor typos; maximum of -0.3p for poor balancing; maximum of 0.3p for an equation in other than ionic form)

The unknowns are identical mixtures for every student in different order. Most are mixed in 1:1 ratio by volume.

Characteristic reactions are marked with bold letters. One of these or equivalent has to be shown on the answer sheet.

NH_3

$AgNO_3$, B)	$2\ Ag^+ + 2\ OH^- = Ag_2O + H_2O$ *(if* Ag^+ *is not mixed with* Fe^{3+}*)*
C)	$Ag_2O + H_2O + 4\ NH_3 = 2\ [Ag(NH_3)_2]^+ + 2\ OH^-$ *(if* Ag^+ *is not with* Fe^{3+}*)*
$Fe(NO_3)_3$, B)	**$Fe^{3+} + 3\ OH^- = Fe(OH)_3$**
$Al_2(SO_4)_3$, A)	**$Al^{3+} + 3OH^- = Al(OH)_3$ (or $[Al(H_2O)_6]^{3+} + 3\ OH^- = Al(OH)_3 + 6\ H_2O$)**
$MgCl_2$, A)	**$Mg^{2+} + 2\ OH^- = Mg(OH)_2$**
NaOH, J)	**$NH_4^+ + OH^- = NH_3 + H_2O$**
$(KIO_3) + AgNO_3$, C)	**$AgIO_3 + 2\ NH_3 = [Ag(NH_3)_2]^+ + IO_3^-$**

$Fe(NO_3)_3$

NaOH, B)	**$Fe^{3+} + 3\ OH^- = Fe(OH)_3$**
NH_3, B)	**$Fe^{3+} + 3\ OH^- = Fe(OH)_3$**
KI, D) or E)	**$2\ Fe^{3+} + 2\ I^- = 2\ Fe^{2+} + I_2$**
$MgCl_2$, E)	**$Fe^{3+} + Cl^- = [FeCl]^{2+}$ (or $Fe^{3+} + 3\ Cl^- = FeCl_3$ etc.)**

$Al_2(SO_4)_3$

NaOH, A)	$Al^{3+} + 3\ OH^- = Al(OH)_3$ (or $[Al(H_2O)_6]^{3+} + 3\ OH^- = Al(OH)_3 + 6\ H_2O$)
C)	**$Al(OH)_3 + OH^- = [Al(OH)_4]^-$**
(NaOH +) HNO_3 A)	**$[Al(OH)_4]^- + H^+ = Al(OH)_3 + H_2O$**
$Ba(NO_3)_2$, A)	**$Ba^{2+} + SO_4^{2-} = BaSO_4$**
Na_2CO_3, A)	$Al^{3+} + 3\ OH^- = Al(OH)_3$ (or $[Al(H_2O)_6]^{3+} + 3\ OH^- = Al(OH)_3 + 6\ H_2O$)

$AgNO_3$

NaOH, B)	**$2 Ag^{+} + 2 OH^{-} = Ag_2O + H_2O$**
KI, B)	**$Ag^{+} + I^{-} = AgI$**
NH_3, B)	$2 Ag^{+} + 2 OH^{-} = Ag_2O + H_2O$ *(if Ag^{+} is not mixed with Fe^{3+})*
C)	$Ag_2O + H_2O + 4 NH_3 = 2 [Ag(NH_3)_2]^{+} + 2 OH^{-}$ *(if Ag^{+} is not with Fe^{3+})*
$MgCl_2$, A)	**$Ag^{+} + Cl^{-} = AgCl$**
Na_2CO_3, A) or B)	$2 Ag^{+} + CO_3^{2-} = Ag_2CO_3$
Na_2SO_3, A)	$2 Ag^{+} + SO_3^{2-} = Ag_2SO_3$
C)	**$Ag_2SO_3 + 3 SO_3^{2-} = 2 [Ag(SO_3)_2]^{3-}$**
KIO_3, A)	$Ag^{+} + IO_3^{-} = AgIO_3$

KIO_3

$Na_2SO_3 + HNO_3$, B) or E) (+ hexane, G)	**$5 SO_3^{2-} + 2 IO_3^{-} + 2 H^{+} = I_2 + 5 SO_4^{2-} + H_2O$**
$KI + HNO_3$, B) or E) (+ hexane, G)	**$5 I^{-} + IO_3^{-} + 6 H^{+} = 3 I_2 + 3 H_2O$**
$AgNO_3$, A)	$Ag^{+} + IO_3^{-} = AgIO_3$
$Ba(NO_3)_2$, A)	$Ba^{2+} + 2 IO_3^{-} = Ba(IO_3)_2$

Na_2CO_3

HNO_3, I)	**$CO_3^{2-} + 2 H^{+} = H_2O + CO_2$**
$Ba(NO_3)_2$, A)	$Ba^{2+} + CO_3^{2-} = BaCO_3$
$+ HNO_3$, C), I)	**$BaCO_3 + 2 H^{+} = Ba^{2+} + H_2O + CO_2$**
$AgNO_3$, A) or B)	$2 Ag^{+} + CO_3^{2-} = Ag_2CO_3$
$+ HNO_3$, C), I)	**$Ag_2CO_3 + 2 H^{+} = 2 Ag^{+} + H_2O + CO_2$**
$MgCl_2$, A)	$Mg^{2+} + CO_3^{2-} = MgCO_3$
$+ HNO_3$, C), I)	**$MgCO_3 + 2 H^{+} = Mg^{2+} + H_2O + CO_2$**

$MgCl_2$

NaOH, A)	**$Mg^{2+} + 2 OH^{-} = Mg(OH)_2$**
NH_3, A)	**$Mg^{2+} + 2 OH^{-} = Mg(OH)_2$**
$AgNO_3$, A)	**$Ag^{+} + Cl^{-} = AgCl$**
Na_2CO_3, A)	$Mg^{2+} + CO_3^{2-} = MgCO_3$
$Fe(NO_3)_3$, E)	**$Fe^{3+} + Cl^{-} = [FeCl]^{2+}$ (or $Fe^{3+} + 3 Cl^{-} = FeCl_3$ etc.)**

Na_2SO_3

HNO_3, J	**$SO_3^{2-} + 2 H^{+} = H_2O + SO_2$**
$KIO_3 + HNO_3$, B) or E) (+hexane, G)	**$5 SO_3^{2-} + 2 IO_3^{-} + 2 H^{+} = I_2 + 5 SO_4^{2-} + H_2O$**
$Ba(NO_3)_2$, A)	$Ba^{2+} + SO_3^{2-} = BaSO_3$
$+ HNO_3$, C)	**$BaSO_3 + 2 H^{+} = Ba^{2+} + SO_2 + H_2O$**
$AgNO_3$, A)	**$2 Ag^{+} + SO_3^{2-} = Ag_2SO_3$**
C)	**$Ag_2SO_3 + 3 SO_3^{2-} = 2 [Ag(SO_3)_2]^{3-}$**
$KI + KIO_3$, D)	**$I_2 + SO_3^{2-} + H_2O = 2 I^{-} + SO_4^{2-} + 2 H^{+}$**

$Ba(NO_3)_2$

$Al_2(SO_4)_3$, A)	**$Ba^{2+} + SO_4^{2-} = BaSO_4$**
KIO_3, A)	$Ba^{2+} + 2\ IO_3^- = Ba(IO_3)_2$
Na_2CO_3, A)	$Ba^{2+} + CO_3^{2-} = BaCO_3$
Na_2SO_3, A)	$Ba^{2+} + SO_3^{2-} = BaSO_3$
+ HNO_3, C)	**$BaSO_3 + 2\ H^+ = Ba^{2+} + SO_2 + H_2O$**

KI

$Fe(NO_3)_3$, E) or D)	**$2\ Fe^{3+} + 2\ I^- = 2\ Fe^{2+} + I_2$**
$AgNO_3$, B)	**$Ag^+ + I^- = AgI$**
KIO_3, + HNO_3, B) or E) (+hexane, G)	**$5\ I^- + IO_3^- + 6\ H^+ = 3\ I_2 + 3\ H_2O$**

Labware

Item	Quantity
General equipment for all tasks, for each student, on the table	
Test tube rack (60 holes)	1
Paper tissue	5
Permanent marker	1
Glass stirring rod, 20 cm	1
Polypropylene funnel, diam. 3.5 cm	1
Soft plastic cups	3
Strong plastic cup	1
Caps for polystyrene test tubes	22
Tasks 2 and 3, for each student, on the table	
Container with a screw cap for waste,3 dm^3, labeled “Liquid Waste, Tests 2&3”	1
Task 2, for each student, on the table	
Storage box labeled “Task 2”	1
Laboratory stand with double burette clamp	1
Burette, 25.00 cm^3	2
Graduated pipette, 10.0 cm^3	1
Graduated pipette, 1.00 cm^3	1
Bulb (Mohr) pipette, 10.00 cm^3	1
Erlenmeyer flask, 100 cm^3	2
Graduated cylinder, 10.0 cm^3	2
Brush	1
Polypropylene funnel, 5.5 cm	1
Task 2, for each student, in the storage box “Task 2”	
Polystyrene test tubes, 10 cm^3	8
Pipette filler	1
Pasteur pipettes for indicators	2
Task 3, for each student, get from the lab assistants	
Storage box labeled “Task 3”	1
Task 3, for each student, in the storage box “Task 3”	
Polystyrene test tubes, 10 cm^3	20
Alcohol lamp	1
Test tube holders, wooden	1
Glass test tubes	10
Pasteur pipettes	10
Strong plastic cup	1

Chemicals

Name	State	Conc.	Q-ty	Placed in	Labeled
Task 2, for each student, on the table					
Nitric acid	Aqueous solution	2 M	-*	Glass bottle with dropper cap, 250 cm^3	HNO_3
Task 2, for each student, in the storage box “Task 2”					
Water sample solution	Aqueous solution	To be determined	100 cm^3	Glass bottle with screw cap, 100 cm^3	Water sample
Sodium fluoride	Aqueous solution	9 mg/dm^3 in fluoride	50 cm^3	Glass bottle with screw cap, 50 cm^3	F^-, 9 mg/dm^3
Zirconyl Alizarin indicator	Acidic aqueous solutions	0.055% $ZrOCl_2$, 0.028% Alizarin Red S	10 cm^3	Glass bottle with screw cap, 25 cm^3	Zirconyl Alizarin
Sodium chloride	Aqueous solution	0.0500 M	50 cm^3	Glass bottle with screw cap, 50 cm^3	NaCl, 0.0500 M
Ammonium iron(III) sulfate dodecahydrate	Aqueous acidic solution	20 g/dm^3	10 cm^3	Glass bottle, 15 cm^3	Fe^{3+} ind.
Silver nitrate	Aqueous solution	To be determined	200 cm^3	Amber glass bottle, 250 cm^3	$AgNO_3$
Ammonium thiocyanate	Aqueous solution	See exact concentration on the label	100 cm^3	Glass bottle with screw cap, 100 cm^3	NH_4SCN, X.XXXX M
Potassium chromate	Aqueous solution	10%	5 cm^3	Glass bottle, 15 cm^3	K_2CrO_4
Task 3, for each student, on the table					
Ethanol	Liquid	95 %	150 cm^3	Glass bottle with dropper cup, 250 cm^3	C_2H_5OH
Task 3, for each student, in the storage box “Task 3”					
Organic unknowns 1 to 8	Liquid	-	0.5 cm^3	Syringes, 2 cm^3	1 to 8
Potassium permanganate	Aqueous solution	0.13 %	5 cm^3	Amber glass bottle, 50 cm^3	$KMnO_4$
Ammonium cerium(IV) nitrate reagent	2.0 M HNO_3 aqueous solution	28.6 %	5 cm^3	HDPE bottle, 30 cm^3	Ce(IV)
Acetonitrile	Liquid	-	45 cm^3	Glass bottle, 50 cm^3	CH_3CN

Name	**State**	**Conc.**	**Q-ty**	**Placed in**	**Labeled**
2,4-Dinitrophenylhydrazine reagent	Sulfuric acid solution in aqueous ethanol	3 %	20 cm^3	HDPE bottle, 30 cm^3	DNPH
Iron(III) chloride	0.5 M HCl aqueous solution	2.5 %	1 cm^3	HDPE bottle, 30 cm^3	$FeCl_3$
Hydroxylamine hydrochloride	Ethanolic solution	0.5 M	10 cm^3	HDPE bottle, 30 cm^3	$NH_2OH\times HCl$
Sodium hydroxide	Aqueous solution	6 M	5 cm^3	HDPE bottle, 30 cm^3	NaOH
Hydrochloric acid	Aqueous solution	1 M	25 cm^3	HDPE bottle, 30 cm^3	HCl

*In the quantity left after doing Task 1.

Periodic table with relative atomic masses

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

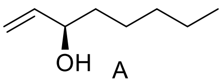
57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

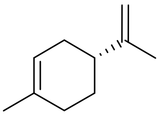
Task 3

Identifying flavors and fragrances

Tourists coming to Georgia admire many specialties, local cuisine occupying one of the top positions in the list of adventures. Excellent meat, fresh vegetables and greens, ripe fruits, home-made jams… What else is needed to satisfy true gourmets? Of course, unique flavors and fragrances!

You are given 8 samples of unknown organic compounds (labeled 1 to 8), which are industrially used as flavors and fragrances. All samples are pure individual compounds. Their possible structures are found among **A**-**M** given here.


A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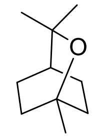
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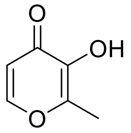
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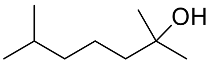
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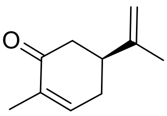
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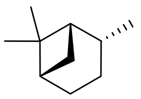
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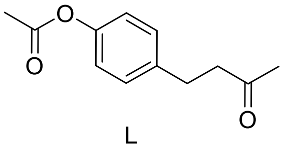
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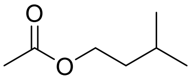
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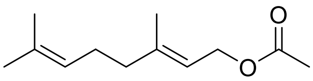
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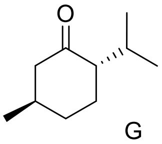
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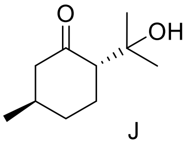
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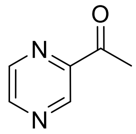

M

The organic compounds in your unknown samples are readily soluble in ether, and insoluble in dilute aqueous NaOH and HCl. These compounds, but the unknown No. 6. are insoluble in water, the latter being slightly soluble (3.5 g/dm^3).

3.1. <u>Perform</u> test reactions described below to identify the samples **1**-**8**. <u>Indicate</u> the results of the tests by giving the Roman numeral of the appropriate observation (choose one or more from the list). <u>Fill</u> in all cells of the table. <u>Use</u> **+** and **–** to indicate positive and negative tests.

3.2. Identify the unknowns based on the test results and the information given above. <u>Write</u> the structure codes (of **A** to **M**) of the identified samples in the appropriate box.

Test procedures

$KMnO_4$ test (Baeyer test)

Place appr. 1 cm^3 of 95% ethanol in a <u>plastic</u> test tube and add 1 drop of an unknown. Add 1 drop of $KMnO_4$ solution and shake the mixture. Treat the test as positive if the permanganate color disappears immediately after shaking.

3.3. Write the reaction scheme for a positive Baeyer test with one of the compounds **A**-**M**.

Cerium(IV) nitrate test

Place 2 drops of the **Ce(IV) reagent** into a glass test tube, add 2 drops of acetonitrile and then 2 drops of an unknown (the sequence is important!). Shake the mixture. In the case of positive test the mixture color promptly changes from yellow to orange-red.

Note 1. Use only glass test tubes to perform the test. In case you need to wash the glass test tubes, carefully choose the appropriate solvent. Use caps to prevent the strong odor.

Note 2. Comparison with blank (no unknown) and reference (with ethanol) tests is recommended for adequate interpretation.

Note 3. Ce(IV) ions initially form brightly colored coordination compounds with alcohols. Complexes formed from primary or secondary alcohols react further (within 15 seconds to 1 hour) with the disappearance of the color.

2,4-dinitrophenylhydrazine (2,4-DNPH) test

Add only 1 drop of an unknown to 1 cm^3 of 95% ethanol in a plastic test tube. Add 1 cm^3 of the DNPH reagent to the prepared solution. Shake the mixture and let it stand for 1-2 min. Observe formation of yellow to orange-red precipitate if the test is positive.

3.4. Write the reaction scheme for a positive 2,4-DNPH test with one of the compounds **A**-**M**.

Ferric hydroxamate test

Ask a lab assistant to light up your alcohol lamp. Mix 1 cm^3 of 0.5 mol/dm^3 ethanolic hydroxylamine hydrochloride solution with 5 drops of 6 mol/dm^3 sodium hydroxide aqueous solution in a glass test tube. Add 1 drop of an unknown and use the alcohol lamp to heat the mixture to boiling while gently swirling the test tube to avoid splashes of the reaction mixture. Allow it to cool down slightly and add 2 cm^3 of 1 mol/dm^3 HCl solution. Add 1 drop of 2.5% iron(III) chloride solution. Observe appearance of magenta color if the test is positive. Close the alcohol lamp with the cap when finished.

Note 1. Use glass test tubes only to perform the test; use the test tube holder when heating. In case you need to wash the glass test tubes, use an appropriate solvent. Stopper the test tubes with a green cap after completing the test to prevent a strong odor.

Note 2. Fe(III) ions form a colored 1:1 complex with hydroxamic acids (R-CO-NHOH).

3.5. Write the reaction scheme for a positive ferric hydroxamate test with one of the compounds **A**-**M**.

Note: After the STOP signal reattach the corresponding needles on the syringes with the unknown compounds, and place them into the plastic cup and leave them on the table.

Task 3 13% of the total

3.1.	3.2.	3.3.	3.4.	3.5.	Sum
32	16	4	4	4	60

3.1. Indicate the results and observations of tests by giving the Roman numerals of the appropriate observations in the table. Fill in all cells of the table. Use **+** and **–** to indicate positive and negative tests. Choose one or more codes from the list below.

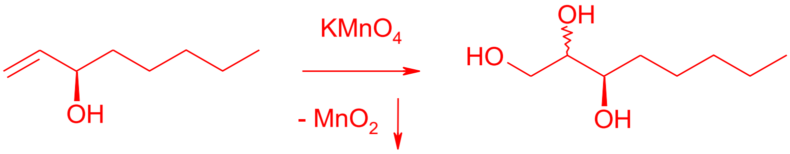
I – Immediate disappearance of purple color
II – Slow disappearance of purple color
III - Disappearance of yellow color
IV – Formation of a brown or black precipitate
V - Formation of a white precipitate
VI - Formation of a yellow or orange-red precipitate
VII - Appearance of orange or red color in solution
VIII - Appearance of magenta color
IX - The unknown compound is insoluble in ethanol
X – no visible changes

Sample No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Baeyer test result (**+**/**–**)	**+**	**–**	**+**	**–**	**–**	**–**	**–**	**+**
Baeyer test observations (**I**-**X**)	**I**, IV	**X**	**I**, IV	**II**, IV	**X**	**II**, IV	**X**	**I**, IV
Ce(IV) nitrate test result (**+**/**–**)	**+**	**+**	**–**	**–**	**–**	**–**	**–**	**–**
Ce(IV) nitrate test observations (**I**-**X**)	**VII**	**VII**	**III**, V	**III**	**X**	**X or III**	**X**	**III**
2,4-DNPH test result (**+**/**–**)	**–**	**–**	**–**	**+**	**–**	**–**	**–**	**–**
2,4-DNPH test observations (**I**-**X**)	**X**	**X**	**X**	**VI**	**X**	**X**	**X**	**X**
Fe(III) hydroxamate test result (**+**/**–**)	**–**	**–**	**–**	**–**	**+**	**–**	**–**	**+**
Fe(III) hydroxamate test observations (**I**-**X**)	**X**	**X**	**X**	**X**	**VIII**	**X**	**X or IX**	**VIII**

3.2. Write the structure codes (of **A** to **M**) of the identified samples in the appropriate boxes when you are certain in your assignments.

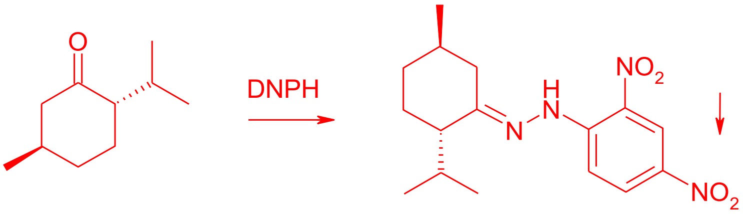
Sample No.	1	2	3	4	5	6	7	8
Structure code	**A**	**B**	**E**	**G**	**C**	**H**	**I**	**D**

3.3. Write the reaction scheme for a positive Baeyer test with one of the compounds **A-M**.



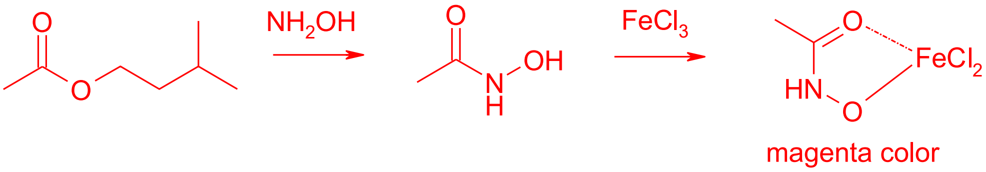
Or analogous 4p

3.4. Write the reaction scheme for a positive 2,4-DNPH test with one of the compounds **A-M**.



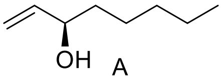
4p

3.5. Write the reaction scheme for a positive ferric hydroxamate test with one of the compounds **A-M**.



Or analogous 4p (any 1:1 hydroxamate – Fe(III) complex is acceptable)

The problem can be approached in many ways. A systematic solution for one variant of the unknown compounds encoding is given below (other variants are processed similarly).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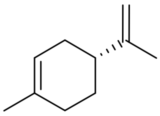
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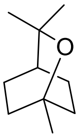
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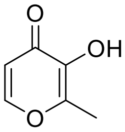
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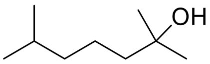
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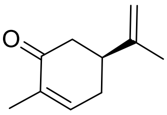
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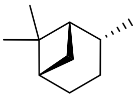
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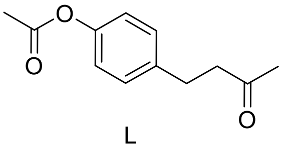
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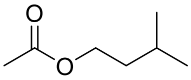
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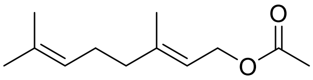
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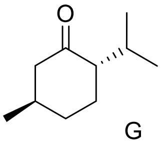
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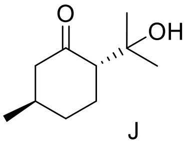
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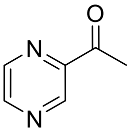

M

Step 1. Solubility data analysis.

The data given allow excluding compounds K (presence of phenol-like moiety) and M (presence of azine nitrogen) soluble in aqueous NaOH and aqueous HCl, respectively.

Step 2. Tests for the functional groups.

2.1 Unsatured compounds excluding those aromatic give positive Baeyer test, and those with keto- or aldehyde group give positive 2,4-DNPH test

2.2 For avoiding mistakes in true-positive / false-positive interpretation the precise description of true-positive tests is given in the test procedures.

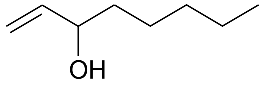
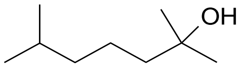
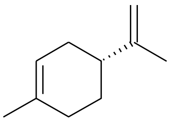
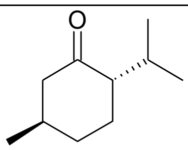
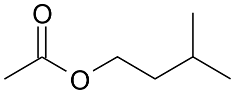
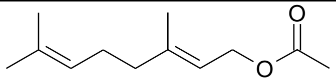
2.3 The information given in the Notes after the test procedures CLEARLY indicates the following prompts:

Note	Prompt
Comparison with blank (no unknown) and reference (with ethanol) tests is recommended for adequate interpretation of the test.	The cerium(IV) nitrate test is one for alcohols
Brightly colored Ce(IV) coordination compounds bearing C_{sp3}-O→Ce(IV) moiety have the formation constant in the range of 0.51 (MeOH, kinetically unstable) to 2.76 (t-BuOH, kinetically stable).	Red color appearing as a result of a positive cerium(IV) nitrate test can disappear due to further oxidation of alcohols by Ce(IV) in the case of primary and secondary alcohols
Brightly colored Fe(III)-hydroxamic acids coordination compounds have the formation constants $K_1 \sim 42$; $K_2 \sim 2.5$; $K_3 \sim 1.2 \cdot 10^{-2}$ (for acetohydroxamate in ethanol–water 1:1 mixture).	The ferric hydroxamate test is the one for the compounds capable of forming the hydroxamic acids in the reaction with NH_2OH. ONLY ESTERS are appropriate candidates for the positive test. Amides (J) do not afford hydroxamic acid under NH_2OH treatment, thus giving negative test.

The results of the experimental work can be summed up in the hereunder table.

# of sample	$KMnO_4$	$Ce(NH_4)_2(NO_3)_6$	2,4-DNPH	Ferric Hydroxamate Test
1	+	+	–	–
2	–	+	–	–
3	+	–	–	–
4	–	–	+	–
5	–	–	–	+
6	–	–	–	–
7	–	–	–	–
8	+	–	–	+

Analysis of the table allows unanimously identifying **A**, **B**, **E**, C, and **G**. **L** (Ferric hydroxamate and 2,4-DNPH), **J** (2,4-DNPH and Cerium(IV) nitrate test), and **F** ($KMnO_4$ and 2,4-DNPH tests) can be excluded from further consideration, since these provide for two positive tests each.

#	Structure	$KMnO_4$	$Ce(NH_4)_2(NO_3)_6$	2,4-DNPH	Ferric Hydroxamate Test
1		+	+	–	–
2		–	+	–	–
3		+	–	–	–
4		–	–	+	–
5		–	–	–	+
6	?	–	–	–	–
7	?	–	–	–	–
8		+	–	–	+

Step 3. Choosing of right structures of the samples 6 and 7 based on additional data given.

Among all compounds in the list, only H and I cannot give any positive test, the attribution requiring consideration of the solubility data. Sample 7 in the above table is soluble in ether only (attributed as I), whereas Sample 6 is partially soluble in water (attributed as H).

The final assignment is given below.

Sample No	1	2	3	4	5	6	7	8
Structure code	A	B	E	G	C	H	I	D

1 points for each test (1p × 4 tests × 8 unknowns=32p)

2 points for each correct assignment (2p× 8 unknowns=16p)

Titolazione acido-base

International Chemistry Olympiad

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

An unknown sample is a mixture of 1.2-molar H_2SO_4 and 1.47-molar HCl. By means of available solutions and facilities determine:

1. the total amount of substance (in val) of the acid being present in 1 dm^3 of the solution,
2. the mass of sulphuric acid as well as hydrochloric acid present in 1 dm^3 of the sample.

PROBLEM 2 (Practical)

By means of available reagents and facilities perform a qualitative analysis of the substances given in numbered test tubes and write down their chemical formulas.

Give 10 equations of the chemical reactions by which the substances were proved:
5 equations for reactions of precipitation,
2 equations for reactions connected with release of a gas,
3 equations for redox reactions.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Determine unknown samples in ten numbered test tubes using reagents and facilities available on the laboratory desk. Write chemical equations for the most important reactions that were used to identify each substance. In case that the reactions take place in solutions, write equations in a short ionic form.

PROBLEM 2 (Practical)

On June 10th, a mixture of formic acid with an excess of ethanol was prepared. This mixture was kept in a closed vessel for approximately one month. Determine quantitatively the composition of the mixture on the day of the competition, using only reagents and facilities available on the laboratory desk. Calculate the amounts of the acid and ethanol in per cent by mass which were initially mixed together.

PROBLEM 4 (practical)

A crystalline sodium carbonate loses a part of water when stored for a long time, i. e. its water content is not constant. After a long storage it has an average content of crystal water.

A solution of Na_2CO_3 is in the test-tube and the mass of $Na_2CO_3 \cdot x\ H_2O$ used in its preparation is marked on the test-tube.

Determine the content of crystal water per mole of sodium carbonate in the sample. Make calculations with an accuracy of 0.01 mol.

Procedure:

Transfer the solution from the test tube quantitatively into a 100 cm^3 volumetric flask and dilute it up to the mark with distilled water free of carbon dioxide (having been boiled and cooled to room temperature). Measure 10.00 cm^3 of the solution into a 100 cm^3 Erlenmeyer flask and dilute it to about 30 cm^3 with the above mentioned distilled water. Add 2 – 3 drops of methyl orange indicator and titrate with a 0.1-molar HCl volumetric solution to a colour transition of the indicator. On boiling for 1 – 2 minutes the carbon dioxide dissolved in the solution is expelled. If the colour of the solution changes to yellow, cool it and titrate again to the colour transition of the indicator. Calculate the carbonate content in the sample from the total consumption of the 0.1-molar HCl solution.

A_r(Na) = 22.99; A_r(C) = 12.01; A_r(O) = 16.00; A_r(H) = 1.01.

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

A sample contains two of the following cations: Ag^+, Pb^{2+}, Fe^{2+}, Cr^{3+}, Co^{2+}, Al^{3+}, Mn^{2+}, and one of the following anions: SO_4^{2-}, Cl^-, NO_3^-.

Prove the cations and anions in the sample by means of the following reagents:
2 N-HCl, concentrated H_2SO_4, 2 N-H_2SO_4, 2 N-HNO_3, 2 N-CH_3COOH, NaOH, NH_4OH, H_2O_2, Na_2CO_3, KNO_3/Na_2CO_3, NH_4SCN, $Na_2B_4O_7$, NaF, C_2H_5OH, $BaCl_2$, $AgNO_3$, NH_4Cl, $(NH_4)_2Fe(SO_4)_2$, alizarin B.

Write the results into the attached table in the following way:

a) into the column "Reagent" write the formula of the reagent which was needed to prove whether the cation or anion is present or absent in the sample;

b) into the column "+/–" mark the presence or absence of an ion, proved in the sample, by the sign "+" and "–" , respectively.

PROBLEM 2 (practical)

A solution contains sodium oxalate and oxalic acid.

Determine how many milligrams of sodium oxalate and oxalic acid are contained in the solution under investigation.

The following solutions are at your disposal: $KMnO_4$ (c = 0.01972 mol dm^{-3}), NaOH (c = 0.1019 mol dm^{-3}), concentrated H_2SO_4, and a solution of phenolphthalein.

PROBLEM 3 (practical)

If a known excess of hydroxide solution with a known concentration is added to a weighed sample of ammonium salt and the liberated ammonia is removed by boiling, it is possible to determine the unreacted quantity of hydroxide by titration with a volumetric solution of an acid.

Procedure:

Three samples of an ammonium salt, weighed with accuracy of 0.001 g, are at your disposal. Introduce each of them into a 250 cm^3 Erlenmeyer flask. Add 50.0 cm^3 of a 0.2-normal sodium hydroxide solution to each sample. Put several boiling stones into each mixture and heat the flasks slowly on a small flame till there is no more ammonia in the liberating vapours. After expelling ammonia, cool the solution to the laboratory temperature, add 2 or 3 drops of indicator solution (Bromothymol blue) and titrate with a 0,2-normal volumetric solution of oxalic acid to the first lasting yellow colour of the solution.

Problems:

3.1 Calculate the molar mass of ammonium salt from the experimental data.

3.2 The sample is a salt of a monobasic inorganic acid. Consider which one.

3.3 Calculate the absolute and relative error of your determination.

3.4 Give reactions by means of which ions of the salt can be proved in the solution.

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Four aqueous solutions are available on the laboratory desk. These are solutions of HCl, NaOH, NH_3, and CH_3COOH whose concentrations are approximately 1 mol dm^{-3}. The concentration of HCl solution is the only one that is exactly determined and known.

Using the volumetric solution of HCl, determine the exact concentrations of the other solutions. A burette, pipette, titration flasks and indicators methyl orange and phenolphthalein are at your disposal. Perform twice each titration and calculate the mean value for concentration. The third determination is needed to be carried out only in such a case when the results of the previous two titrations differ more than by 2 %.

Now you will perform the following thermochemical measurements of neutralisation heat evolved in the reactions of the above given solutions of acids and bases:

a) Measure quantitatively exactly 50.0 cm^3 of the hydrochloric acid solution into a beaker. Measure into another equal beaker a volume of NaOH solution that contains such a number of moles of NaOH as that of HCl being present in the first beaker. Then measure the temperatures of both solutions with a precision of 0.2 K. Pour quickly the content of the first beaker into the other using the thermometers as a glass stick and stir the resulting solution with the thermometer. Determine the final highest temperature of the mixture.

b) Perform analogous measurement with the following pairs of acids and bases:
HCl – NH_3, CH_3COOH – NaOH, CH_3COOH – NH_3.

Problems:

1.1 What indicators have been used for the individual determinations? Give approximately pH regions in which the mentioned indicators show colour transitions. Give reasons for the use of the individual indicators using only ionic equations for the reactions which are characteristic of specific properties of salts being formed in the individual neutralisation reactions. Calculate the concentrations of all solutions under investigations.

1.2 Write the calorimetric equation in its general form by means of which the neutralisation heat can be calculated. Calculate the thermal effect for each neutralisation reaction under investigation and give the value in relation to one mole of the water formed.

Densities of the solutions are as follows:

$\rho(HCl) = 1.02\ g\ cm^{-3}$

$\rho(NaOH) = 1.04\ g\ cm^{-3}$

$\rho(NH_3) = 0.99\ g\ cm^{-3}$

$\rho(CH_3COOH) = 1.01\ g\ cm^{-3}$

In the calculations consider the specific heat capacity value for the solutions equal to 4.19 J g^{-1} K^{-1} whereas the heat capacity of glass and thermometer may be neglected.

1.3. Have you obtained equal results in all four cases? If not, order the particular reaction systems according to the decreasing value of reaction heat. What reactions cause the above mentioned differences? Express the reactions by means of chemical equations.

1.4 The exact methods showed that neutralisation heat in the reaction of the strong acid with a strong base (i. e. the reaction heat when 1 mole of water is formed from H^+ and OH^- ions) is equal to 57.57 kJ mol^{-1}. Calculate the relative error of your determination.

SOLUTION

1.1. In titrating a strong acid with a strong base, both phenolphthalein and methyl orange can be used as acid-base indicators. The drop on the titration curve covers the colour changes of both indicators (pH values from 4 – 10).

Only phenolphthalein can be used in the case when a weak acid is titrated with a strong base because the neutralisation occurs at higher pH values (the colour transition of phenolphthalein is in the region of pH = 8 – 10). A salt formed undergoes hydrolysis (more precisely its anion) and the solution exhibits a basic reaction:

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

In titrating a strong acid with a weak base or vice versa, methyl orange is used (pH = 3 – 4.5) and due to hydrolysis the resulting solution shows an acidic reaction:

$$NH_4^+ + 2\,H_2O \rightleftharpoons NH_3\,.\,H_2O + H_3O^+$$

The exact concentrations of the aqueous solutions of sodium hydroxide and ammonia are determined by titrations with the volumetric solution of hydrochloric acid. The exact concentration of the acetic acid solution is then determined by a titration with the sodium hydroxide solution.

1.2 When the specific heat capacities of glass and thermometer are neglected the neutralisation heat can be then calculated according to a simple relation:

$\Delta H_{neutr.} = (m_1 + m_2)\,c\,(T_2 - T_1)$

m_1 – mass of the first solution,

m_2 – mass of the second solution,

c – specific heat capacity of the solutions,

T_1 – temperatures of the solutions before mixing,

T_2 – temperatures of the solutions after mixing.

If the temperatures of the solutions before mixing are not equal then T_1 will be the mean temperature of both. Finally, the neutralisation heat value should be related to 1 mole of water formed.

1.3 The results obtained for the neutralisation of a strong base with a weak acid and vice versa, as well as for the reaction of a weak acid with a weak base, are lower than those obtained for the neutralisation of a strong acid with a strong base. A part of the heat is consumed for ionisation of a weak electrolyte:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

A similar equation can be written for $NH_3.H_2O$.

PROBLEM 3 (practical)

Volumetric determination of sodium carbonate and sodium hydrogen carbonate simultaneously.

A) *Procedure:*

1. Determination of the precise concentration of an HCl solution (0.1 mol dm^{-3}) using borax $Na_2B_4O_7 . 10\ H_2O$ as a standard.

   Principle:

   An aqueous solution of sodium tetraborate reacts with hydrochloric acid to form trihydrogenboric acid.

   Procedure:

   25.00 cm^3 of a standard borax solution with a concentration of about 0.05 mol dm^{-3} (the exact borax concentration is written on the label on the volumetric flask; the solution needs not be diluted with water to a volume of 100 cm^{-3}) is transferred into a titration flask, 1 to 2 drops of methyl red are added and the solution is titrated to the first orange coloration of the yellow solution. The titration should be carried out at least twice. The consumption of hydrochloric acid should be designated by symbol V_1.

2. Volumetric determination of Na_2CO_3 and $NaHCO_3$ simultaneously.

   Procedure:

   The sample in a volumetric flask (250 cm^3) should be diluted to the mark with distilled water from which the carbon dioxide has been removed by boiling, and mix.

   a) Part of the solution (25 cm^3) is titrated with an HCl solution using methyl orange (2 drops) to the first red coloration of the originally yellow solution. The sample is boiled 2 to 3 minutes to release carbon dioxide. Then the solution is cooled and the titration is continued to a clear red coloration of the solution. The titration should be carried out at least twice. The consumption of hydrochloric acid should be designated as V_2 (average of titration values).

   b) A further part of the sample (25.00 cm^3) is transferred to an Erlenmeyer flask and mixed with 25.00 cm^3 of the NaOH solution with a concentration of 0.1 mol dm^{-3}. Add 10 cm^3 of a 10 % solution of $BaCl_2$ and 2 drops of phenolphthalein. Excess hydroxide should be titrated immediately in the presence of a white precipitate formed, using an HCl solution whose precise concentration has been determined

c) in part 1. The consumption of hydrochloric acid should be denoted as V_3 (average values of at least two titrations).

d) Carry out the same titration as in part b) without the sample (blank). The consumption of HCl is designated as V_4 (average of two titrations).

Use the results of the above experiments to calculate the amounts of Na_2CO_3 and $NaHCO_3$ in the sample.

B) Results

The results should be written into the form provided in which you should note the following:

a) The ionic equation for the reaction according to which the concentration of the HCl solution was determined.

b) The ionic equation for the reaction used in the determination of Na_2CO_3 and $NaHCO_3$ simultaneously.

c) The volume of hydrochloric acid consumed in the titration of 25.00 cm^3 of borax solution.

d) Calculation of the HCl concentration (in mol dm^{-3}).

e) Consumption of the HCl solution – V_2, V_3, and V_4.

f) Mass amounts of Na_2CO_3 and $NaHCO_3$ in the sample in grams.

$M(Na_2CO_3) = 105.989 \text{ g mol}^{-1}$

$M(NaHCO_3) = 84.007 \text{ g mol}^{-1}$

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

A pH buffer solution has a well defined acidity which changes only very slightly upon addition of moderate quantities of strong acid or base. The larger is the quantity of acid or base that must be added to a certain volume of a buffer solution in order to change its pH by a specific amount, the better is its action. A buffer solution is prepared by mixing a weak acid and its conjugate base in appropriate amounts in a solution. An example of a useful buffer system in aqueous solution is the phosphate system.

Your task is to prepare a phosphate buffer with properties specified by the following two conditions:

(1) pH = 7.20 in the buffer solution,

(2) pH = 6.80 in a mixture of 50.0 cm^3 of the butter solution and 5.0 cm^3 hydrochloric acid with a concentration of 0.100 mol dm^{-3}.

Chemicals and equipment

Aqueous solution of phosphoric acid, sodium hydroxide solution of known concentration, hydrochloric acid (0.100 mol dm^{-3}), solution of bromocresol green, distilled water.

Burettes, pipettes (25 and 5 cm^3), Erlenmeyer flasks (100 and 250 cm^3), volumetric flask (100 cm^3), beaker, and funnel.

Procedure

Determine the concentration of the phosphoric acid solution by titration with a sodium hydroxide solution using bromocresol green as an indicator (pH range $3.8 < pH < 5.4$).

Make a buffer solution by mixing calculated volumes of phosphoric acid and sodium hydroxide solutions in the volumetric flask and filling the flask to the mark with distilled water.

Mix in an Erlenmeyer flask 50.0 cm^3 of the buffer solution with 5.0 cm^3 of the hydrochloric acid.

Hand in your answer sheet to the referee who will also measure the pH of your two solutions and note your results.

The pK_a values for phosphoric acid are:

pK_{a1} = 1.75, pK_{a2} = 6.73, pK_{a3} = 11.50

SOLUTION

The buffer solution must contain

$H_2PO_4^-$ (concentration **a** mol dm^{-3}) and

HPO_4^{2-} (concentration **b** mol dm^{-3}).

The concentrations should satisfy the condition

$$\frac{\mathbf{b}}{\mathbf{a}} = \frac{10^{-6.73}}{10^{-7.20}}$$

After addition of HCl the condition will be

$$\frac{50.0\,b\ -\ 0.50}{50.0\,a\ +\ 0.50} = \frac{10^{-6.73}}{10^{-6.80}}$$

From these equations,

a = 0.0122 **b** = 0.0361

Total concentration of the phosphate system = 0.0483 mol dm^{-3}

Total concentration of Na^+ = (**a** + 2 **b**) mol dm^{-3} = 0.0844 mol dm^{-3}

If the concentration of both phosphoric acid and sodium hydroxide solution are 0.500 mol dm^{-3}, then 100.0 cm^3 buffer solution will require:

$$\text{volume of } H_3PO_4 \text{ solution} = \frac{0.0483 \times 0.1000}{0.500\,dm^3} = 9.7\,cm^3$$

$$\text{volume of NaOH solution} = \frac{0.0844 \times 0.1000}{0.500\,dm^3} = 16.9\,cm^3$$

PROBLEM 2 (practical)

A solution in a graduated flask contains a mixture of oxalic acid and ammonium oxalate.

One of the bottles denoted X, Y, and Z contains a solution of a calibration substance with reducing character at a concentration of 0.1000 mol dm^{-3}.

You are required to solve the following tasks:

a) Determine the quantity of oxalic acid and of ammonium oxalate in the solution in the graduated flask. (The result will be given in grams.)

b) Write the formula for the substance with reducing character and the equations of the chemical reactions which led to its determination.

In order to carry out the analyses the following solutions are available:
HCl (c = 0.1000 mol dm^{-3}), NaOH (c = 2 mol dm^{-3}), $KMnO_4$ (c = 0.02 mol dm^{-3}), 25 % H_2SO_4, HNO_3 (c = 2 mol dm^{-3}), 5 % $BaCl_2$, 5 % $AgNO_3$, 5 % $Hg_2(NO_3)_2$, phenolphthalein 0.1 %, methyl red 1 %.

c) Describe the procedure used in the individual steps, indicators employed and partial results.

$M_r(H_2C_2O_4) = 90.04$

$M_r((NH_4)_2C_2O_4) = 124.11$

SOLUTION

ANSWER SHEET:

A$_1$ – Identification of the solution with the reducing substance X, Y, Z: $Fe(NH_4)_2(SO_4)_2$

A$_2$ – Identification reactions for the ions of the substance

- $Fe^{2+} + 2\ NaOH \rightarrow Fe(OH)_2 + 2\ Na^+$
- $NH_4^+ + NaOH \rightarrow NH_3\uparrow + H_2O + Na^+$
- $4\ NH_3 + 2\ Hg_2(NO_3)_2 + H_2O \rightarrow O(Hg)_2NH_2.NO_3 + 3\ NH_4OH$
- $SO_4^{2-} + BaCl_2 \rightarrow BaSO_4 + 2\ Cl^-$

B$_1$– Preparation of the 0.1 M NaOH solution

. . . . cm^3 in 200.0 cm^3

B_2 – Concentration of the NaOH in its solution: . . . . M

Indicator used: . . . .

C – Concentration of $KMnO_4$ in its solution . . . . M

D_1 – Mass of oxalic acid in the initial solution . . . . g

Indicator used . . . .

D_2 – Mass of ammonium oxalate in the initial solution . . . . g

Solution

A_1 – 1-2 cm^3 of solution X, Y and Z are put into three test tubes. 6 N H_2SO_4 and a drop of $KMnO_4$ solution are added. The solution which loses colour is the one with reducing character.

A_2 – Establishment of the formula:

. . . . + NaOH – greenish white precipitate $\Rightarrow$ Fe^{2+}

. . . . + NaOH at the upper end of the test-tube, filter paper with a drop of $Hg_2(NO_3)_2$, black spot $\Rightarrow$ NH_4^+

. . . . + $BaCl_2$ – white precipitate $\Rightarrow$ SO_4^{2-}

. . . . + $AgNO_3$ + HNO_3 $\Rightarrow$ Cl^- is absent

Accordingly the substance used is $Fe(NH_4)_2(SO_4)_2$.

The chemical reactions:

$$Fe^{2+} + 2\ Na^+ + 2\ OH^- \rightarrow Fe(OH)_2 + 2\ Na^+$$

$$NH_4^+ + Na^+ + OH^- \rightarrow NH_3 + H_2O + Na^+$$

$$4\ NH_3 + 2\ Hg_2(NO_3)_2 \rightarrow O(Hg)_2NH_2\ .\ NO_3 + 2\ Hg + 3\ NH_4NO_3$$

$$SO_4^{2-} + Ba^{2+} + 2\ Cl^- \rightarrow BaSO_4 + 2\ Cl^-$$

B_1 – 5 cm^3 2 M solution $\Rightarrow$ 100 cm^3 0.1 M solution

B_2 – V cm^3 0.1000 N HCl + 0.1 N NaOH in the presence of phenolphthalein.

C – V cm^3 solution X + 10.0 cm^3 H_2SO_4 + H_2O is titrated at elevated temperature with $KMnO_4$.

D_1 – The solution which is to be analyzed is filled to the mark; *V* cm^3 of this solution is titrated with NaOH in the presence of methyl red. The quantity of oxalic acid (moles and g) is calculated.

D_2 – *V* cm^3 solution to be analyzed + 10.0 cm^3 6 N H_2SO_4 + H_2O are heated and titrated with $KMnO_4$ solution.

The total amount of oxalate is calculated (in mol).

The difference gives the amount of ammonium oxalate (moles and g).

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Determination of the relative molecular mass of a weak acid by acid-base titration in a non-aqueous solvent

Weak acid whose dissociation constants, K_a, are smaller than 1×10^{-7} can be satisfactorily titrated in ethanol or in a mixture of ethanol and benzene, using a standard ethanolic solution of potassium hydroxide or potassium alkoxide in the presence of phenolphthalein or thymolphthalein as an indicator.

Task:

Determine the molecular weight (chemical equivalent) of a weak monobasic acid by titration with potassium ethoxide in ethanolic solution using phenolphthalein as an indicator (the acid has the general formula $C_xH_yO_z$).

Chemicals and equipment:
Standard solution of potassium ethoxide in ethanol of concentration c = 0.1000 mol dm^{-3}
Indicator: 0.1% solution of phenolphthalein in ethanol
Solvent: A mixture of ethanol and benzene
1.000 g of sample, accurately weighed,
3 titration flasks of volume 200 or 500 cm^3, one 25 cm^3 burette, one 50 cm^3 pipette, one 250 cm^3 volumetric flask, one 100 cm^3 measuring cylinder, small funnels, beakers, filter paper.

Procedure:

You are provided with 1.000 g of the monobasic acid $C_xH_yO_z$. This sample is labelled with a number. This should be written clearly at the top of your answer paper.

Carefully transfer all the acid into the graduated (volumetric) flask and fill the solution in the flask with ethanol up to 250 ml. A portion of 50.00 ml of this solution should be titrated with the 0.1000 M alcoholic solution of potassium ethoxide using 5 drops of phenolphthalein as indicator. The first titration should be a rough titration for estimating the approximate volume necessary to determine the endpoint. Subsequent titrations should be carried out with precision, using the same quantity of indicator each time.

Record all titration values. An extra titration should be carried out to eliminate any error that might be due to the action of the potassium hydroxide on the solvent, indicator or ethanol. This type of titration is known as a blank titration, its value should be recorded and used to correct the results of previous titrations. Care should be taken to use the same quantity of indicator as in previous titrations.

The correct titration values should be used to calculate the relative molecular mass (molecular weight) of the sample.

Note: The waste material containing organic solvents must not be discharged in a sink. Use labelled containers for this purpose.

Questions:

1) Suggest the name and formula of a common, monobasic acid which corresponds to the value you determined experimentally for your sample.
2) Write a general equation for the neutralisation of a monocarboxylic acid with:
    i) potassium ethoxide,
    ii) potassium hydroxide.
3) During the titration of some weak carboxylic (fatty) acids, similar to the titration that you have carried out, turbidity or cloudiness is observed. Suggest an explanation for this turbidity.
4) How would you produce 1 dm^3 of a standard solution of 0.1 M potassium ethoxide? Which compound would you use, as a standard solution?
5) Why are the titrations of weak acids carried out in non-aqueous media?
6) Name another solvent which is suitable for use in the titration of weak acids.
7) How would you recover the organic solvent used in your experiment?
8) Sketch a schematic titration curve (pH as a function of volume) for the titration of 20 ml of a 0.1 M aqueous solution of a weak monobasic acid with a standard aqueous solution of 0.1 M potassium hydroxide.
9) Calculate the pH of 0.1 M aqueous solution of an acid which has a dissociation constant of 1×10^{-7}.

PROBLEM 2 (practical)

Analysis of the Nickel Salt:

For the analysis of the salt, only one sample solution is prepared. The determination of the components is achieved by titrating each time 25 ml of the sample solution in duplicate.

For the determination of the ammonia and chlorine content a back titration is carried out. For that purpose a certain amount of reagent is added in excess. The total amount of reagent, available for the sample, is determined by following the same procedure for 25 ml of a blank solution. This titration should not be carried out in duplicate.

Prepare the following solutions:

A) Sample solution:

Pipette 25.0 ml of 1.6 M nitric acid into a volumetric flask of 250 ml. Add a sample of about 1.2 g of the amminenickel(II) chloride and dilute with water to a volume of 250 ml.

B) Blank solution:

Pipette 25.0 ml of the same 1.6 M nitric acid and dilute it with water to a volume of 250 ml.

Note:

1) For the chlorine determination use conical (Erlenmeyer) flasks with a ground glass stopper.
2) The nitric acid contains a small amount of hydrochloric acid. The total acid content is 1.6 M.

a) *Determination of the ammonia content*

Titrate the solutions with a standard solution of NaOH (about 0.1 M). Indicator: methylred, 0.1 % solution in ethanol.

Calculate the percentage of ammonia in the salt.

b) *Determination of the nickel content*

Add about 100 ml of water, 2 ml of ammonia solution (25 %) and 5 drops of murexide solution to the nickel solution, which now should have a yellow colour. Titrate the solution with a standard solution of EDTA (about 0.025 M) until a sharp colour change from yellow to violet is observed. Calculate the percentage of nickel in the salt.

c) *Determination of the chlorine content*

Execute the titration as quickly as possible after the addition of the reagent!

Add to each solution 25 ml of 0.1 M silver nitrate solution. Add about 5 ml of toluene, shake vigorously, add indicator and titrate with the standard solution of ammonium thiocyanate (-rhodanide, about 0.05 M) until a permanent colour change to red is observed. At the end of the titration, shake vigorously again. The red coloration should persist.

Indicator: 1 ml of a saturated solution of iron(III) sulphate.

Calculate the percentage of chlorine in the salt.

Data: Relative atomic masses: H = 1, Cl = 35.5, Ni = 58.7, N = 14.

Questions:

Calculate from the results obtained the molar ratio of the components to two decimal points and enter this on the report form in the format: Ni : Cl : NH_3 = 1.00 : x : y.

PROBLEM 2 (Practical)

Analysis

Determination of Mass of a given Sample of 2-Ethanoyl-oxybenzoic Acid (Acetylsalicylic Acid, or Aspirin) by Volumetric Back Titration after Hydrolysis with Excess of Sodium Hydroxide.

Reagents

Aqueous solution of sodium hydroxide (about 0.5 mol dm^{-3})
Standard aqueous solution of hydrochloric acid (0.4975 mol dm^{-3})
Ethanolic phenolphthalein solution (indicator dropping bottle II)
Deionised/distilled water

Part 1:

Determine accurately the concentration of the about 0.5 mol dm^{-3} sodium hydroxide solution using the standard hydrochloric acid solution. (Record the answer as mol dm^{-3} with four places after decimal point.)

Procedure:

Pipette 20.00 cm^3 of the sodium hydroxide solution into a 300 cm^3 Erlenmeyer flask and dilute it to about 100 cm^3 with deionized water. Titrate the obtained solution with the standard 0.4975 mol dm^{-3} hydrochloric acid solution using the phenolphthalein indicator. Repeat the procedure to produce three acceptable values and calculate the mean volume.

Part 2:

Determine accurately the mass of aspirin in Erlenmeyer flask I. Record your answer in g with three places after the decimal point.

Procedure:

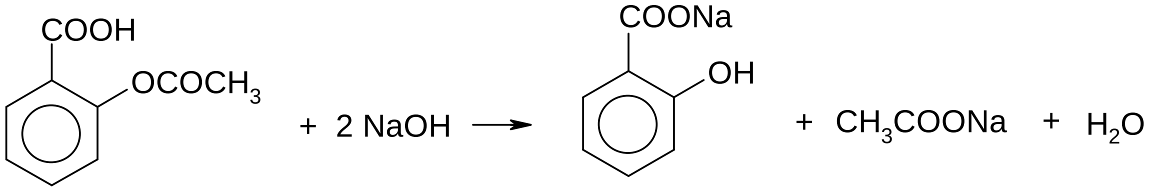
Pipette 50.00 cm^3 of your standardized sodium hydroxide solution into the Erlenmeyer flask I (with a ground glass joint) which contains your unknown mass of aspirin. Add 3 – 5 boiling stones to the flask and boil the reaction mixture for 15 minutes using a reflux condenser and the electrical hot plate. After cooling, remove the reflux condenser and rinse it with a small quantity of deionised water into Erlenmeyer flask I. Pour the whole solution into a 100.0 cm^3 volumetric flask and fill it exactly to the mark with deionised water. Pipette 20.00 cm^3 of this solution into a 300 cm^3 Erlenmeyer flask and dilute to about 100 cm^3 with deionised water. Back titrate the residual sodium hydroxide with the standard hydrochloric acid solution (0.4975 mol dm^{-3}) using a 10 cm^3 burette and phenolphthalein indicator. Repeat the volumetric procedure to produce three acceptable values and calculate the mean volume.

Questions:

1) Write the balanced chemical equation for the ester hydrolysis of aspirin by sodium hydroxide using structural formulae. Note that 1000 cm^3 aqueous solution of 0.5000 mol dm^{-3} sodium hydroxide is equivalent to 0.0450 g of aspirin.
2) Calculate the mass of aspirin that you were given.

SOLUTION

1.

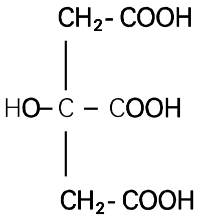


PROBLEM 2 (Practical)

Analysis

Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) is widely distributed in plants and in animal tissues. Lemon juice contains from 5 to 8% of this acid. It is produced by mycological fermentation on an industrial scale using crude sugar solutions, such as molasses, and stains of *Aspergillus niger*.

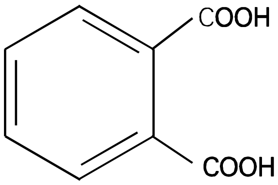
It is utilized as an acidulant and antioxidant in several beverages.



$$\begin{array}{c} CH_2-COOH \\ | \\ HO-C-COOH \\ | \\ CH_2-COOH \end{array}$$

MM = 192.12 g/mol

$pK_1 = 3.06$; $pK_2 = 4.74$; $pK_3 = 5.40$



MM = 204.23 g/mol

a) Standardization of NaOH solution (ca 0.1 mol dm^{-3}) by potassium hydrogen phthalate

Procedure:

A preweighed quantity (2.050 g) of potassium hydrogen phthalate is in the 100 cm^3 volumetric flask B. Dilute this sample with water to the mark. Phenolphthalein indicator (2 - 3 drops) is added to an aliquot of 25.0 cm^3 of the resulting solution and the solution is then titrated with the NaOH solution that has to be standardized.

Give the concentration of the NaOH solution.

b) Titrimetric determination of citric acid

Procedure:

The unknown sample of citric acid is in the 100 cm^3 volumetric flask C. Dilute the sample with water to the mark. Transfer 25.0 cm^3 of the resulting solution into a 250 cm^3 Erlenmeyer flask and dilute with water. Add 2 – 3 drops of phenolphthalein indicator and titrate with the previously standardized NaOH solution.

Give the mass of citric acid.

SOLUTION

Marks were given accordingly to determined mass of citric acid.

Some additional points were given for correct calculations.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Determination of Fatty Acids

A mixture of an unsaturated monoprotic fatty acid and an ethyl ester of a saturated monoprotic fatty acid has been dissolved in ethanol (2.00 cm^3 of this solution contain a total of 1.00 g acid plus ester). By titration the acid number$^{1)}$, the saponification number$^{2)}$ and the iodine number$^{3)}$ of the mixture shall be determined. The acid number and the saponification number shall be used to calculate the number of moles of free fatty acid and ester present in 1.00 g of the sample. The iodine number shall be used to calculate the number of double bonds in the unsaturated fatty acid.

Note: The candidate must be able to carry out the whole exam by using the delivered amount of unknown sample (12 cm^3). There will be no supplementation.

1) Acid number: The mass of KOH in milligram that is required to neutralize *one* gram of the acid plus ester.
2) Saponification number: The mass of KOH in milligram that is required to saponify *one* gram of the acid plus ester.
3) Iodine number: The mass of iodine (I) in g that is consumed by 100 g of acid plus ester.

Relative atomic masses:

A_r(I) = 126.90 A_r(O) = 16.00

A_r(K) = 39.10 A_r(H) = 1.01

1) Determination of the Acid Number

Reagents and Apparatus

Unknown sample, 0.1000 M KOH, indicator (phenolphthalein), ethanol/ether (1 : 1 mixture), burette (50 cm^3), Erlenmeyer flasks (3 x 250 cm^3), measuring cylinder (100 cm^3), graduated pipette (2 cm^3), funnel.

Procedure:

Pipette out aliquots (2.00 cm^3) from the unknown mixture into Erlenmeyer flasks (250 cm^3). Add first ca. 100 cm^3 of an ethanol/ether mixture (1:1) and then add the indicator (5 drops). Titrate the solutions with 0.1000 M KOH.

Calculate the acid number.

2) Determination of the Saponification Number

Reagents and Apparatus

Unknown sample, 0.5000 M KOH in ethanol, 0.1000 M HCl, indicator (phenolphthalein), volumetric flask (50 cm^3), round bottom flask (250 cm^3), Liebig condenser, burette (50 cm^3), Erlenmeyer flasks (3 x 250 cm^3), volumetric pipette (25 cm^3), volumetric pipette (10 cm^3), graduated pipette (2 cm^3), funnel, glass rod. The round bottom flask and Liebig condenser are to be found in the fume hoods.

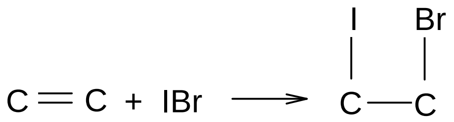
Procedure

Pipette out a 2.00 cm^3 aliquot of the unknown sample into a round bottom flask (250 cm^3) and add 25.0 cm^3 0.5000 M KOH/EtOH. Reflux the mixture with a heating mantle for 30 min in the fume hood (start the heating with the mantle set to 10, then turn it down to 5 after 7 min.). Bring the flask back to the bench and cool it under tap water. Transfer quantitatively the solution to a 50 cm^3 volumetric flask and dilute to the mark with a 1:1 mixture of ethanol/water. Take out aliquots of 10 cm^3 and titrate with 0.1000 M HCl using phenolphthalein as indicator (5 drops).

Calculate the saponification number.

3) Determination of the Iodine Number

In this experiment iodobromine adds to the double bond.



$$C{=}C + IBr \longrightarrow \overset{I}{C}-\overset{Br}{C}$$

The Hanus solution (IBr in acetic acid) is added in excess. After the reaction is complete, excess iodobromine is reacted with iodide forming I_2, ($IBr + I^- \rightarrow I_2 + Br^-$) which in turn is determined by standard thiosulphate solution.

Warning: Be careful when handling the iodobromine solution. Treat any spill immediately with thiosulphate solution.

Reagents and Apparatus

Unknown sample, 0.2000 M Hanus solution, dichloro-methane, 15 % KI solution in distilled water, distilled water, 0.2000 M sodium thiosulphate, starch indicator, Erlenmeyer flasks (3 x 500 cm^3), buret (50 cm^3), graduated pipette (2 cm^3), measuring cylinders (10 and 100 cm^3), volumetric pipette (25 cm^3), aluminium foil.

Procedure

Pipette out aliquots (1.00 cm^3) of the unknown mixture into Erlenmeyer flasks (500 cm^3) and add 10 cm^3 of dichloromethane. With a pipette add 25.0 cm^3 Hanus solution, cover the opening with aluminium foil and place your labelled flasks in the dark in the cupboard (under the fume hood) for 30 min. with occasionally shaking. Add 10 cm^3 of the 15 % KI solution, shake thoroughly and add 100 cm^3 of dist. water. Titrate the solution with 0.2000 M sodium thiosulphate until the solution turns pale yellow. Add starch indicator (3 cm^3) and continue titration until the blue colour entirely disappears.

Calculate the iodine number.

4) Use the results from 1) 2) and 3) to:

i) Calculate the amount of ester (in mol) in 1 g of the acid plus ester.

ii) Calculate the number of double bonds in the unsaturated acid.

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} × 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} × (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} × 0.100 dm^3 = 1.351×10^{-3} mol

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

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

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

$n(H^+)$ = 1.351×10^{-3} mol – 1.250×10^{-4} mol = 1.226×10^{-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) × 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 %

PROBLEM 2 (Practical)

Reverse-phase Chromatography:

Acid-Base Titration of Acetic Acid and Salicylic Acid

Acetic acid (AA) and salicylic acid (SA) are slightly different in polarity and thus can be separated on a reverse-phase cartridge using distilled water as eluent. AA is eluted first. The total amount of AA and SA in a mixed solution will be determined by titration. Then, AA and SA will be separately determined following chromatographic separation.

2-1. Determination of the Total Amount of AA and SA in a Mixed Acid (MA) Solution

a) Titrate 10 cm^3 of distilled water with the NaOH (< 5 mM) solution provided. Report blank acidity in 1 cm^3 of distilled water in terms of the volume of the NaOH solution. Take this blank acidity into account for all solutions in subsequent data analyses. Show corrections in the calculation part in the answer sheet.

b) Standardize NaOH solution with 2.00 cm^3 of the standard KHP (potassium hydrogen phthalate) solution (1.00 x 10^{-2} M) provided. Repeat and report the concentration of the NaOH solution. Show how you accounted for the blank acidity.

c) Withdraw 1.00 cm^3 of Solution MA and determine the total acidity. Repeat and report the total number of moles of AA and SA combined in 1.00 cm^3 of Solution MA.

2-2. Reverse-phase Separation and Titration

a) Elute a new C-18 cartridge with about 10 cm^3 of distilled water using 10 cm^3 syringe.

b) Load 1.00 cm^3 of Solution MA onto the cartridge. Collect the liquid eluting at the outlet in tube 1 (Fraction 1).

c) Elute with 1 cm^3 of distilled water. Collect the eluent in a test tube (Fraction 2). Repeat until Fraction 20 is collected. You will have 20 test tubes with about 1 cm^3 liquid in each tube.

d) Titrate acidity in each test tube. Report volume of the NaOH solution consumed and the amount of acid(s) in each test tube. Make a graph in the answer sheet (Fig. 2-2) showing the amount of acid(s) in each test tube.

e) Blank acidity and the background (due to leaching out of residual materials from the column) must be subtracted. In determining the amount of eluted AA, disregard tubes containing only trace amounts of acids. Tube 2 and 3 contain most AA. Calculate the total amount of AA eluted by adding the amount of AA in tubes. Similarly calculate the total amount of SA eluted. Indicate, in Fig. 2-2, which fractions you used to get the amount of each acid.

f) Calculate the mole percent of AA in solution MA.

PROBLEM 2 (Practical)

Determination of Carbonate and Hydrogen Phosphate in an Abrasive Sample

Na_2CO_3, $CaCO_3$ and Na_2HPO_4 are the main constituents of abrasive powders. In this task you will have to determine carbonate and hydrogen phosphate ions in an abrasive sample by two acid-base titrations.

First, the exactly known amount of hydrochloric acid (taken in an excess) is added to the sample. As a result, hydrogen phosphates are transformed into H_3PO_4, whereas carbonates into CO_2 which is further removed by boiling. Calcium ions initially present in the sample pass into the solution. Because of possible interference in subsequent analysis, they are precipitated as CaC_2O_4 and filtered off prior to the titration.

Next, the phosphoric acid formed is subjected to two titrations with pre-standardized NaOH solution and two different indicators: Bromocresol Green (BCG) and Thymolphthalein (TP). First, H_3PO_4 (and excess of HCl) is titrated to $H_2PO_4^-$ ion, the endpoint lying in slightly acidic medium (*pH* of ~4.5). It corresponds to the colour change of BCG from yellow to blue. The second titration proceeds till HPO_4^{2-} is formed. The endpoint of the second titration corresponds to the color change of TP from colourless to blue (moderately alkaline medium, *pH* of ~10).

The content of CO_3^{2-} ions in the sample is calculated by finding the difference between:

a) the amount of the titrant equivalent to the initial amount of HCl (taken for the sample dissolution) and

b) the amount of the titrant corresponding to the second endpoint (TP).

The content of HPO_4^{2-} is calculated by finding the difference between the amounts of the titrant consumed to achieve two endpoints (TP and BCG).

Procedure

Step 1. Dissolution of the sample and removal of CO_2

To the sample of the abrasive powder in a beaker covered with watch glass add 10.00 cm^3 (exactly, with a pipette! Carefully, not removing the glass and avoiding losses because of splashing!) of ca. 1 mol dm^{-3} HCl (see the exact concentration of the acid on the label). After the most intensive stage of gas evolution is completed, heat carefully the solution in the beaker (covered with watch glass) on a heating plate until the gas evolution stops. Then bring the solution to boiling and boil it carefully for 2 – 3 min.

Step 2. Precipitation of calcium

Remove the beaker from the plate; wash the steam condensate from the watch glass down to the beaker with distilled water. Add 1 – 2 cm^3 of 15 % $K_2C_2O_4$ solution with measuring cylinder. Put the beaker aside until the most part of the precipitate is formed (usually takes 10 to 20 min). Spend this time for standardization of the titrant solution of NaOH (see the procedure hereunder).

Step 3. Standardization of NaOH solution

Place with a pipette 10.00 cm^3 of HCl solution into a 100 cm^3 volumetric flask, make up to the mark with distilled water and mix. Fill the burette with NaOH solution. Transfer with a pipette 10.00 cm^3 of the diluted HCl solution from the volumetric flask to an Erlenmeyer flask. Add 1 – 2 drops of Thymolphthalein solution and titrate with NaOH solution until blue coloration stable on swirling for 5 – 10 s appears.

Here and after. Repeat the titrations as necessary. It is desirable that the highest and the lowest titrant volume values differ not more than by 0.10 cm^3. Report all the final volume values with 0.01 cm^3 accuracy.

2.1 a Complete the table in the Answer Sheet.

2.1 b Calculate the concentration of NaOH solution (in mol dm^{-3}).

Step 4. Filtering off calcium oxalate

After the most part of CaC_2O_4 precipitates filter the precipitate off collecting the filtrate into a 100 cm^3 volumetric flask. Slight turbidity in the filtrate is admissible, since small amounts of calcium oxalate do not interfere in the titration. Wash the filter with distilled water; make up the solution in the flask to the mark with distilled water and mix. Put the used filter into the waste basket.

Step 5. Sample titration against Bromocresol Green

Transfer with a pipette a 10.00 cm^3 aliquot of the sample solution coming from the step 4 from the volumetric flask to an Erlenmeyer one, and add 3 drops of BCG solution. Prepare in another Erlenmeyer flask a reference solution by adding 3 drops of 15 % NaH_2PO_4 solution and 3 drops of BCG solution to 15 – 20 cm^3 of distilled water. Titrate the sample solution with NaOH solution until the colour coincides with that of the reference solution.

2.2 Complete the table in the Answer Sheet.

Step 6. Sample titration against thymolphthalein

Transfer with a pipette a 10.00 cm^3 aliquot of the sample solution coming from the step 4 from the volumetric flask to an Erlenmeyer one. Add 2 drops of TP solution and titrate with NaOH solution until blue coloration stable on mixing for 5 – 10 s appears.

2.3 Complete the table in the Answer Sheet.

Step 7. Calculations

2.4 Calculate the mass of CO_3^{2-} in the sample.

2.5 Calculate the mass of HPO_4^{2-} in the sample.

Step 8. Additional questions to the problem

Answer the additional questions in the Answer Sheets.

2.6a Indicate one reaction (write down the equation) for a process interfering in the sample analysis you have carried out in the presence of Ca^{2+}.

2.6b A list of mistakes possible at different steps is given in the table in the answer sheet. Indicate which of the mistakes can lead to errors in CO_3^{2-} and/or HPO_4^{2-} content determination. Use the following symbols: “0” if no error is expected, “+”or “–“ if the result is higher (positive error) or lower (negative error) than the true one.

SOLUTION

2.1 a, 2.2, 2.3

The values of the final volumes $V_{1,f}$, $V_{2,f}$, and $V_{3,f}$, (as reported in the Answer Sheet) were graded according to a scheme approved by the International Jury.

The values of $\Delta V_{\text{expected}}$ and $\Delta V_{\text{acceptable}}$ (in cm^3) are listed in the table below.

	ΔV, cm^3	
	expected	acceptable
$V_{1,f}$	**0.10**	**0.25**
$V_{2,f}$	**0.15**	**0.40**
$V_{3,f}$	**0.15**	**0.40**

2.1 b Calculation of NaOH concentration

$$c(\text{NaOH}) = \frac{c(\text{HCl})\times V(\text{HCl})\times V(\text{aliquot})}{V(\text{flask})\times V(\text{NaOH})} = \frac{1.214\ \text{mol dm}^{-3}\times 10.00\ \text{cm}^3\times 10.00\ \text{cm}^3}{100.0\ \text{cm}^3\times V_{1,\text{f}}\text{cm}^3}$$

2.4 Calculation of the mass of CO_3^{2-}

$$\text{m}(CO_3^{2-}) = M(CO_3^{2-})\times 1/2\times\frac{c(\text{NaOH})\times(V_{1,f}-V_{3,f})\times V(\text{flask})}{V(\text{aliquot})} =$$

$$= 60.01\ \text{g mol}^{-1}\times 1/2\times\frac{c(\text{NaOH})\ \text{mol dm}^{-3}\times(V_{1,f}-V_{3,f})\ \text{cm}^3\times 100.0\ \text{cm}^3}{10.00\ \text{cm}^3}\times 0.001\ \text{dm}^3/\text{cm}^3 =$$

2.5 Calculation of the mass of HPO_4^{2-}

$$m(HPO_4^{2-}) = M(HPO_4^{2-})\times\frac{c(\text{NaOH})\times(V_{3,f}-V_{2,f})\times V(\text{flask})}{V(\text{aliquot})} =$$

$$= 95.98\ \text{g mol}^{-1}\times\frac{c(\text{NaOH})\ \text{mol dm}^{-3}\times(V_{3,\text{f}}\text{-}V_{2,\text{f}})\ \text{cm}^3\times 100.0\ \text{cm}^3}{10.00\ \text{cm}^3}\times 0.001\ \text{dm}^3/\text{cm}^3 =$$

2.6 a

$Ca^{2+} + H_2PO_4^- \rightarrow CaHPO_4 + H^+$

or

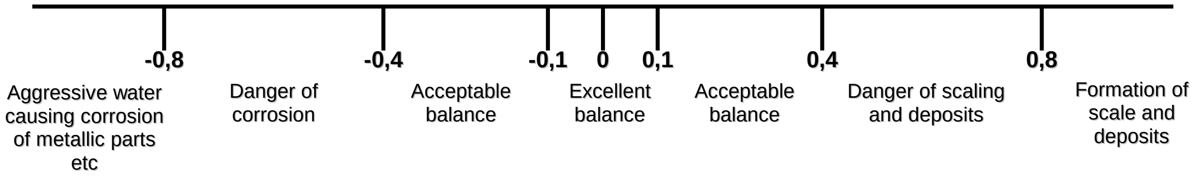
$3\ Ca^{2+} + 2\ HPO_4^{2-} \rightarrow Ca_3(PO_4)_2 + 2\ H^+$

PROBLEM 2 (Practical)

Determination of the Langelier Saturation Index of a pool water

The Langelier Saturation Index (LI) is a measure of swimming pool water corrosivity as well as its ability to dissolve or deposit calcium carbonate. If LI is approximately zero, the water is considered “balanced”. If the index LI is a positive number, the water tends to deposit calcium carbonate and is scale-forming. If the index LI is a negative number, the water is corrosive and dissolves calcium carbonate. The LI is a combination of the physical values factors taken from Table 1 and can be calculated by the formula:

$$\text{LI} = \text{pH} + \text{FT} + \text{FD} + \text{FA} - \text{FTDS}$$



pH : pH value
FT : Temperature factor
FD : Calcium hardness (CH) factor
FA : Total alkalinity (TA) factor
FTDS: Total dissolved solids (TDS) factor

Table 2.1 Values and corresponding factors

Temperature, °C	FT	Calcium hardness (CH), mg dm^{-3} $CaCO_3$	FD	Total alkalinity (TA), mg dm^{3} $CaCO_3$	FA	Total dissolved solids (TDS), mg dm^{-3} NaCl	FTDS
0	0.0	5	0.3	5	0.7	0	12.0
3	0.1	25	1.0	25	1.4	-	-
8	0.2	50	1.3	50	1.7	1000	12.1
12	0.3	75	1.5	75	1.9	-	-
16	0.4	100	1.6	100	2.0	2000	12.2
19	0.5	150	1.8	125	2.1	-	-
24	0.6	200	1.9	150	2.2	3000	12.25
29	0.7	250	2.0	200	2.3	-	-

Table 2.1 continued

34	0.8	300	2.1	300	2.5	4000	12.3
41	0.9	400	2.2	400	2.6	-	-
53	1.0	600	2.35	800	2.9	5000	12.35
-	-	800	2.5	1000	3.0	-	-
-	-	1000	2.6	-	-	6000	12.4

In this task you will have to determine the LI value of a given water sample. Note that hardness is expressed as the equivalent to the concentration of $CaCO_3$ (expressed in mg dm^{-3}). Total alkalinity, being the acid equivalent to the total amount of carbonate and hydrogen carbonate, can also be expressed in mg dm^{-3} of $CaCO_3$, whereas TDS is recalculated as concentration of NaCl (mg dm^3).

Chemicals

- EDTA, standard aqueous solution, c = 0.0443 mol $dm^{–3}$,
- HCl, standard aqueous solution, c = 0.0535 mol $dm^{–3}$,
- Methyl orange, 0.1% in water,
- Murexide, indicator, solid mixture with NaCl (1 : 250 by mass),
- Sample of water.

Procedures

Calcium hardness is determined by complexometric titration with EDTA (Na_2H_2Y). This is performed in a strongly alkaline medium to mask magnesium (large amounts of Mg^{2+} interfere due to the co-precipitation of calcium with $Mg(OH)_2$; moreover, the complexometric indicator is also adsorbed on $Mg(OH)_2$, which impairs the observation of its colour change). When the alkali is added, titration should be carried out immediately to avoid the deposition of $CaCO_3$.

2.1 Write down equation of the reaction occurring during titration with Na_2H_2Y.

Procedure for determination of calcium

a) Put the standard solution of EDTA (precise exact concentration c = 0.0443 mol $dm^{–3}$) in the burette.

b) Pipette a 20 cm^3 aliquot of the water sample into an Erlenmeyer flask.

c) Add 3 cm^3 of NaOH solution (c = 2 mol $dm^{–3}$) with the 10 cm^3 measuring cylinder.

d) Add murexide indicator with spatula to obtain noticeably pink solution.

e) Within few minutes titrate the mixture with EDTA solution until the indicator colour changes from pink to purple.

2.2 Fill in the table 2.2.

Table 2.2

Volume of EDTA solution	Titration No			
Initial reading of the burette, cm^3				
Final reading of the burette, cm^3				
Consumed volume, cm^3				

Accepted volume, cm^3:

2.3 Calculate the hardness of the water sample in mg dm^{-3} of $CaCO_3$. Write down the result in Table 2.4 (see question 2.11).

Measurement of pH

Locate a pH meter in the lab (or ask your lab assistant).

a) Place about 70 -- 90 cm^3 of the water sample into a clean Erlenmeyer flask.

b) Remove the protective cap from the pH-meter (keep the cap standing, since there is solution in it).

c) Rinse the electrode with distilled water using a plastic wash bottle.

d) Turn the pH meter on by sliding the ON/OFF switch.

e) Immerse the electrode in the solution to be tested and stir gently by swirling the flask.

f) Place the flask on the table and wait until the reading stabilizes (not more than 1 min).

g) Read and record the pH value.

h) Switch the pH meter off, rinse the electrode with distilled water and place the protective cap back.

2.4 Write down the pH value in Table 2.4 (see question 2.11).

2.5 Which form of carbonic acid predominates in your water sample?

Confirm your choice with calculation and tick one box.

☐ Carbonate ☐ Hydrogen carbonate ☐ Carbonic acid

Note: The dissociation constants of carbonic acid are as follows:
$K_1 = 4.5 \cdot 10^{-7}$;
$K_2 = 4.8 \cdot 10^{-11}$.

2.6 Write down the ionic equation of the predominant reaction of titration of the water sample with HCl solution.

Determination of the total alkalinity

To obtain the value of the total alkalinity the water sample should be titrated to H_2CO_3. An acid-base indicator used is methyl orange, which starts changing its colour from yellow to orange at pH of about 4.5.

a) Rinse the burette with distilled water and fill it with the standard HCl solution (exact concentration of HCl is 0.0535 mol dm^{-3}).

b) Pipette a 50.0 cm^3 aliquot of water sample into an Erlenmeyer flask and add 3 drops of methyl orange solution.

c) If the sample is orange prior to addition of the acid the total alkalinity is zero. If the solution is yellow titrate it with the standard acid solution until the first noticeable colour change towards orange is observed. Record the volume of the titrant used.

2.7 Fill in the Table 2.3.

Table 2.3

Volume of the standard HCl solution	Titration No			
Initial reading of the burette, cm^3				
Final reading of the burette, cm^3				
Consumed volume, cm^3				
Accepted volume, cm^3 ______				

2.8 Calculate the total alkalinity (in mg dm^{-3} $CaCO_3$). Write down the result in Table 2.4 (see question 2.11).

2.9 Temperature measurement

Read the thermometer located at the table of common use and write down the value into Table 2.4 (see question 2.11).

2.10 TDS determination in the water sample with the test strip.

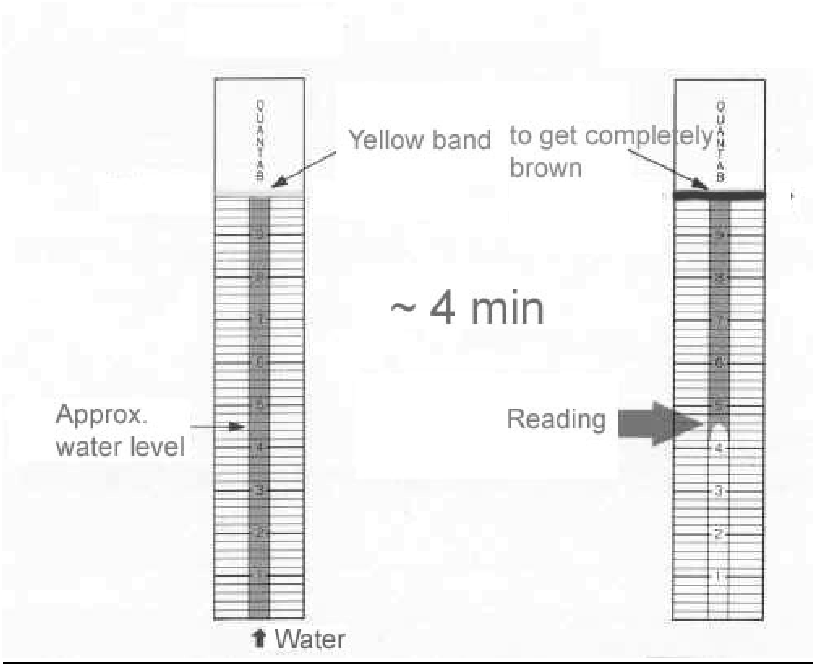
a) Fill a beaker with the water sample to a level of about 3 cm of height. Immerse the strip into water; be sure that the yellow band on the top of the strip does not touch the liquid.

b) Wait for 3 - 4 minutes until the yellow band turns completely brown. Take the reading as shown in the picture hereunder. Give it to one decimal digit.

c) Report the reading.

d) Find your TDS concentration as that of NaCl in mg dm^{-3} in the table to the right of the picture.

e) Write down the concentration of NaCl in Table 2.4 (see question 2.11).



Reading	NaCl conc., mg dm^{-3}
1.4	360
1.6	370
1.8	420
2.0	430
2.2	470
2.4	530
2.6	590
2.8	660
3.0	730
3.2	800
3.4	880
3.6	960
3.8	1050
4.0	1140
4.2	1240
4.4	1340
4.6	1450
4.8	1570
5.0	1700

2.11 Fill in all the blank boxes in the Table 2.4. Calculate LI and write down the result in Table 2.4. Take the values of the factors to the accuracy of two decimal digits.

Table 2.4. Calculation of LI of the water sample

Water sample Number ______					
CH, mg dm^{-3} $CaCO_3$	TA, mg dm^{-3} $CaCO_3$	*t*, °C	pH	TDS, mg dm^{-3} NaCl	**LI**
FD	FA	FT		FTDS	

Theoretical questions. Water balance correction.

If LI significantly deviates from zero, it is needed to be adjusted to zero.

Imagine you are given a sample of pool water analyzed as you have done above. The results of the analysis are as follows: CH = 550 mg dm^{-3}, FD = 2.31, TA = 180 mg dm^{-3}, FA = 2.26, t = 24 °C, FT = 0.6; TDS = 1000 mg dm^{-3}, FTDS = 12.1, pH = 7.9, LI = 0.97. The pool serviceman added 10 cm^3 of 0.0100 mol dm^{-3} solutions of reagents ($NaHCO_3$, NaOH, $NaHSO_4$, $CaCl_2$, EDTA (disodium salt dihydrate) and HCl) to 200 cm^3 of different pool water samples (one reagent for one sample).

2.12 Decide whether $CaSO_4$ is deposited upon addition of $NaHSO_4$.

Yes ☐ No ☐

Tick one box and confirm your choice with calculation.

Note: $CaSO_4$ solubility product is $5 \cdot 10^{-5}$. Assume that no precipitate of $CaCO_3$ is formed upon addition of any of the above reagents.

2.13 Fill in the hereunder table 2.5 by showing the trends of changes resulting from addition of each reagent to this particular water sample (use "+" if the factor increases, "–" if it decreases, and "0" if it does not change).

Table 2.5

Reagent	pH	FA	FD	FTDS	LI
$NaHCO_3$					
NaOH					
$NaHSO_4$					
$CaCl_2$					
Na_2H_2Y					
HCl					

SOLUTION

2.1 $H_2Y^{2-} + Ca^{2+} = CaY^{2-} + 2\ H^+$

Reactions with other forms of EDTA are also acceptable.

2.5 We observe pH ~8 ⇒ this is carbonic acid - hydrogen carbonate buffer, then:

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{K_1}{[H^+]} = 45$$

i.e. ~ 98 % of hydrogen carbonate

☐ Carbonate ☑ Hydrogen carbonate ☐ Carbonic acid

2.6 $HCO_3^- + H^+ = H_2CO_3$ (or $H_2O + CO_2$)

2.12 $[Ca^{2+}] = \frac{V_{EDTA} \times c_{EDTA}}{20}\ \frac{200}{200+10} = \frac{2.2 \times 0.05}{\frac{20 \times 200}{210}} = 0.00524\ \text{mol dm}^{-3}$

When $NaHSO_4$ is added, $[SO_4^{2-}] = \frac{0.01 \times 10}{(200+10)} = 0.000476\ \text{mol dm}^{-3}$

Then $[Ca^{2+}]\ [SO_4^{2-}] = 0.00524 \times 0.000476 = 2.5 \cdot 10^{-6} < K_{sp}$

⇒ no precipitate of $CaSO_4$ is formed.

Your answer (tick one) Yes ☐ No ☑

2.13

Reagent	pH	FA	FD	FTDS	LI
$NaHCO_3$	+	+	0	+	+
NaOH	+	+	0	+	+
$NaHSO_4$	–	–	0	+	–
$CaCl_2$	0	0	+	+	+
Na_2H_2Y	–	–	–	+	–
HCl	–	–	0	0	–

Titolazione complessometrica

Titolazione complessometrica

IChO

International Chemistry Olympiad

PROBLEM 3 (practical)

Determination of the solubility product of lead(II) chloride

Shake solid lead(II) chloride:

a) with water,

b) with three solutions of sodium chloride of different concentrations,

until equilibrium is attained. Then determine the lead ion concentration by titration with EDTA. Calculate the solubility product of lead(II) chloride.

Equipment and chemicals

Volumetric flask (100 cm^3), pipettes (20 cm^3 and 10 cm^3), graduated cylinder (100 cm^3 and 25 cm^3), 4 Erlenmeyer flasks (200 – 250 cm^3) with stoppers, spatula, 4 filter funnels, filter papers, thermometer, 4 Erlenmeyer flasks (100 cm^3), titrating flasks (200 – 250 cm^3), beakers, stand with burette (50 cm^3), burette funnel, wash bottle with distilled water, glass rod.

Standard solutions of sodium chloride (0.1000 mol dm^{-3}) and EDTA (0.01000 mol dm^{-3}), solid lead(II) chloride, xylenol orange solution in a dropping bottle (0.5 % in water), solid hexamine (urotropine), nitric acid (2.5 mol dm^{-3}) in a dropping bottle.

Procedure

1. Prepare 100 cm^3 of sodium chloride solutions with concentrations of 0.0600 mol dm^{-3}, 0.0400 mol dm^{-3}, and 0.0200 mol dm^{-3}, respectively. Place the solutions in Erlenmeyer flasks with stoppers. Place 100 cm^3 of water in the fourth flask with a stopper. Add 5 spatulas of solid lead(II) chloride (about 2 g) to each, stopper the flasks and shake vigorously. Let the flasks stand for 30 minutes. Shake them occasionally. Prepare for filtration and titration in the meanwhile.
2. Measure the temperatures of the lead(II) chloride solutions and report them in the table of results. Filter the solutions through dry filters into small, dry Erlenmeyer flasks.
3. Using a pipette, transfer 10.00 cm^3 of the filtrate into a titration flask. Dilute with approximately 25 cm^3 of water, add 3 drops of xylenol orange (indicator) and 5 drops of nitric acid. Then add 5 spatulas (about 0.5 g) of solid hexamine (a weak base) and swirl gently until the solution is clear. Titrate with EDTA.

4. Calculate the concentration of lead ions and that of chloride ions in the solutions and give the solubility product K_s. Report the results in the table.
5. Answer the questions in the answer sheet.

Questions

3.1 Give the structure of EDTA. Mark those atoms which can coordinate to a metal ion with an asterisk (*).

3.2 Give the equation for the filtration reaction. EDTA may be written as H_2X^{2-}.

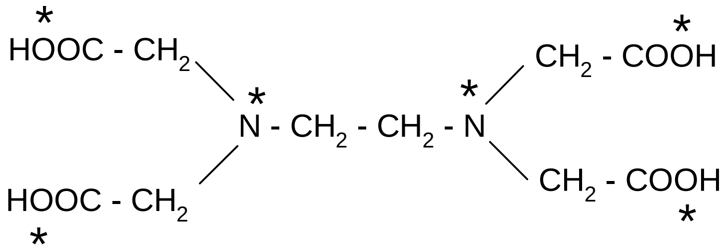
SOLUTION

A typical result:

c(NaCl) (mol dm^{-3})	Temperature (°C)	Volume EDTA solution (cm^3)	[Pb^{2+}] (mol dm^{-3})	[Cl$^-$] (mol dm^{-3})	K_s
0.0600	21	18.7	0.0187	0.0974	1.77×10^{-4}
0.0400	21	22.7	0.0227	0.0854	1.66×10^{-4}
0.0200	21	27.8	0.0278	0.0756	1.59×10^{-4}
-	21	34.2	0.0342	0.0684	1.60×10^{-4}

Answers to the questions:

3.1



3.2 $H_2Y^{2-} + Pb^{2+} \rightarrow PbY^{2-} + 2\,H^+$

PROBLEM 2 (practical)

Analysis of the Nickel Salt:

For the analysis of the salt, only one sample solution is prepared. The determination of the components is achieved by titrating each time 25 ml of the sample solution in duplicate.

For the determination of the ammonia and chlorine content a back titration is carried out. For that purpose a certain amount of reagent is added in excess. The total amount of reagent, available for the sample, is determined by following the same procedure for 25 ml of a blank solution. This titration should not be carried out in duplicate.

Prepare the following solutions:

A) Sample solution:

Pipette 25.0 ml of 1.6 M nitric acid into a volumetric flask of 250 ml. Add a sample of about 1.2 g of the amminenickel(II) chloride and dilute with water to a volume of 250 ml.

B) Blank solution:

Pipette 25.0 ml of the same 1.6 M nitric acid and dilute it with water to a volume of 250 ml.

Note:

1) For the chlorine determination use conical (Erlenmeyer) flasks with a ground glass stopper.
2) The nitric acid contains a small amount of hydrochloric acid. The total acid content is 1.6 M.

a) *Determination of the ammonia content*

Titrate the solutions with a standard solution of NaOH (about 0.1 M). Indicator: methylred, 0.1 % solution in ethanol.

Calculate the percentage of ammonia in the salt.

b) *Determination of the nickel content*

Add about 100 ml of water, 2 ml of ammonia solution (25 %) and 5 drops of murexide solution to the nickel solution, which now should have a yellow colour. Titrate the solution with a standard solution of EDTA (about 0.025 M) until a sharp colour change from yellow to violet is observed. Calculate the percentage of nickel in the salt.

c) *Determination of the chlorine content*

Execute the titration as quickly as possible after the addition of the reagent!

Add to each solution 25 ml of 0.1 M silver nitrate solution. Add about 5 ml of toluene, shake vigorously, add indicator and titrate with the standard solution of ammonium thiocyanate (-rhodanide, about 0.05 M) until a permanent colour change to red is observed. At the end of the titration, shake vigorously again. The red coloration should persist.

Indicator: 1 ml of a saturated solution of iron(III) sulphate.

Calculate the percentage of chlorine in the salt.

Data: Relative atomic masses: H = 1, Cl = 35.5, Ni = 58.7, N = 14.

Questions:

Calculate from the results obtained the molar ratio of the components to two decimal points and enter this on the report form in the format: Ni : Cl : NH_3 = 1.00 : x : y.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Effects of CO_2 on Solubility

Calcium carbonate is a partially soluble material commonly known as limestone, marble, chalk, or calcite. In the presence of CO_2-rich groundwater, calcium carbonate dissolves to form cavities and caves in limestone formations.

In this experiment you will determine the solubility of calcium carbonate in an aqueuos solution saturated with carbon dioxide and in solution free of carbon dioxide. The $[Ca^{2+}]$ will be determined by complexometric titration with EDTA (ethylenediamine-tetraacetic acid).

a) Procedure for the determination of $[Ca^{2+}]$

1. Calibrate your *pH* meter.
2. Measure and record the *pH* of the sample equilibrated with solid $CaCO_3$ and CO_2 gas.
3. Filter all your sample into a second 250 cm^3 plastic bottle to remove any suspended $CaCO_3$. Quickly cap the bottle when the filtering is complete.
4. Uncap the bottle long enough to measure and record the pH of the filtered solution and recap the bottle until you are ready for the next step.
5. As rapidly as possible, transfer three 25 cm^3 aliquots of this sample to three Erlenmeyer flasks. Recap the sample bottle after removing each 25 cm^3 aliquot.
6. Add 15 drops of 6 M HCl to each of the three flasks with stirring. Any $CaCO_3$ that may have formed should dissolve. Before proceeding with the next step, make sure there is no solid $CaCO_3$ in the Erlenmeyer flasks. If a flask has some solid present, then more stirring is necessary.
7. To one, and only one flask, add 5 cm^3 of a pH 10 NH_3 buffer. Proceed immediately with steps 8 - 10.
8. Add 20 drops of 0.001 M $Mg^{2+}/EDTA^{4-}$ solution to the flask in order for the indicator to function properly.
9. Add 5 drops of Calmagite indicator to the sample.

10. Titrate the sample with an approximately 0.01 M EDTA solution provided (to be standardized as directed below) to a colour change from red to blue. You may wish to make a reference for colour with water, buffer, two drops EDTA and indicator.
11. Quickly repeat steps 7 - 10 for each remaining flask, one at a time.
12. After steps 1 - 11 have been completed to your satisfaction, transfer the remaining filtered, saturated solution from step 3 to a suitable beaker. Heat this solution to 96 – 99 °C and allow it to remain at that temperature, with magnetic stirring, for 5 minutes. A stirrer setting on 6 is adequate, and an initial high setting of heat will be required. You should see CO_2 being evolved and some $CaCO_3$ may precipitate.
13. At the end of the five minutes heating period, use the beaker tongs to remove the beaker from the hot plate and place it in an ice bath. Allow the solution to cool to room temperature.
14. Measure and record the *pH* of the cooled solution.
15. Filter the solution to remove any suspended $CaCO_3$.
16. Transfer three 25 cm^3 aliquots of this filtered solution to three Erlenmeyer flasks. Add about 25 cm^3 of deionized water to each flask, followed by 15 drops of 6 M HCl.
17. Titrate each sample according to steps 7 - 11.

b) Procedure for standardization of EDTA

1. Weigh approximately 0.35 g of dried primary standard $CaCO_3$, (molar mass 100.09 g mol^{-1}) which will be found in the weighing bottle in the desiccator. Note: $CaCO_3$ is hygroscopic.
2. Add 25 cm^3 of deionized water to the $CaCO_3$, then carefully add 5 cm^3 of 6 M HCl. Quickly cover with a watch glass.
3. When the $CaCO_3$ has dissolved, quantitatively transfer the solution to a 250 cm^3 volumetric flask and dilute to the mark.
4. Transfer three 25 cm^3 aliquots of the standard Ca^{2+} solution to three Erlenmeyer flasks.
5. Proceed to titrate each sample according to steps 7 - 11, following each step in sequence.

Tasks:

1.1 Calculate the solubility of calcium carbonate (expressed in mol dm^{-3}) in a solution saturated with both $CaCO_3$ and CO_2 and in solution free of CO_2.

1.2 List all the ionic species that increase in concentration as a result of the dissolving of $CaCO_3$ in water.

1.3 Given below are brief descriptions of two solutions. Circle the one in which the concentration of CO_3^{2-} would be highest:

a) a solution produced by dissolving $CaCO_3$(s) in CO_2 -saturated water

b) a solution produced by dissolving $CaCO_3$(s) in CO_2 -free water

1.4 Will the solubility of $CaCO_3$ increase or decrease in a solution from which the CO_2 has been removed?

SOLUTION

1.1 The results of the titration (volumes of titrants, mass of $CaCO_3$) and calculation of the concentration of the standardized EDTA solution were required to be written on the Answer Sheet.

Moreover, it was necessary to measure and record *pH* values of the sample at steps 2, 4, and 14.

It was expected to show the calculation of the solubility of $CaCO_3$ in its saturated solutions containing CO_2 and in those without CO_2.

The other tasks to be solved:

1.2 The ionic species mentioned above are as follows: Ca^{2+}, HCO_3^-, OH^-.

1.3 Correct answer: (b) A solution produced by dissolving $CaCO_3$(s) in CO_2-free water.

1.4 The solubility of $CaCO_3$ will decrease.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Determination of Mg^{2+} and Ca^{2+} in Bottled Water

- The K_{sp} for calcium oxalate is 2.3×10^{-9} and the K_{sp} for magnesium oxalate is 8.6×10^{-5}.
- In a solution buffered to maintain *pH* 10, Calmagite indicator is pink when bound to Mg^{2+} and blue in the absence of available magnesium ions. Calcium ions are not bound by Calmagite.
- EDTA binds to Mg^{2+} and Ca^{2+} even in the presence of Calmagite. The stoichiometry of the EDTA-metal complex formed with both Mg^{2+} and Ca^{2+} is 1:1.
- Molar masses: M(Ca) = 40.08 g mol^{-1} M(Mg) = 24.31 g mol^{-1}

Chemicals Available

500 cm^3 sample of “Bottled Water”
aqueous buffer (pH 10)
Calmagite indicator
aqueous saturated ammonium oxalate
aqueous ethylenediaminetetraacetic acid
aqueous standardized* Mg^{2+}
distilled water
*0.928 mg Mg^{2+}/cm^3 solution, 0.0382 moles Mg^{2+}/dm^3

Procedure

A. Precipitation of calcium ions

Precipitate the calcium ions in a 25.00 cm^3 aliquot of the “Bottled Water” sample by accurately adding approximately 0.50 cm^3 of saturated ammonium oxalate solution (from the common burettes in each lab room). Carefully swirl the solution to ensure uniform mixing. Allow at least 45 minutes for complete precipitation to occur.

B. Standardization of the EDTA solution

Using distilled water, dilute 5.00 cm^3 of the standardized magnesium solution to a final volume of 100.0 cm^3. Add 40 cm^3 of distilled water, 5 cm^3 of *pH* 10 buffer solution, and some Calmagite indicator to 5.00 cm^3 of diluted magnesium solution. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

C. Titration of Mg^{2+} and Ca^{2+}

Add 40 cm^3 of distilled water, 5 cm^3 of *pH* 10 buffer solution, and some Calmagite indicator to 5.00 cm^3 of the “Bottled Water” sample. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

D. Titration of Mg^{2+}

Add 40 cm^3 of distilled water, 5 cm^3 of *pH* 10 buffer solution, and some Calmagite indicator to 5.00 cm^3 of the calcium-free “Bottled Water” sample prepared in part **A**. The presence of a small amount of calcium oxalate will not interfere with your titration. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

Calculations

Calculate the concentration of Mg^{2+} (in mg dm^{-3}) in the “Bottled Water” sample.

Calculate the concentration of Ca^{2+} (in mg dm^{-3}) in the “Bottled Water” sample.

PROBLEM 2 (Practical)

Estimation of Mn(II) and Mg(II) Present in the Given Sample

In this experiment, estimation of the amounts of Mn (II) and Mg (II) present in the given sample is carried out by complexometric titration using standard Na_2EDTA solution. Total metal ion content is obtained from the first titration. At this stage, by using adequate solid NaF, selective and quantitative release of EDTA present in Mg-EDTA complex is achieved. The EDTA thus released is bound again by the addition of a known excess of standard Mn (II) solution. The unused Mn (II) is estimated by a back titration using the same standard Na_2EDTA solution. From these two different titre values, individual amounts of metal ions present can be obtained. Both the titrations are performed using a buffer (*pH* = 10) and Erichrome black T indicator.

The sample in duplicate is given in two 250 cm^3 conical flasks (labelled as Trial I and Trial II). Perform the titrations for both and record your readings on the answer sheet.

Procedure

Two burettes (25 cm^3) are supplied to you. Fill one with the given standard Na_2EDTA solution and the other with the given standard Mn (II) solution.

Titration 1

To the sample solution (supplied in the 250 cm^3 conical flask), add all of the solid hydroxylamine hydrochloride given in one vial followed by 50 cm^3 of distilled water. With the help of a measuring cylinder, add 10 cm^3 buffer solution (*pH* = 10) and one metal spatula full of the solid indicator. Shake the contents of the flask thoroughly and titrate the solution against the standard Na_2EDTA solution until the colour changes from wine red to blue. Record your burette reading (**A** cm^3). Ensure that you shake the contents of the flask thoroughly throughout the titration.

Titration 2

To the same flask, add all of the solid NaF given in one vial and shake the contents well for a minute. To this add 20 cm^3 of the given standard Mn (II) solution from the other burette. The addition of the Mn (II) solution should be done in small increments (2 – 3 cm^3) with thorough shaking. After addition of the total Mn (II) solution, shake the contents for two to three minutes. The colour of the solution will change from blue to wine red. Titrate the excess of Mn (II) in the solution against the standard Na_2EDTA solution till the colour changes from wine red to blue. Record your burette reading (**B** cm^3).

Repeat the same procedure for Trial II.

SOLUTION

The results of the titration (volumes) were required to be written on the Answer Sheet.

The other tasks to be solved:

2.2 Give the balanced chemical equation for the reactions of Mg(II) and Mn(II) with Na_2EDTA . (Use the symbol Na_2HY for Na_2EDTA.)

Answer: $Mg^{2+} + H_2Y^{2-} \rightarrow MgY^{2-} + 2\,H^+$

$Mn^{2+} + H_2Y^{2-} \rightarrow MnY^{2-} + 2\,H^+$

2.3 Give the equation for the release of EDTA by the addition of NaF to the MgEDTA complex.

Answer: $MgY^{2-} + 2\,F^- \rightarrow MgF_2 + Y^{4-}$

2.4 Calculate the amount of Mg (II) and Mn (II) in gram for any one of the two trials. (Show the main steps in your calculation.)

2.5 The colour change at the end point (wine red to blue) in Titration 1 is due to

a) the formation of metal-indicator complex, ☐

b) the release of free indicator from metal-indicator complex, ☐

c) the formation of metal-EDTA complex. ☐

[Mark X in the correct box.]

Correct answer is (b).

PROBLEM 2 (Practical)

Qualitative and Quantitative Analysis of a Superconductor

Introduction

Superconductors based on lanthanum cuprate (La_2CuO_4) have the general composition of $La_xM_{(2-x)}CuO_4$ (M = Ca, Sr, Ba).

This problem consists of two parts:

- the qualitative determination of the alkaline earth metal(s)
- the quantitative determination of lanthanum and copper.

Read the burette as accurately as possible. Report your results on the answer sheets.
Answer the additional questions and write the results with adequate accuracy.
The qualitative and quantitative parts of this experiment may be done in any order.

Procedures

2.1 *Qualitative determination of the alkaline earth metal(s)*

(If the hood is occupied start with the titration 2.2)

In this experiment you have to use the superconductor as a solid ($La_xM_{(2-x)}CuO_4$; No. **14**).
At the beginning, lanthanum has to be separated as an insoluble residue.
All steps must be carried out in the hood!
Dissolve the complete sample in a beaker in about 5 cm^3 of perchloric acid (No. **22**) by heating the mixture. Add 5 cm^3 of demineralized water afterwards.
Cool down the solution until it is lukewarm.

Add about 5 cm^3 of demineralized water and then ammonia solution (No. **17**), until the reaction mixture shows a basic reaction. Lanthanum precipitates as hydroxide and copper forms an intense blue-coloured tetraammine complex. The precipitate is filtered off and washed with a small amount of demineralized water.

An excess of ammonium-carbonate solution (No. **18**) is added to the filtrate and the mixture is being boiled for some minutes. The alkaline earth metal(s) will precipitate as carbonate(s). The precipitate is filtered off and washed a few times with a small amount of demineralized water.

Then, the precipitate is dissolved in acetic acid (No. **16**). Add sodium acetate (No. **9**) and an excess of potassium-dichromate solution (No. **23**). In the presence of barium, yellow $BaCrO_4$ precipitates. After boiling the mixture for one minute barium chromate is filtered off and washed with demineralized water.

(If there is no barium chromate precipitation, proceed in a way as if there were precipitation.)

Ammonia solution (No. **17**) is added to the clear filtrate until it is basic. Add an excess of ammonium-carbonate solution (No. **18**) and boil the mixture for some minutes. In the presence of strontium and/or calcium, white carbonate(s) precipitate(s).

The precipitate is filtered off and washed a few times with demineralized water.

Then it is dissolved in a mixture of about 2 cm^3 of demineralized water and a few drops of hydrochloric acid (No. **3**). This solution is devided between two test tubes:

- Saturated calcium-sulfate solution (No. **21**) is added to one of the test tubes. In the presence of strontium a small amount of white strontium sulfate precipitates. To accelerate the precipitation, you can grind the inner surface of the test tube with a glass rod for a few minutes.
- Ammonium-sulfate solution (No. **20**) is added to the second test tube. In the presence of strontium and/or calcium, white sulfate(s) precipitate(s). The precipitate is filtered off and washed with a very small amount of demineralized water.

  1 cm^3 of ammonium-oxalate solution (No. **19**) is added to the filtrate. In the presence of calcium, white calcium oxalate precipitates after a few minutes.

Preparation of the superconductor parent solution

There is a superconductor solution ($La_xM_{(2-x)}CuO_4$ in perchloric acid; No. 13) in a volumetric flask.

Fill it up with demineralized water to a volume of 250.0 cm^3. From now on this solution is called “parent solution”.

2.2 *Quantitative determination of the total content of lanthanum and copper*

Transfer 25.00 cm^3 of the parent solution into an Erlenmeyer flask. Add about 5-6 piled spatula of sodium acetate (CH_3COONa; No. **8**) and 2 micro spatula of xylenol orange indicator (No. **15**) to this solution and make up with demineralized water to a volume of

about 75 cm^3. The *pH*-value has to be about ***pH* 6** before the determination, otherwise add more sodium acetate.

Titrate the solution with Na_2-EDTA solution (No. **7**). The color of the solution changes from light violet to intensely light-green. (In between, the color changes a few times.)

Repeat this procedure as many times as necessary.

2.3 *Quantitative determination of the copper content*

Transfer 25.00 cm^3 of your parent solution (No. **13**) into the 100 cm^3 volumetric flask and fill up with demineralized water to a volume of 100.0 cm^3. For each titration, transfer 25.00 cm^3 of this solution into an Erlenmeyer flask and add sodium hydroxide solution (No. **6**), until the solution shows an alkaline reaction. During this procedure, a blue precipitate forms. Add sulfuric acid (No. **12**) until the blue precipitate dissolves. The solution has to be acidic (**pH 1-2**) and will contain a small amount of a white precipitate.

Add 10 cm^3 of sodium-iodide solution (No. **9**), and swirl the Erlenmeyer flask for about 1 minute. Titrate the solution with sodium-thiosulfate solution (No. **10**). Add some starch solution (No. **11**) as an indicator just before the end of the titration. At the end, the solution has to be colourless for at least 60 seconds.

Repeat this procedure as many times as necessary.

SOLUTION

2.1 Which alkaline earth metal(s) can be found in the superconductor? Mark only one box!

Ca ☐ Sr ☐ Ba ☒

Ca and Sr ☐ Ca and Ba ☐ Sr and Ba ☐

Ca and Sr and Ba ☐

Complete the following reaction equations:

$$Ca^{2+} + C_2O_4^{2-} \rightleftharpoons CaC_2O_4$$

$$Sr^{2+} + CO_3^{2-} \rightleftharpoons SrCO_3$$

$2\ Ba^{2+} + Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\ BaCrO_4 + 2\ H^+$

2.2 Quantitative determination of the total content of lanthanum and copper.

Appropriate consumption of 0.1000 mol dm^{-3} EDTA solution: V = 11.60 cm^3

(accoding to 100 cm^3 of superconductor solution)

2.3 Quantitative determination of the copper content.

Appropriate consumption of 0.01000 mol dm^{-3} $Na_2S_2O_3$ solution: V = 10.50 cm^3
(according to 100 cm^3 of superconductor solution)

Complete the following reaction equations:

$2\ Cu^{2+} + 4\ I^- \rightleftharpoons I_2 + 2\ CuI$

$I_2 + 2\ S_2O_3^{2-} \rightleftharpoons 2\ I^- + S_4O_6^{2-}$

2.4 Mass (in mg) of copper in your parent solution,
mass (in mg) of lanthanum in your parent solution.

[M(Cu) = 63.55 g mol^{-1}; M(La) = 138.91 g mol^{-1}]

Amount of copper:

10,50 cm^3 × 0.01 mol dm^{-3} × 4 × 10 × 63.55 g mol^{-1} = 266.9 mg

Amount of lanthanum:

[11.60 – (10.50 / 10 × 4)] cm^3 × 0.1 mol dm^{-3} × 10 × 138.91 g mol^{-1} = 1028 mg

Mass Cu: m(Cu) = 266.9 mg
Mass La: m(La) = 1028 mg

2.5 Assume a fictive consumption of 39.90 cm^3 of 0.1000 mol dm^{-3} EDTA solution and 35.00 cm^3 of 0.01000 mol dm^{-3} $Na_2S_2O_3$ solution. Calculate the coefficient x in the formula $La_xM_{(2-x)}CuO_4$ (M = Ca and/or Sr and/or Ba) and give the exact formula of the superconductor

Consumption for lanthanum = [39.90 – (35.00/10 × 4)] cm^3 = 25.90 cm^3

Consumption for copper = (39.90 – 25.90) cm^3 = 14.00 cm^3

n(La) : n(Cu) = 25.90 : 14.00 = 1.85 : 1

coefficient x: 1.85 formula: $La_{1.85}Ba_{0.15}CuO_4$

PROBLEM 2 (Practical)

Analysis of a Copper(II) Complex

You are provided with a sample of an inorganic copper(II) complex, the anion of which is made from copper, chlorine, and oxygen. The counter ion is the tetramethyl ammonium cation. There is no water of crystallisation. You are required to determine proportions of copper ions and chloride ions by titration and hence determine the composition of the complex.

Chemicals

- Inorganic complex: three samples of approximately 0.1 g, accurately pre-weighed in vials labelled ‘Sample 1’, ‘Sample 2’, ‘Sample 3’.
- Inorganic complex: three samples of approximately 0.2 g, accurately pre-weighed in vials labelled ‘Sample 4’, ‘Sample 5’ and ‘Sample 6’.
- pH 10 ammonia buffer, 10 cm^3.
- Murexide indicator, solution in H_2O, 10 cm^3.
- EDTA disodium salt, aqueous solution, c = 0.0200 mol dm^{-3}, 150 cm^3.
- Ethanoic acid, 10 cm^3.
- 2,7-Dichlorofluorescein indicator, solution in 7 : 3 EtOH : H_2O), 10 cm^3.
- Dextrin, 2 % solution in H_2O, 25 cm^3.
- Silver nitrate, aqueous solution, c = 0.1000 mol dm^{-3}, 150 cm^3.

Procedure

Titration to determine the proportion of copper ions

(a) You are provided with three accurately pre-weighed samples of copper complex, each of approximately 0.1 g. These are labelled "Sample 1", "Sample 2", "Sample 3", together with the exact mass of the copper complex. Take the first of these, note down the mass of the sample and quantitatively transfer the contents to a 250 cm^3 conical flask using approximately 25 cm^3 of water.

(b) Add pH 10 ammonia buffer solution until the precipitate which forms initially just redissolves (about 10 drops).

(c) Add 10 drops of the murexide indicator.

(d) Titrate with the 0.0200 mol dm^{-3} EDTA solution until the solution turns violet and the colour persists for at least 15 seconds. Record the volume of solution used in the titration.

(e) Repeat if necessary with samples 2 and 3.

Note: You will be marked only on a single value you report in the answer booklet. This may either be an average value, or a single value you feel most confident in.

2.1 Calculate the volume of EDTA solution needed to react completely with 0.100 g of complex.

2.2 Give an equation for the titration reaction.

2.3 Calculate the percentage by mass of copper in the sample.

You will need to wash out your burette before you start the titration for the determination of chloride ions. Any remaining EDTA solution may be disposed of into the waste containers labelled ‘EDTA’.

Titration to determine the proportion of chloride ions present

(f) You are provided with three accurately pre-weighed samples of copper complex each of approximately 0.2 g. These are labelled "Sample 4", "Sample 5", "Sample 6", together with the exact mass of the copper complex. Take the first of these, note down the mass of the sample and quantitatively transfer the contents to a 250 cm^3 conical flask using approximately 25 cm^3 of water.

(g) Add 5 drops of ethanoic acid, followed by 10 drops of dichlorofluorescein indicator and 5 cm^3 dextrin (2 % suspension in water). Shake the bottle well before adding the dextrin suspension.

(h) Titrate with the 0.1000 mol dm^{-3} silver nitrate solution, swirling constantly until the white suspension turns pink and the colour does not disappear after swirling.

(i) Repeat if necessary.

Note: You will be marked only on a single value you report in the answer booklet. This may either be an average value, or the value you feel most confident in.

2.4 Calculate the volume of silver nitrate solution needed to react completely with 0.200 g of complex.

2.5 Give an equation for the titration reaction.

2.6 Calculate the percentage by mass of chloride ions in the sample.

The percentage of carbon, hydrogen and nitrogen in the complex was determined by combustion analysis and found to be as follows:

Carbon: 20.87 %; Hydrogen: 5.17 %; Nitrogen: 5.96 %.

2.7 Mark in the answer booklet, which element in the complex has the greatest percentage error in the determination of its proportion.

Cu Cl O C H N

2.8 Determine the formula of the copper complex. Show your working.

SOLUTION

2.1 Full marks if answer is $V_{corr.} \pm 0.1$ cm^3. Zero marks if answer is less than ($V_{corr.} - 0.5$ cm^3) or greater than ($V_{corr.} + 0.5$ cm^3), linear point scale is applied in between.

2.2 $Cu^{2+} + EDTA^{4-} \rightarrow [Cu(EDTA)]^{2-}$

2.3 $n(\text{EDTA}) = 0.0200 \text{ mol dm}^{-3} \times V(\text{EDTA}) \text{ (in dm}^3) = (0.0200 \text{ mol dm}^{-3} \times V) \text{ mol}$

$n(\text{Cu}^{2+}) = (0.0200 \text{ mol dm}^{-3} \times V) \text{ mol}$

$m(\text{Cu}) = M(\text{Cu}) \times n(\text{Cu}) = 63.55 \text{ g mol}^{-1} \times (0.0200 \text{ mol dm}^{-3} \times V) \text{ mol}$

$$\% \text{ Cu} = \frac{m(\text{Cu})}{m(\text{sample})} \times 100$$

2.4 Full marks if answer is $V_{corr.} \pm 0.1$ cm^3.

Zero marks if answer is less than ($V_{corr.} - 0.5$ cm^3) or greater than ($V_{corr.} + 0.5$ cm^3), linear point scale is applied in between.

2.5 $Ag^+ + Cl^- \rightarrow AgCl$

2.6 $n(\text{Ag}^+) = 0.100 \text{ mol dm}^{-3} \times V(\text{Ag}^+) \text{ (in dm}^3) = (0.100 \text{ mol dm}^{-3} \times V) \text{ mol}$

$n(\text{Cl}^-) = (0.100 \text{ mol dm}^{-3} \times V) \text{ mol}$

$m(\text{Cl}) = M(\text{Cl}) \times n(\text{Cl}) = 35.45 \text{ g mol}^{-1} \times (0.100 \text{ mol dm}^{-3} \times V) \text{ mol}$

$$\% \text{ Cl} = \frac{m(\text{Cl})}{m(\text{sample})} \times 100$$

2.7 If the percentage of oxygen is calculated by subtracting all the others from 100, it has all the errors from the determination of the other elements combined. In practice this leads to a large error which affects the subsequent calculation of the formula unless this point is appreciated.

Cu Cl [✓ O] C H N

2.8 Full marks if the formula is correctly calculated from the student data and the large error in oxygen is taken into account (either by using one of the proportions of the other elements to determine the elemental ratios, or by a consideration of charge balance).

PROBLEM 3 (Practical)

Polymers in Analysis

Polymers can be used in various analyses. In this task, you are first required to analyze a polysaccharide using a polymer-polymer interaction, which will then be utilized to identify polymers in the second part.

I. Analysis of Polysaccharide by Colloid Titration

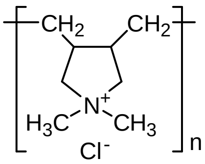
You are provided with a solution of a polysaccharide containing sulfonate ($-SO_3^-$) and carboxylate ($-COO^-$) groups. You are asked to determine the concentrations of these two groups by colloid titration under the basic and acidic conditions based on the differences in the protonation behaviour of these acid groups. A back-titration technique is utilized.

When these acid groups are ionized, the polysaccharide becomes a polyanion. Upon addition of polycation, poly(diallyldimethylammonium) (provided as its chloride salt, PDAC), it forms a polyion complex. PDAC solution is standardized using the standard solution of potassium poly(vinyl sulphate) (PVSK). At the endpoint of colloid titration, the number of anionic groups becomes equal to that of cationic groups.

Chemicals

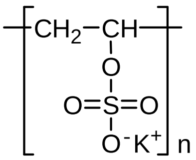
- Polysaccharide solution, 50 cm^3
- Poly(diallyldimethylammonium chloride), (**PDAC**), aqueous solution

  Formula:



- Potassium poly(vinyl sulfate) aqueous solution, c = 0.0025 mol dm^{-3}; (monomer unit concentration)

  Formula:



- sodium hydroxide, aqueous solution, c = 0.5 mol dm^{-3}
- toluidine blue, $C_{15}H_{16}N_3SCl$, (TB), aqueous solution, c = 1 g dm^{-3}
- Solutions X-1 – X- 5 for Part II.

Procedure

(1) Take precisely 20 cm^3 of the PDAC solution using a volumetric pipette into a 100 cm^3 conical beaker. Add 2 drops of toluidine blue (TB) into the conical beaker. Titrate the resulting blue solution with the standard solution of PVSK (c = 0.0025 mol dm$^{–3}$ - monomer unit concentration). At the endpoint the colour turns purple. Note that the solution becomes gradually turbid as the endpoint approaches. The endpoint is determined when the colour remains purple for 15 – 20 seconds. Repeat if necessary.

3.1 Report the PVSK solution volume (**z** cm^3) consumed in the standardization of PDAC. Record your reading to 0.05 cm^3.

(2) Take precisely 5 cm^3 of the polysaccharide solution and 20 cm^3 of the PDAC solution using volumetric pipettes into a conical beaker. Add 0.4 cm^3 of NaOH solution (c = 0.5 mol dm$^{–3}$) and 2 drops of TB to the solution. Titrate the resulting blue solution with the PVSK standard solution in a similar manner. Repeat if necessary.

(The appearance of coagulation may be different, depending on the pH of the solution.)

3.2 Report the PVSK solution volume, (**x** cm^3) consumed in the titration under basic conditions. Record your reading to 0.05 cm^3.

3.3 Mark the acid group(s) ionized under the basic conditions on the answer sheet.

(3) Repeat procedure (2) above with the addition of 0.5 cm^3 of HCl solution (c = 0.5 mol dm$^{–3}$) instead of NaOH solution (c = 0.5 mol dm$^{–3}$).

3.4 Report the PVSK solution volume (**y** cm^3) consumed in the titration under acidic conditions. Record your reading to 0.05 cm^3.

3.5 Mark the acid group(s) fully ionized under acidic conditions on the answer sheet.

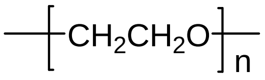
3.6 Calculate the concentrations of the $–SO_3^-$ (or $–SO_3H$) groups and the $–COO^-$ (or –COOH) groups (in mol dm$^{–3}$) in the given polysaccharide solution.

II. Identification of compounds

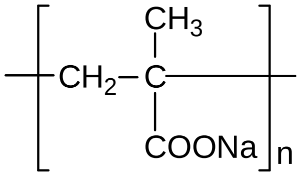
You are provided with five solutions **(1 – 5)** and each solution contains one of the compounds below (all of which are used). The concentration is 0.05 mol dm^{-3} (for polymers, monomer unit concentration). Your task is to identify all the compounds by carrying out the following procedures.

$$HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$$

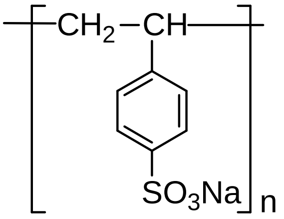
(TEG)



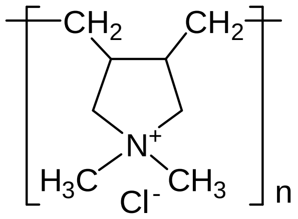
(PEO)



(PMANa)



(PSSNa)



(PDAC)

Abbreviations:

TEG = triethylene glycol;

PEO = poly(ethylene oxide);

PMANa = poly(sodium methacrylate);

PSSNa = poly(sodium 4-styrenesulfonate);

PDAC = poly(diallyldimethylammonium chloride) MW. stands for molecular weight.

Helpful comments

i) Aggregates observed in part I could be observed when mixing two polymer solutions in an appropriate combination in which an interaction takes place between the two polymers. They can be utilized to identify polymer samples.

ii) The volume of a solution measuring 5 mm in height from the bottom of the vial is approximately 1 cm^3. Remember that you have only 10 cm^3 of each solution.

Procedures

(4) Mix similar volumes of two solutions together in a vial.

(5) If necessary, you can acidify the resulting mixture. Ten drops of hydrochloric acid (c = 0.5 mol dm^{-3}) from a plastic Pasteur pipette are sufficient for this purpose.

3.7 Identify the compound in each solution based on the experimental results. Mark one of the five boxes to indicate your identification of the samples.

Sample					
1	☐ TEG	☐ PEO	☐ PMANa	☐ PSSNa	☐ PDAC
2	☐ TEG	☐ PEO	☐ PMANa	☐ PSSNa	☐ PDAC
3	☐ TEG	☐ PEO	☐ PMANa	☐ PSSNa	☐ PDAC
4	☐ TEG	☐ PEO	☐ PMANa	☐ PSSNa	☐ PDAC
5	☐ TEG	☐ PEO	☐ PMANa	☐ PSSNa	☐ PDAC

SOLUTION

I. Analysis of Polysaccharide by Colloid Titration

3.1 V = 20.06 cm^3; z = 20.06

3.2 Sample A: V = 13.14 cm^3 ; x = 13.14
Sample B: V = 12.07 cm^3 x = 12.07
Sample C: V = 10.91 cm^3 x = 10.91

3.3 Under basic conditions: The acid groups are $–SO_3H$ and –COOH.

3.4 Sample A: V = 15.26 cm^3 ; y = 15.26
Sample B: V = 14.61 cm^3 y = 14.61
Sample C: V = 13.59 cm^3 y = 13.59

3.5 Under acidic conditions: The acid group is $–SO_3H$.

3.6 The concentrations (in mol dm$^{–3}$) of:
$–SO_3^-$ (or $–SO_3H$) groups = 0.0005 (z – y)
$–COO^–$ (or –COOH) groups = 0.0005 (y – x)

II. Identification of compounds

PMANa and PSSNa are polyanions and they interact with a polycation (PDAC) to form a precipitate. Under acidic conditions the carboxylate ($–COO^–$) groups in PMANa undergo protonation and PMANa changes to protonated poly(metacrylic acid) (PMA). The resulting carboxy groups (–COOH) interact with the ether oxygen atoms in PEO through hydrogen bonding to form a precipitate. Since the protonated PMA is no longer a polyanion, the precipitate (the complex between PMANa and PDAC) disappears after the addition of HCl.

On the other hand, PSSNa does not exist as a protonated form even under acidic condition.

The expected results of mutual reactions are summarized in the table below. The signs in upper rows correspond to the reactions before addition of HCl while those in lower rows to the reactions after addition of HCl.

	TEG	PEO	PMANa	PSSNa	PDAC
TEG					
PEO	– –				
PMANa	– –	– +			
PSSNa	– –	– –	– –		
PDAC	– –	– –	+ –	+ +	

Note: (+) precipitation is formed; **(–)** no precipitation occurs (or the precipitation disappears)

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.

SOLUTION

1.1 – 1.3

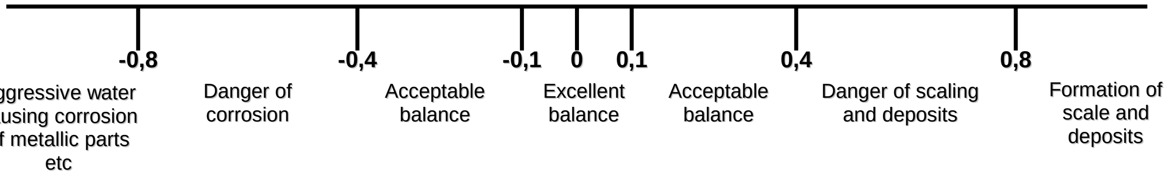
- Some distribution graphs were proposed by the organizer and approved by the International Jury that could be applied for evaluating of accuracy of the titrations and, consequently, for awarding points.
- For determinations of amounts of substance of Cl^- and Mg^{2+} ions, as well concentrations of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

PROBLEM 2 (Practical)

Determination of the Langelier Saturation Index of a pool water

The Langelier Saturation Index (LI) is a measure of swimming pool water corrosivity as well as its ability to dissolve or deposit calcium carbonate. If LI is approximately zero, the water is considered "balanced". If the index LI is a positive number, the water tends to deposit calcium carbonate and is scale-forming. If the index LI is a negative number, the water is corrosive and dissolves calcium carbonate. The LI is a combination of the physical values factors taken from Table 1 and can be calculated by the formula:

$$\text{LI} = \text{pH} + \text{FT} + \text{FD} + \text{FA} - \text{FTDS}$$



pH : pH value
FT : Temperature factor
FD : Calcium hardness (CH) factor
FA : Total alkalinity (TA) factor
FTDS: Total dissolved solids (TDS) factor

Table 2.1 Values and corresponding factors

Temperature, °C	FT	Calcium hardness (CH), mg dm^{-3} $CaCO_3$	FD	Total alkalinity (TA), mg dm^{3} $CaCO_3$	FA	Total dissolved solids (TDS), mg dm^{-3} NaCl	FTDS
0	0.0	5	0.3	5	0.7	0	12.0
3	0.1	25	1.0	25	1.4	-	-
8	0.2	50	1.3	50	1.7	1000	12.1
12	0.3	75	1.5	75	1.9	-	-
16	0.4	100	1.6	100	2.0	2000	12.2
19	0.5	150	1.8	125	2.1	-	-
24	0.6	200	1.9	150	2.2	3000	12.25
29	0.7	250	2.0	200	2.3	-	-

Table 2.1 continued

34	0.8	300	2.1	300	2.5	4000	12.3
41	0.9	400	2.2	400	2.6	-	-
53	1.0	600	2.35	800	2.9	5000	12.35
-	-	800	2.5	1000	3.0	-	-
-	-	1000	2.6	-	-	6000	12.4

In this task you will have to determine the LI value of a given water sample. Note that hardness is expressed as the equivalent to the concentration of $CaCO_3$ (expressed in mg dm^{-3}). Total alkalinity, being the acid equivalent to the total amount of carbonate and hydrogen carbonate, can also be expressed in mg dm^{-3} of $CaCO_3$, whereas TDS is recalculated as concentration of NaCl (mg dm^3).

Chemicals

- EDTA, standard aqueous solution, c = 0.0443 mol dm$^{–3}$,
- HCl, standard aqueous solution, c = 0.0535 mol dm$^{–3}$,
- Methyl orange, 0.1% in water,
- Murexide, indicator, solid mixture with NaCl (1 : 250 by mass),
- Sample of water.

Procedures

Calcium hardness is determined by complexometric titration with EDTA (Na_2H_2Y). This is performed in a strongly alkaline medium to mask magnesium (large amounts of Mg^{2+} interfere due to the co-precipitation of calcium with $Mg(OH)_2$; moreover, the complexometric indicator is also adsorbed on $Mg(OH)_2$, which impairs the observation of its colour change). When the alkali is added, titration should be carried out immediately to avoid the deposition of $CaCO_3$.

2.1 Write down equation of the reaction occurring during titration with Na_2H_2Y.

Procedure for determination of calcium

a) Put the standard solution of EDTA (precise exact concentration c = 0.0443 mol dm$^{–3}$) in the burette.

b) Pipette a 20 cm^3 aliquot of the water sample into an Erlenmeyer flask.

c) Add 3 cm^3 of NaOH solution (c = 2 mol dm$^{–3}$) with the 10 cm^3 measuring cylinder.

d) Add murexide indicator with spatula to obtain noticeably pink solution.

e) Within few minutes titrate the mixture with EDTA solution until the indicator colour changes from pink to purple.

2.2 Fill in the table 2.2.

Table 2.2

Volume of EDTA solution	Titration No			
Initial reading of the burette, cm^3				
Final reading of the burette, cm^3				
Consumed volume, cm^3				

Accepted volume, cm^3:

2.3 Calculate the hardness of the water sample in mg dm^{-3} of $CaCO_3$. Write down the result in Table 2.4 (see question 2.11).

Measurement of pH

Locate a pH meter in the lab (or ask your lab assistant).

a) Place about 70 -- 90 cm^3 of the water sample into a clean Erlenmeyer flask.

b) Remove the protective cap from the pH-meter (keep the cap standing, since there is solution in it).

c) Rinse the electrode with distilled water using a plastic wash bottle.

d) Turn the pH meter on by sliding the ON/OFF switch.

e) Immerse the electrode in the solution to be tested and stir gently by swirling the flask.

f) Place the flask on the table and wait until the reading stabilizes (not more than 1 min).

g) Read and record the pH value.

h) Switch the pH meter off, rinse the electrode with distilled water and place the protective cap back.

2.4 Write down the pH value in Table 2.4 (see question 2.11).

2.5 Which form of carbonic acid predominates in your water sample?

Confirm your choice with calculation and tick one box.

☐ Carbonate ☐ Hydrogen carbonate ☐ Carbonic acid

Note: The dissociation constants of carbonic acid are as follows:

$K_1 = 4.5 \cdot 10^{-7}$;

$K_2 = 4.8 \cdot 10^{-11}$.

2.6 Write down the ionic equation of the predominant reaction of titration of the water sample with HCl solution.

Determination of the total alkalinity

To obtain the value of the total alkalinity the water sample should be titrated to H_2CO_3. An acid-base indicator used is methyl orange, which starts changing its colour from yellow to orange at pH of about 4.5.

a) Rinse the burette with distilled water and fill it with the standard HCl solution (exact concentration of HCl is 0.0535 mol dm^{-3}).

b) Pipette a 50.0 cm^3 aliquot of water sample into an Erlenmeyer flask and add 3 drops of methyl orange solution.

c) If the sample is orange prior to addition of the acid the total alkalinity is zero. If the solution is yellow titrate it with the standard acid solution until the first noticeable colour change towards orange is observed. Record the volume of the titrant used.

2.7 Fill in the Table 2.3.

Table 2.3

Volume of the standard HCl solution	Titration No			
Initial reading of the burette, cm^3				
Final reading of the burette, cm^3				
Consumed volume, cm^3				
Accepted volume, cm^3 ______				

2.8 Calculate the total alkalinity (in mg dm^{-3} $CaCO_3$). Write down the result in Table 2.4 (see question 2.11).

2.9 Temperature measurement

Read the thermometer located at the table of common use and write down the value into Table 2.4 (see question 2.11).

2.10 TDS determination in the water sample with the test strip.

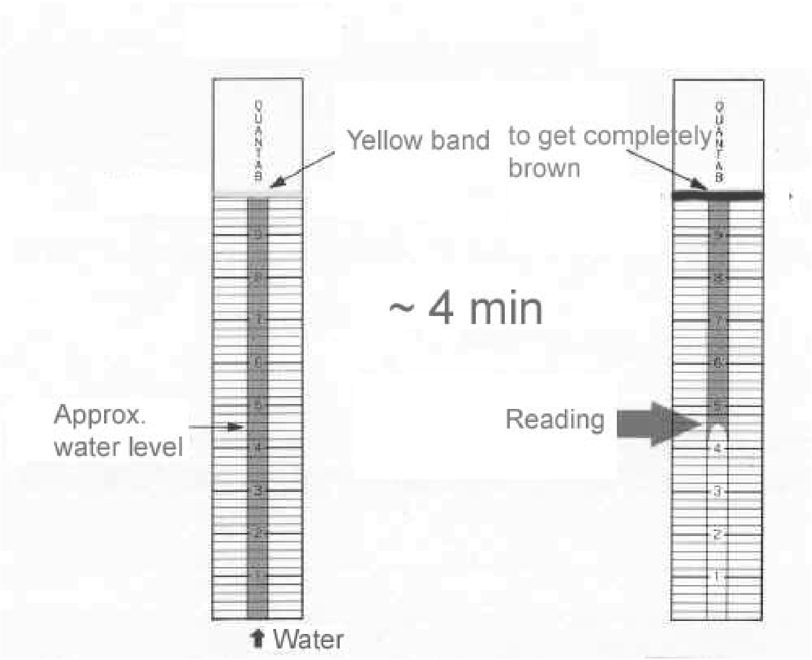
a) Fill a beaker with the water sample to a level of about 3 cm of height. Immerse the strip into water; be sure that the yellow band on the top of the strip does not touch the liquid.

b) Wait for 3 - 4 minutes until the yellow band turns completely brown. Take the reading as shown in the picture hereunder. Give it to one decimal digit.

c) Report the reading.

d) Find your TDS concentration as that of NaCl in mg dm^{-3} in the table to the right of the picture.

e) Write down the concentration of NaCl in Table 2.4 (see question 2.11).



Reading	NaCl conc., mg dm^{-3}
1.4	360
1.6	370
1.8	420
2.0	430
2.2	470
2.4	530
2.6	590
2.8	660
3.0	730
3.2	800
3.4	880
3.6	960
3.8	1050
4.0	1140
4.2	1240
4.4	1340
4.6	1450
4.8	1570
5.0	1700

2.11 Fill in all the blank boxes in the Table 2.4. Calculate LI and write down the result in Table 2.4. Take the values of the factors to the accuracy of two decimal digits.

Table 2.4. Calculation of LI of the water sample

Water sample Number ______					
CH, mg dm^{-3} $CaCO_3$	TA, mg dm^{-3} $CaCO_3$	*t*, °C	pH	TDS, mg dm^{-3} NaCl	**LI**
FD	FA	FT		FTDS	

Theoretical questions. Water balance correction.

If LI significantly deviates from zero, it is needed to be adjusted to zero.

Imagine you are given a sample of pool water analyzed as you have done above. The results of the analysis are as follows: CH = 550 mg dm^{-3}, FD = 2.31, TA = 180 mg dm^{-3}, FA = 2.26, t = 24 °C, FT = 0.6; TDS = 1000 mg dm^{-3}, FTDS = 12.1, pH = 7.9, LI = 0.97. The pool serviceman added 10 cm^3 of 0.0100 mol dm^{-3} solutions of reagents ($NaHCO_3$, NaOH, $NaHSO_4$, $CaCl_2$, EDTA (disodium salt dihydrate) and HCl) to 200 cm^3 of different pool water samples (one reagent for one sample).

2.12 Decide whether $CaSO_4$ is deposited upon addition of $NaHSO_4$.

Yes ☐ No ☐

Tick one box and confirm your choice with calculation.

Note: $CaSO_4$ solubility product is $5 \cdot 10^{-5}$. Assume that no precipitate of $CaCO_3$ is formed upon addition of any of the above reagents.

2.13 Fill in the hereunder table 2.5 by showing the trends of changes resulting from addition of each reagent to this particular water sample (use “+” if the factor increases, “–“ if it decreases, and “0” if it does not change).

Table 2.5

Reagent	pH	FA	FD	FTDS	LI
$NaHCO_3$					
NaOH					
$NaHSO_4$					
$CaCl_2$					
Na_2H_2Y					
HCl					

SOLUTION

2.1 $H_2Y^{2-} + Ca^{2+} = CaY^{2-} + 2\ H^+$

Reactions with other forms of EDTA are also acceptable.

2.5 We observe pH ~8 ⇒ this is carbonic acid - hydrogen carbonate buffer, then:

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{K_1}{[H^+]} = 45$$

i.e. ~ 98 % of hydrogen carbonate

☐ Carbonate ☑ Hydrogen carbonate ☐ Carbonic acid

2.6 $HCO_3^- + H^+ = H_2CO_3$ (or $H_2O + CO_2$)

2.12 $[Ca^{2+}] = \dfrac{V_{EDTA} \times c_{EDTA}}{20}\,\dfrac{200}{200+10} = \dfrac{2.2 \times 0.05}{\dfrac{20 \times 200}{210}} = 0.00524\ \text{mol dm}^{-3}$

When $NaHSO_4$ is added, $[SO_4^{2-}] = \dfrac{0.01 \times 10}{(200+10)} = 0.000476\ \text{mol dm}^{-3}$

Then $[Ca^{2+}]\,[SO_4^{2-}] = 0.00524 \times 0.000476 = 2.5 \cdot 10^{-6} < K_{sp}$

⇒ no precipitate of $CaSO_4$ is formed.

Your answer (tick one) Yes ☐ No ☑

2.13

Reagent	pH	FA	FD	FTDS	LI
$NaHCO_3$	+	+	0	+	+
NaOH	+	+	0	+	+
$NaHSO_4$	–	–	0	+	–
$CaCl_2$	0	0	+	+	+
Na_2H_2Y	–	–	–	+	–
HCl	–	–	0	0	–

Practical Problem 3 **13 %** of the total	**Code:**		Task	1	2	3	4	5	6	7	8	9	10	Total
	Examiner		Mark	0	25	2	25	3	4	3	2	5	2	**71**
			Grade											

Practical Problem 3. Analysis of a hydrated zinc iron(II) oxalate double salt

Zinc iron(II) oxalate double salt is a common precursor in the synthesis of zinc ferrite which is widely used in many types of electronic devices due to its interesting magnetic properties. However, such double salts may exist with different compositions and different amount of water depending on how the sample was synthesized.

You will analyze a pure sample of hydrated zinc iron(II) oxalate double salt (**Z**) in order to determine its empirical formula.

Procedure

The concentration of the standard $KMnO_4$ is posted on the lab walls.

Bring a clean 250 mL beaker to the lab assistant who will be waiting by the balance. You will receive a pure sample of **Z** for analysis. Accurately weigh between 0.7-0.8 g of the pure sample **Z** onto the weighing paper (***m***, grams). This should then be immediately quantitatively transferred into your 250 mL beaker for analysis, and its mass recorded in table below.

<u>Task 3.1:</u> Record the mass of the sample of pure Z taken.

Mass of sample, *m* (gram)	**Lab assistant's signature**
------------------	---------------------

Analysis of Z

- Using the 100 mL graduated measuring cylinder, measure *ca.* 30 mL of 30 wt% H_2SO_4 solution and add it into the 250-mL beaker containing your accurately weighed pure sample of **Z**. To speed up the dissolving of your sample you may use the hotplate stirrer to warm up the mixture, **but be careful not to boil** it. *You should not use the digital thermometer as the acid may damage it.* After the solid has dissolved, remove the beaker from the hotplate stirrer and cool it to close to room temperature. After the solution has cooled, quantitatively transfer it into the 100 mL volumetric flask. Add distilled water up to the 100 mL–mark. We will now call this solution **C.**

- Use an appropriately labeled beaker to transfer the standardized **$KMnO_4$** solution into the burette graduated with **brown** marks.
- Use another appropriately labeled beaker to transfer the standardize **EDTA** solution into the burette graduated with **blue** marks.

Titration with $KMnO_4$

a) Using the 5 mL graduated pipette add 5.00 mL of the solution **C** into a 250 mL conical flask.

b) To this conical flask add about 2 mL of 30 wt% H_2SO_4 solution, about 3 mL of 3.0 M H_3PO_4 solution, and about 10 mL of distilled water. Heat the mixture on the hot plate stirrer until hot, **but be careful not to boil** it.

c) Titrate the hot solution with the standardized $KMnO_4$ solution, recording your burette readings in the table below. At the end point of the titration, the pink color of the solution appears. Repeat the titration as desired and report your accepted volume of $KMnO_4$ solution consumed (V_1 mL) in the table.

<u>Task 3.2</u>: Record volumes of standardized $KMnO_4$ solution consumed

(You DO NOT need to fill in the entire table)

	Titration No			
	1	**2**	**3**	**4**
Initial reading of the burette of $KMnO_4$, mL				
Final reading of the burette of $KMnO_4$, mL				
Consumed volume of $KMnO_4$, mL				

Accepted volume, V_1 = ________ mL

***Task 3.3*: Can aqueous HCl or HNO_3 be used instead of H_2SO_4 for the dissolving of sample Z and the subsequent analyses?**

HCl	**YES** ☐	**NO** ☐
HNO_3	**YES** ☐	**NO** ☐

Titration with EDTA

- Clean both the 250 mL beakers ready for the next part of the experiment. Pipette 10.00 mL of solution **C** into a 250 mL beaker. Heat and stir the solution on the hotplate stirrer, **but be careful not to boil** it. Add *ca.* 15 mL of 20 wt% NaOH solution to the beaker and keep it on the hotplate for *ca. 3*-*5* min in order to complete the precipitation of iron hydroxide, and to convert all Zn^{2+} ions into the ionic complex $[Zn(OH)_4]^{2-}$.
- Using a glass funnel and the large quantitative filter paper, filter the hot suspension directly into the 250 mL conical flask. **From this point take care with the volumes as you will be preparing a standard solution of exactly 100 mL from the filtrate**. As it is filtering, prepare some warm distilled water in a 250 mL beaker (*ca.* 50 mL). Wash the precipitate on the filter paper (at least 5 times) with small portions (*ca.* 5 mL) of the warm distilled water. Cool the filtrate down and then quantitatively transfer it into the 100 mL volumetric flask via a glass funnel. Add distilled water to make up to the 100 mL mark. This will now be referred to as solution **D**.
- Pipette 10.00 mL of solution **D** into a 250 mL conical flask. Add *ca.*10 mL ammonia buffer solution ($pH = 9 – 10$) and a small quantity of the ETOO indicator using the glass spatula spoon. Mix well to obtain a purple solution. Titrate the solution with the standardized 2.00×10^{-3} M EDTA solution, recording your burette readings in table below. At the end point, the color of the solution turns blue. Repeat the titration as desired and report your accepted volume of EDTA solution consumed (V_2 mL) in the table.

***Task 3.4*: Record the volumes of EDTA solution consumed**

(You DO NOT need to fill in the entire table)

	Titration No			
	1	**2**	**3**	**4**
Initial reading of the burette of EDTA, mL				
Final reading of the burette of EDTA, mL				
Consumed volume of EDTA, mL				

Accepted volume, $\mathbf{V_2}$ = ________ **mL**

Determination of the empirical formula of Z

***Task 3.5:* Calculate the number of moles of Zn^{2+}, $n_{Zn^{2+}}$, present in 100 mL of solution C.**

$n_{Zn^{2+}}$ (mol): ……………

***Task 3.6:* Give the ionic equations for the reduction-oxidation reactions taking place in the titration with $KMnO_4$.**

<u>Task 3.7:</u> Calculate the number of moles of Fe^{2+}, $n_{Fe^{2+}}$, present in 100 mL of solution C. **[YOU WILL NEED THE PRECISE CONCENTRATION OF $KMnO_4$ POSTED ON THE WALLS IN YOUR LAB]**

V_1, mL = …………………………………….

$n_{Fe^{2+}}$ (mol): …………………………

<u>Task 3.8:</u> Calculate the number of moles of $C_2O_4^{2-}$ anion, $n_{C_2O_4^{2-}}$, in 100 mL of solution C.

$n_{C_2O_4^{2-}}$ = …………………………………………..

Task 3.9: ***Calculate the number of moles of water,*** n_{H_2O}***, in the original sample of Z taken for analysis.***

Task 3.10*: Give the empirical formula of Z:*

Titolazione iodometrica

Titolazione iodometrica

International Chemistry Olympiad

PROBLEM 3 (practical)

You are required to determine the concentrations of hydrochloric acid and potassium iodate in the diluted solution containing both.

Procedure:

A solution containing potassium iodate and hydrochloric acid has already been measured into the volumetric flask provided. Fill the flask to the mark with distilled water using the wash bottle, close it with a stopper and shake it thoroughly. Fill the burette with the standard sodium thiosulphate solution using one of the beakers provided. (The exact concentration of the thiosulphate is given on the label of the bottle.)

a) First titration

Pipette a 10.00 cm^3 aliquot (portion) of the solution from the volumetric flask into a glass stoppered conical flask. Dilute it with 10 cm^3 of distilled water, add 1 g (a small spatula end-full) of potassium iodide and acidify with 10 cm^3 of 10 % sulphuric acid using a measuring cylinder. Titrate immediately the iodine formed with the standard sodium thiosulphate solution until the solution in the flask is pale yellow. Add with a pipette 1 cm^3 of starch indicator solution and continue the titration to completion. Repeat the titration twice more and record your readings on the result sheet.

b) Second titration

Pipette a 10.00 cm^3 aliquot of the solution into another glass stoppered conical flask, dilute with 10 cm^3 of distilled water, add 1 g of solid potassium iodide, and leave to stand for 10 minutes. Then titrate the iodine formed using the standard sodium thiosulphate solution, adding 1 cm^3 of starch indicator solution when the mixture is pale yellow. Repeat the titration twice more, recording your readings on the result sheet.

Task:

Calculate the concentration of the HCl and the KIO_3 in the solution that you prepared by dilution (in mol dm^{-3}).

SOLUTION

The reaction:

$$IO_3^- + 5\ I^- + 6\ H^+ = 3\ I_2 + 3\ H_2O$$

occurs to be quantitative both with respect to IO_3^- and H^+. Consequently the first titration (in the presence of sulphuric acid) is suitable for the determination of iodate, while the second one for the determination of the hydrochloric acid content.

PROBLEM 3 (Practical)

Titration of Oxygen Dissolved in Water

(Winkler's method)

In aqueous alkaline solution, dissolved oxygen oxidizes manganese(II) hydroxide to hydrated manganese(III) oxide (written as $Mn(OH)_3$ for simplification). In acidic solution, manganese(III) ions oxidize iodide ions to iodine. The iodine formed is titrated with a sodium thiosulphate solution.

Data:

Redox couple	Electrode potentials (in V)	
	at *pH* = 0	at *pH* = 14
Mn^{3+} / Mn^{2+}	1.51	
$Mn(OH)_3$ / $Mn(OH)_2$		0.13
O_2 / H_2O	1.23	0.39
I_2 / I^-	0.62	0.62
$S_4O_6^{2-}$ / $S_2O_3^{2-}$	0.09	0.09

Solubility products: $K_{sp}(Mn(OH)_2) = 1\times10^{-13}$

$K_{sp}(Mn(OH)_3) = 1\times10^{-36}$

Gas constant: $R = 8.315\ J\ K^{-1}mol^{-1}$

Procedure:

Preliminary remarks: To reduce volume variations, the reagents are added either as solids (sodium hydroxide pellets ...), or as concentrated solutions (sulphuric acid).

1. The water to be tested is stored in a large container located on the general-use bench. Place two glass beads into a 250 cm^3 ground top Erlenmeyer (conical) flask. Fill it to the rim with the water to be tested. At this stage of the manipulation the

Erlenmeyer flask should be standing in the basin provided to avoid overflow of water onto the bench. Measure the temperature of the water.

2. Add to the water, avoiding any loss of reagent:
   a) 2 g of manganese(II) chloride, preweighed within a decigram and contained in the bag.
   b) about 8 pellets of sodium hydroxide (yielding a basic medium, *pH* = 14). The pellets will be found on the general-use bench.
3. Stopper the Erlenmeyer flask, avoiding air bubbles, and swirl it until complete dissolution of the sodium hydroxide and of the manganese chloride has occurred. A brown precipitate forms.
4. Let the flask stand for at least 30 minutes.
5. Open the Erlenmeyer flask, add concentrated sulphuric acid dropwise, stirring with a glass rod until the solution is definitely acidic (check with the *pH* indicator paper); make sure that nearly all the precipitate has disappeared.
   Sulphuric acid will be found on the general-use bench.
6. Add to the Erlenmeyer flask 3 g of potassium iodide, preweighed within a decigram and contained in a bag. Stopper the flask and shake it until the potassium iodide has dissolved. The solution should now be clear.
7. Remove a 50 cm^3 sample of the solution and titrate it with a X mol dm^{-3} sodium thiosulphate solution (the numerical value of X will be shown on the board). For this titration, the endpoint can be determined using the indicator thiodene which is equivalent to starch. A small quantity of this solid indicator should be dissolved in the solution being titrated just prior to the endpoint.

Questions:

3.1 Justify that the oxidation of manganese(II) by dissolved oxygen is possible only in alkaline solution.

3.2 Write the equation of the reaction between:

- dissolved oxygen and manganese(II) hydroxide (in alkaline solution),
- manganese(III) ions and iodide ions,
- iodine and thiosulphate.

3.3 Record the volume of thiosulphate required to reach the endpoint.

3.4 Derive an expression that relates the dissolved oxygen concentration in water (expressed as mol dm^{-3}) to the volume in cm^3 of thiosulphate added at the endpoint. Determine that concentration for the water tested.

Deduce the volume of oxygen (in cm^3), determined at 0 °C and at a pressure of 101,325 Pa, contained in a litre of water (measured at ambient temperature). Give the temperature of the water.

SOLUTION

3.1 $E^0(O_2/H_2O) > E^0(Mn(III)/Mn(II))$ at $pH = 14$

3.2

$$\begin{array}{l} O_2 + 4\,e^- + 2\,H_2O \rightarrow 4\,OH^- \\ Mn(OH)_2 + HO^- \rightarrow Mn(OH)_3 + e^- \\ \hline O_2 + 4\,Mn(OH)_2 + 2\,H_2O \rightarrow 4\,Mn(OH)_3 \end{array}$$

$$\begin{array}{l} 2\,I^- \rightarrow I_2 + 2\,e^- \\ Mn^{3+} + e^- \rightarrow Mn^{2+} \\ \hline 2\,I^- + 2\,Mn^{3+} \rightarrow I_2 + 2\,Mn^{2+} \end{array}$$

$$\begin{array}{l} I_2 + 2\,e^- \rightarrow 2\,I^- \\ 2\,S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\,e^- \\ \hline I_2 + 2\,S_2O_3^{2-} \rightarrow 2\,I^- + S_4O_6^{2-} \end{array}$$

3.4 1 mol $O_2 \triangleq$ 4 mol Mn(II) $\triangleq$ 4 mol Mn(III)

4 mol Mn(III) $\triangleq$ 4 mol I^- $\triangleq$ 2 mol I_2

2 mol $I_2 \triangleq$ 4 mol $S_2O_3^{2-}$

$$c(S_2O_3^{2-}) \times V(S_2O_3^{2-}) = 4 \times c(O2) \times 50$$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Determination of Fatty Acids

A mixture of an unsaturated monoprotic fatty acid and an ethyl ester of a saturated monoprotic fatty acid has been dissolved in ethanol (2.00 cm^3 of this solution contain a total of 1.00 g acid plus ester). By titration the acid number$^{1)}$, the saponification number$^{2)}$ and the iodine number$^{3)}$ of the mixture shall be determined. The acid number and the saponification number shall be used to calculate the number of moles of free fatty acid and ester present in 1.00 g of the sample. The iodine number shall be used to calculate the number of double bonds in the unsaturated fatty acid.

Note: The candidate must be able to carry out the whole exam by using the delivered amount of unknown sample (12 cm^3). There will be no supplementation.

1) Acid number: The mass of KOH in milligram that is required to neutralize *one* gram of the acid plus ester.
2) Saponification number: The mass of KOH in milligram that is required to saponify *one* gram of the acid plus ester.
3) Iodine number: The mass of iodine (I) in g that is consumed by 100 g of acid plus ester.

Relative atomic masses:

A_r(I) = 126.90 A_r(O) = 16.00
A_r(K) = 39.10 A_r(H) = 1.01

1) Determination of the Acid Number

Reagents and Apparatus

Unknown sample, 0.1000 M KOH, indicator (phenolphthalein), ethanol/ether (1 : 1 mixture), burette (50 cm^3), Erlenmeyer flasks (3 x 250 cm^3), measuring cylinder (100 cm^3), graduated pipette (2 cm^3), funnel.

Procedure:

Pipette out aliquots (2.00 cm^3) from the unknown mixture into Erlenmeyer flasks (250 cm^3). Add first ca. 100 cm^3 of an ethanol/ether mixture (1:1) and then add the indicator (5 drops). Titrate the solutions with 0.1000 M KOH.

Calculate the acid number.

2) Determination of the Saponification Number

Reagents and Apparatus

Unknown sample, 0.5000 M KOH in ethanol, 0.1000 M HCl, indicator (phenolphthalein), volumetric flask (50 cm^3), round bottom flask (250 cm^3), Liebig condenser, burette (50 cm^3), Erlenmeyer flasks (3 x 250 cm^3), volumetric pipette (25 cm^3), volumetric pipette (10 cm^3), graduated pipette (2 cm^3), funnel, glass rod. The round bottom flask and Liebig condenser are to be found in the fume hoods.

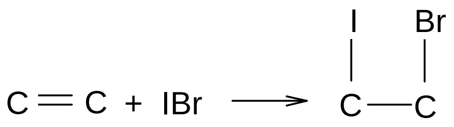
Procedure

Pipette out a 2.00 cm^3 aliquot of the unknown sample into a round bottom flask (250 cm^3) and add 25.0 cm^3 0.5000 M KOH/EtOH. Reflux the mixture with a heating mantle for 30 min in the fume hood (start the heating with the mantle set to 10, then turn it down to 5 after 7 min.). Bring the flask back to the bench and cool it under tap water. Transfer quantitatively the solution to a 50 cm^3 volumetric flask and dilute to the mark with a 1:1 mixture of ethanol/water. Take out aliquots of 10 cm^3 and titrate with 0.1000 M HCl using phenolphthalein as indicator (5 drops).

Calculate the saponification number.

3) Determination of the Iodine Number

In this experiment iodobromine adds to the double bond.



$$C=C + IBr \longrightarrow \underset{}{\overset{I}{C}}-\overset{Br}{C}$$

The Hanus solution (IBr in acetic acid) is added in excess. After the reaction is complete, excess iodobromine is reacted with iodide forming I_2, ($IBr + I^- \rightarrow I_2 + Br^-$) which in turn is determined by standard thiosulphate solution.

Warning: Be careful when handling the iodobromine solution. Treat any spill immediately with thiosulphate solution.

Reagents and Apparatus

Unknown sample, 0.2000 M Hanus solution, dichloro-methane, 15 % KI solution in distilled water, distilled water, 0.2000 M sodium thiosulphate, starch indicator, Erlenmeyer flasks (3 x 500 cm^3), buret (50 cm^3), graduated pipette (2 cm^3), measuring cylinders (10 and 100 cm^3), volumetric pipette (25 cm^3), aluminium foil.

Procedure

Pipette out aliquots (1.00 cm^3) of the unknown mixture into Erlenmeyer flasks (500 cm^3) and add 10 cm^3 of dichloromethane. With a pipette add 25.0 cm^3 Hanus solution, cover the opening with aluminium foil and place your labelled flasks in the dark in the cupboard (under the fume hood) for 30 min. with occasionally shaking. Add 10 cm^3 of the 15 % KI solution, shake thoroughly and add 100 cm^3 of dist. water. Titrate the solution with 0.2000 M sodium thiosulphate until the solution turns pale yellow. Add starch indicator (3 cm^3) and continue titration until the blue colour entirely disappears.

Calculate the iodine number.

4) Use the results from 1) 2) and 3) to:

i) Calculate the amount of ester (in mol) in 1 g of the acid plus ester.

ii) Calculate the number of double bonds in the unsaturated acid.

PROBLEM 3 (Practical)

Determination of Copper(II) Content in Cu(gly)$_2$. x H_2O

The Cu(II) content in Cu(gly)$_2$. *x* H_2O crystals prepared yourself can be determined by iodometry with starch solution as indicator. Based on the data obtained one can calculate
the moles of hydrate in Cu(gly)$_2$. *x* H_2O.

Reagents:
Standard KIO_3 (see the label on the bottle to get the accurate concentration)
H_2SO_4 (1.0 mol dm^{-3}) as indicator.
KI (0.6 mol dm^{-3})
KSCN (2 mol dm^{-3})
Starch (0.5 %)
$Na_2S_2O_3$ (to be standardized)

1. *Standardization of* <u>*$Na_2S_2O_3$ solution*</u>

Procedure
(1) Transfer 25.00 cm^3 of standard KIO_3 solution to an Erlenmeyer flask.
(2) Add 5 cm^3 of water, 10 cm^3 of KI solution and 5 cm^3 of H_2SO_4 (1.0 mol dm^{-3}) to the flask.
(3) Titrate immediately with $Na_2S_2O_3$ solution.
(4) Add 2 cm^3 starch solution when the colour of the titrand turns pale yellow.
(5) Continue titrating until the blue colour of the solution disappears.
(6) Proceed with step (1) – (5) twice parallel.

2. <u>*Determination of Cu(II) content in Cu(gly)$_2$.xH_2O*</u>

(1) Weigh 1.0 – 1.2 g (precision of ±0.0002 g) of Cu(gly)$_2$. *x* H_2O with a dry 100 cm^3 beaker as the container.
(2) Dissolve it with 40 cm^3 of water and 8 cm^3 of H_2SO_4 (1.0 mol dm^{-3}).
(3) Transfer the above solution quantitatively to a 100 cm^3 volumetric flask and dilute to the mark.

(4) Transfer 25.00 cm^3 of the Cu(II) solution to an Erlenmeyer flask, add 50 cm^3 of water and 10 cm^3 of KI solution to the flask.

(5) Titrate immediately with standardized $Na_2S_2O_3$ solution.

(6) Add 2 cm^3 of starch solution and 3 cm^3 of KSCN solution to the flask when the colour of the titrand turns from brown to pale yellow.

(7) Titrate continuously until the blue colour of the solution disappears.

(8) Proceed with steps (4) – (7) twice parallel.

SOLUTION

The following values were required to be written on the Answer Sheet :

Part 1

- Volumes of $Na_2S_2O_3$ solution
- Calculation of the concentration of $Na_2S_2O_3$ solution.

Part 2

- Mass of the product.
- Volumes of $Na_2S_2O_3$ solution
- Mass % of Cu(II) in $Cu(gly^-)_2 \cdot x\,H_2O$. Calculation.
- The value of x in the formula of the product. Calculation.

Other Tasks:

1. Write two equations for chemical reactions taking place during the standardization of $Na_2S_2O_3$ solution.
2. Write the equation for the reaction between Cu^{2+} and I^-.

Solutions of the tasks:

1. $IO_3^- + 5\,I^- + 6\,H_3O^+ \rightarrow I_2 + 9\,H_2O$

   $I_2 + 2\,S_2O_3^{2-} \rightarrow 2\,I^- + S_4O_6^{2-}$

2. $2\,Cu^{2+} + 4\,I^- \rightarrow 2\,CuI + I_2$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Iodometric Determination of the Concentration of Copper(II) and Iron(III) in a Sample of Technological Solution

Reagents

- $K_2Cr_2O_7$, 0.008333 M
- KI, 20 % by mass.
- HCl, 1 M
- H_2SO_4, 1 M
- $Na_4P_2O_7$, 5 % by mass.
- Starch, 1 % by mass.
- $Na_2S_2O_3$ (should be standardized)
- The solution to be analyzed in 100 cm^3 volumetric flask.

Procedure

1. Standardization of $Na_2S_2O_3$ solution

   (1) 10 cm^3 of 1 M solution of H_2SO_4 and 2 cm^3 of 20 % KI solution are placed into an Erlenmeyer flask (the solution remains colourless).

   (2) 10.00 cm^3 of $K_2Cr_2O_7$ solution is added.

   (3) The Erlenmeyer flask is covered with a watch glass and kept in a dark place for 3 to 5 min.

   (4) 100 cm^3 of water is added to the flask.

   (5) The mixture is titrated immediately with $Na_2S_2O_3$ solution until the colour of mixture changes to pale yellow. Then 10 drops of starch solution are added. The titration continues until blue colour disappears completely.

   (6) It is recommended to repeat the titration (steps 1 through 5) two more times.

Do the following and fill in the answer sheet form

1.1 Write the reactions involved in the procedure of standardization of $Na_2S_2O_3$ solution

1.2 Calculate the concentration of $Na_2S_2O_3$ solution, and write your calculations.

2. The determination of copper

(1) The solution to be analyzed in a 100 cm^3 volumetric flask is diluted with water to the mark and stirred

(2) A 10.00 cm^3 aliquot of the solution is placed into an Erlenmeyer flask.

(3) 20 cm^3 of 5 % solution of $Na_4P_2O_7$, 7 cm^3 of 1 M solution of HCl, and 10 cm^3 of 20 % solution of KI are added. A precipitate may form upon the addition of $Na_4P_2O_7$.

(4) The Erlenmeyer flask is covered with a watch glass and left in a dark place for 3 - 5 min.

(5) The mixture is titrated immediately with $Na_2S_2O_3$ solution until the colour of suspension changes to pale yellow. Then, 10 drops of starch solution are added. The titration continues until the colour of suspension becomes clear white.

(6) It is recommended to repeat the titration (steps 2 through 5) two more times.

Do the following and fill in the answer sheet form

1.3 Write the reactions involved in the procedure of determination of Cu^{2+} ion.

1.4 Calculate the mass of copper in the solution under analysis, and write your calculations.

3. The determination of total amount of copper and iron

(1) A 10.00 cm^3 aliquot of the solution prepared in the item 2(1) is placed into an Erlenmeyer flask.

(2) 2 cm^3 of 1 M HCl solution and 10 cm^3 of 20 % KI solution are added.

(3) The Erlenmeyer flask is covered with a watch glass and kept in a dark place for 3 to 5 min.

(4) The mixture is titrated immediately with $Na_2S_2O_3$ solution until the colour of suspension changes to pale yellow. Then, 10 drops of starch solution are added. The titration continues until the colour of suspension becomes clear white.

(5) It is recommended to repeat the titration (steps 1 through 4) two more times.

Do the following and fill in the answer sheet form

1.5 Write the reactions involved in the procedure of determination of Fe^{3+} ion.

1.6 Calculate the mass of iron in the solution under analysis, and write your calculations.

SOLUTION

1.1

Equations:

$Cr_2O_7^{2-} + 6\,I^- + 14\,H^+ = 2\,Cr^{3+} + 3\,I_2 + 7\,H_2O$

$I_2 + 2\,S_2O_3^{2-} = 2\,I^- + S_4O_6^{2-}$

i

1.3

Equations:

$2\,Cu^{2+} + 4\,I^- = 2\,CuI + I_2$

$4\,Fe^{3+} + 3\,P_2O_7^{4-} = Fe_4(P_2O_7)_3 \downarrow$

$I_2 + 2\,S_2O_3^{2-} = 2\,I^- + S_4O_6^{2-}$

1.5

Equations:

$2\,Fe^{3+} + 2\,I^- = 2\,Fe^{2+} + I_2$

$2\,Cu^{2+} + 4\,I^- = 2\,CuI + I_2$

$I_2 + 2\,S_2O_3^{2-} = 2\,I^- + S_4O_6^{2-}$

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 sufficient 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 °C 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.

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.

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)

Qualitative and Quantitative Analysis of a Superconductor

Introduction

Superconductors based on lanthanum cuprate (La_2CuO_4) have the general composition of $La_xM_{(2-x)}CuO_4$ (M = Ca, Sr, Ba).

This problem consists of two parts:

- the qualitative determination of the alkaline earth metal(s)
- the quantitative determination of lanthanum and copper.

Read the burette as accurately as possible. Report your results on the answer sheets.
Answer the additional questions and write the results with adequate accuracy.
The qualitative and quantitative parts of this experiment may be done in any order.

Procedures

2.1 *Qualitative determination of the alkaline earth metal(s)*

(If the hood is occupied start with the titration 2.2)

In this experiment you have to use the superconductor as a solid ($La_xM_{(2-x)}CuO_4$; No. **14**).
At the beginning, lanthanum has to be separated as an insoluble residue.
All steps must be carried out in the hood!
Dissolve the complete sample in a beaker in about 5 cm^3 of perchloric acid (No. **22**) by heating the mixture. Add 5 cm^3 of demineralized water afterwards.
Cool down the solution until it is lukewarm.

Add about 5 cm^3 of demineralized water and then ammonia solution (No. **17**), until the reaction mixture shows a basic reaction. Lanthanum precipitates as hydroxide and copper forms an intense blue-coloured tetraammine complex. The precipitate is filtered off and washed with a small amount of demineralized water.

An excess of ammonium-carbonate solution (No. **18**) is added to the filtrate and the mixture is being boiled for some minutes. The alkaline earth metal(s) will precipitate as carbonate(s). The precipitate is filtered off and washed a few times with a small amount of demineralized water.

Then, the precipitate is dissolved in acetic acid (No. **16**). Add sodium acetate (No. **9**) and an excess of potassium-dichromate solution (No. **23**). In the presence of barium, yellow $BaCrO_4$ precipitates. After boiling the mixture for one minute barium chromate is filtered off and washed with demineralized water.

(If there is no barium chromate precipitation, proceed in a way as if there were precipitation.)

Ammonia solution (No. **17**) is added to the clear filtrate until it is basic. Add an excess of ammonium-carbonate solution (No. **18**) and boil the mixture for some minutes. In the presence of strontium and/or calcium, white carbonate(s) precipitate(s).

The precipitate is filtered off and washed a few times with demineralized water.

Then it is dissolved in a mixture of about 2 cm^3 of demineralized water and a few drops of hydrochloric acid (No. **3**). This solution is devided between two test tubes:

- Saturated calcium-sulfate solution (No. **21**) is added to one of the test tubes. In the presence of strontium a small amount of white strontium sulfate precipitates. To accelerate the precipitation, you can grind the inner surface of the test tube with a glass rod for a few minutes.
- Ammonium-sulfate solution (No. **20**) is added to the second test tube. In the presence of strontium and/or calcium, white sulfate(s) precipitate(s). The precipitate is filtered off and washed with a very small amount of demineralized water.

  1 cm^3 of ammonium-oxalate solution (No. **19**) is added to the filtrate. In the presence of calcium, white calcium oxalate precipitates after a few minutes.

Preparation of the superconductor parent solution

There is a superconductor solution ($La_xM_{(2-x)}CuO_4$ in perchloric acid; No. 13) in a volumetric flask.

Fill it up with demineralized water to a volume of 250.0 cm^3. From now on this solution is called “parent solution”.

2.2 *Quantitative determination of the total content of lanthanum and copper*

Transfer 25.00 cm^3 of the parent solution into an Erlenmeyer flask. Add about 5-6 piled spatula of sodium acetate (CH_3COONa; No. **8**) and 2 micro spatula of xylenol orange indicator (No. **15**) to this solution and make up with demineralized water to a volume of

about 75 cm^3. The *pH*-value has to be about ***pH* 6** before the determination, otherwise add more sodium acetate.

Titrate the solution with Na_2-EDTA solution (No. **7**). The color of the solution changes from light violet to intensely light-green. (In between, the color changes a few times.)

Repeat this procedure as many times as necessary.

2.3 *Quantitative determination of the copper content*

Transfer 25.00 cm^3 of your parent solution (No. **13**) into the 100 cm^3 volumetric flask and fill up with demineralized water to a volume of 100.0 cm^3. For each titration, transfer 25.00 cm^3 of this solution into an Erlenmeyer flask and add sodium hydroxide solution (No. **6**), until the solution shows an alkaline reaction. During this procedure, a blue precipitate forms. Add sulfuric acid (No. **12**) until the blue precipitate dissolves. The solution has to be acidic (**pH 1-2**) and will contain a small amount of a white precipitate.

Add 10 cm^3 of sodium-iodide solution (No. **9**), and swirl the Erlenmeyer flask for about 1 minute. Titrate the solution with sodium-thiosulfate solution (No. **10**). Add some starch solution (No. **11**) as an indicator just before the end of the titration. At the end, the solution has to be colourless for at least 60 seconds.

Repeat this procedure as many times as necessary.

SOLUTION

2.1 Which alkaline earth metal(s) can be found in the superconductor? Mark only one box!

Ca	☐	Sr	☐	Ba	☒
Ca and Sr	☐	Ca and Ba	☐	Sr and Ba	☐
Ca and Sr and Ba	☐				

Complete the following reaction equations:

$$Ca^{2+} + C_2O_4^{2-} \rightleftharpoons CaC_2O_4$$

$$Sr^{2+} + CO_3^{2-} \rightleftharpoons SrCO_3$$

$2\ Ba^{2+} + Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\ BaCrO_4 + 2\ H^+$

2.2 Quantitative determination of the total content of lanthanum and copper.

Appropriate consumption of 0.1000 mol dm^{-3} EDTA solution: V = 11.60 cm^3

(accoding to 100 cm^3 of superconductor solution)

2.3 Quantitative determination of the copper content.

Appropriate consumption of 0.01000 mol dm^{-3} $Na_2S_2O_3$ solution: V = 10.50 cm^3

(according to 100 cm^3 of superconductor solution)

Complete the following reaction equations:

$2\ Cu^{2+} + 4\ I^- \rightleftharpoons I_2 + 2\ CuI$

$I_2 + 2\ S_2O_3^{2-} \rightleftharpoons 2\ I^- + S_4O_6^{2-}$

2.4 Mass (in mg) of copper in your parent solution,
mass (in mg) of lanthanum in your parent solution.

[M(Cu) = 63.55 g mol^{-1}; M(La) = 138.91 g mol^{-1}]

Amount of copper:

10,50 cm^3 × 0.01 mol dm^{-3} × 4 × 10 × 63.55 g mol^{-1} = 266.9 mg

Amount of lanthanum:

[11.60 – (10.50 / 10 × 4)] cm^3 × 0.1 mol dm^{-3} × 10 × 138.91 g mol^{-1} = 1028 mg

Mass Cu: m(Cu) = 266.9 mg

Mass La: m(La) = 1028 mg

2.5 Assume a fictive consumption of 39.90 cm^3 of 0.1000 mol dm^{-3} EDTA solution and 35.00 cm^3 of 0.01000 mol dm^{-3} $Na_2S_2O_3$ solution. Calculate the coefficient x in the formula $La_xM_{(2-x)}CuO_4$ (M = Ca and/or Sr and/or Ba) and give the exact formula of the superconductor

Consumption for lanthanum = [39.90 – (35.00/10 × 4)] cm^3 = 25.90 cm^3

Consumption for copper = (39.90 – 25.90) cm^3 = 14.00 cm^3

n(La) : n(Cu) = 25.90 : 14.00 = 1.85 : 1

coefficient x: 1.85 formula: $La_{1.85}Ba_{0.15}CuO_4$

Student Code AAA-1

Practical Problems

"Bonding the World with Chemistry"

49th INTERNATIONAL CHEMISTRY OLYMPIAD
Nakhon Pathom, THAILAND

Practical Exam

Task 1B

Chemicals and Equipment (Task 1B)

I. Chemicals and materials (the actual labeling for each is given in bold font)

	Health Statements[a]
Solution A (KIO_3 10.7042 g in 5.00 dm^3), 60 cm^3 in a plastic bottle	H272-H315-H319-H335
Solution B (Saturated $Ca(IO_3)_2$ solution), 50 cm^3 in a plastic bottle	H272-H315-H319-H335
Solution C (Saturated $Ca(IO_3)_2$ in unknown dilute KIO_3 solution)**,** 50 cm^3 in a plastic bottle	H272-H315-H319-H335
Solution of **$Na_2S_2O_3$** 200 cm^3 in a plastic bottle	
KI 10% (w/v), 100 cm^3 in a plastic bottle	H300+H330-H312-H315-H319-H335
HCl 1 mol dm^{-3}, 100 cm^3 in a plastic bottle	H290-H314-H335
Starch solution 0.1% (w/v), 30 cm^3 in a dropping glass bottle	
Distilled water, 500 cm^3 in a **wash bottle**	
Distilled water, 1000 cm^3 in a plastic **gallon**	

[a]See page xx for definition of Risk and Safety Phrases

II. Equipment and labwares

Personal Labwares	Quantity
Beaker, 100 cm^3	2
Beaker, 250 cm^3	1
Erlenmeyer flask, 125 cm^3	9
Transfer pipette, 5.00 cm^3	2
Transfer pipette, 10.00 cm^3	1
Measuring cylinder, 10.0 cm^3	1
Measuring cylinder, 25.0 cm^3	2
Pasteur pipette	1
Rubber bulb for Pasteur pipette	1
Glass funnel, 7.5 cm diameter	2
Plastic funnel, 5.5 cm diameter	1
Filter paper in a zipped bag	3
Burette, 50.0 cm^3	1
Burette stand and clamp	1
O-ring with bosshead	2

Task 1B	a			b			c			Total
	a1	a2	a3	b1	b2	b3	c1	c2	c3	
Total	1	5	1	6	1	2	6	1	3	26
Score										

Accounted for 13% of Total Score

Task 1B: Calcium iodate

Calcium iodate is an inorganic salt composed of calcium and iodate ions. $Ca(IO_3)_2$ is sparingly soluble in water. Equilibrium is established between the undissolved salt and saturated solution of the salt.

$$Ca(IO_3)_{2\,(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2\,IO_3^-{}_{(aq)}$$

Titration data will be used to determine the concentration of iodate ions in a saturated solution of $Ca(IO_3)_2$ and then to determine the value of Ksp for $Ca(IO_3)_2$.

The concentration of iodate ion will be determined by titration with a standard solution of sodium thiosulfate ($Na_2S_2O_3$), in the presence of potassium iodide (KI). Starch will be used as an indicator.

Part a is associated with the standardization of $Na_2S_2O_3$. Part b is the determination of Ksp for $Ca(IO_3)_2$.

In Part C, solid $Ca(IO_3)_2$ is dissolved in an unknown dilute KIO_3 solution. After standing for 3 days, equilibrium is also established between the undissolved salt and saturated solution of the salt. The concentration of iodate ion will be determined using the same titrimetric method, and then used to calculate the concentration of the dilute KIO_3 solution.

Part a

Standardization of $Na_2S_2O_3$

1. Fill the burette with $Na_2S_2O_3$ solution.
2. Pipette 10.00 cm^3 of standard KIO_3 solution (provided as solution A, KIO_3 10.7042 g in 5.00 dm^3) into an Erlenmeyer flask. Add 10 cm^3 of 10%(w/v) KI and 10 cm^3 of 1 mol dm^{-3} HCl into a flask. The solution should turn dark brown as I_2 is formed.
3. Titrate with $Na_2S_2O_3$ solution until the solution has turned pale yellow. Add 2 cm^3 of 0.1%(w/v) starch solution. The solution should turn dark blue. Titrate carefully to the colorless endpoint. Record the volume of $Na_2S_2O_3$ solution.

a1) Balance relevant chemical equations.

...... $IO_3^-{}_{(aq)}$ + ... $I^-{}_{(aq)}$ + ... $H_3O^+{}_{(aq)}$ → ...... $I_{2(aq)}$ + ... $H_2O_{(l)}$

......$I_{2\,(aq)}$ + ... $S_2O_3^{2-}{}_{(aq)}$ → ...... $I^-{}_{(aq)}$ + ... $S_4O_6^{2-}{}_{(aq)}$

a2) Record volume of $Na_2S_2O_3$ solution.

(You do not need to fill in the entire table)

	Titration no.		
	1	2	3
Initial reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Final reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Consumed volume of $Na_2S_2O_3$ solution, cm^3			

Accepted volume, cm^3; V1 =

a3) Calculate the concentration of the $Na_2S_2O_3$ solution.

Concentration of $Na_2S_2O_3$, mol dm^{-3}: …………… (answer in 4 digits after decimal point)

(If the student cannot find the concentration of $Na_2S_2O_3$, use the concentration of 0.0700 mol dm^{-3} for further calculations.)

Part b

Determination of Ksp of $Ca(IO_3)_2$

1. You are provided with the filtrate of the filtered saturated solution of $Ca(IO_3)_2$. (Solution B)
2. Pipette 5.00 cm^3 of the filtrate into an Erlenmeyer flask. Add 10 cm^3 of 10% (w/v) KI and 10 cm^3 of 1 mol dm^{-3} HCl into a flask.
3. Titrate with $Na_2S_2O_3$ solution until the solution has turned pale yellow. Add 2 cm^3 0.1% (w/v) starch solution. The solution should turn dark blue. Titrate carefully to the colorless endpoint. Record the volume of $Na_2S_2O_3$ solution.

b1) Record volume of $Na_2S_2O_3$ solution.

(You do not need to fill in the entire table)

	Titration no.		
	1	2	3
Initial reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Final reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Consumed volume of $Na_2S_2O_3$ solution, cm^3			

Accepted volume, cm^3; V2 =

b2) Calculate the concentration of the IO_3^- solution.

Concentration of IO_3^-, mol dm^{-3}: …………………(answer in 4 digits after decimal point)

b3) Calculate value of Ksp for **$Ca(IO_3)_2$.**

Ksp for $Ca(IO_3)_2$ = ……………………………………(answer in 3 significant figures)

(If the student cannot find Ksp, use the value of 7×10^{-7} for further calculations.)

Part c

Determination of concentration of unknown dilute KIO_3 solution

1. You are provided with the filtrate of the filtered saturated solution of $Ca(IO_3)_2$ dissolved in the unknown dilute KIO_3 (provided as solution C).
2. Pipette 5.00 cm^3 of the filtrate solution into an erlenmeyer flask. Add 10 cm^3 of 10% (w/v) KI and 10 cm^3 of 1 mol dm^{-3} HCl into a flask.
3. Titrate with $Na_2S_2O_3$ solution until the solution has turned pale yellow. Add 2 cm^3 0.1% (w/v) starch solution. The solution should turn dark blue. Titrate carefully to the colorless endpoint. Record the volume of $Na_2S_2O_3$ solution.

c1) Record volume of $Na_2S_2O_3$ solution

(You do not need to fill in the entire table)

	Titration no.		
	1	2	3
Initial reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Final reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Consumed volume of $Na_2S_2O_3$ solution, cm^3			

Accepted volume, cm^3; V3 =

c2) Calculate the concentration of the IO_3^- in solution C.

Concentration of IO_3^-, mol dm^{-3}: ……………………(answer in 4 digits after decimal point)

c3) Calculate the concentration of the unknown dilute KIO_3 sample.

Concentration of IO_3^- , mol dm^{-3}: ……………… (answer in 4 digits after decimal point)

Student Code **AAA-1**

Task 1B	**a**			**b**			**c**			**Total**
	a1	a2	a3	b1	b2	b3	c1	c2	c3	
Total	1	5	1	6	1	2	6	1	3	26
Score										

a1) Balance relevant chemical equations.

…1… $IO_3^-{}_{(aq)}$ + …5… $I^-{}_{(aq)}$ + …6... $H_3O^+{}_{(aq)}$ → …3… $I_{2(aq)}$ + …9… $H_2O_{(l)}$ (0.5 points)

…1…$I_2{}_{(aq)}$ + …2… $S_2O_3^{2-}{}_{(aq)}$ → …2… $I^-{}_{(aq)}$ + …1… $S_4O_6^{2-}{}_{(aq)}$ (0.5 points)

a2) Record volume of $Na_2S_2O_3$ solution.

(You do not need to fill in the entire table)

	Titration no.		
	1	2	3
Initial reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Final reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Consumed volume of $Na_2S_2O_3$ solution, cm^3			

Accepted volume, cm^3; V1 = 12.08 ± 0.20 (5 points)

a3) Calculate the concentration of the $Na_2S_2O_3$ solution.

$$\frac{(C_{IO3-} \times V_{IO3-}) \times 6}{V_{S2O32-}} = C_{S2O32-}$$

$$\frac{(0.0100 \times 10.00) \times 6}{12.08} = 0.0497$$

Concentration of $Na_2S_2O_3$, mol dm^{-3}: …0.0497… (answer in 4 digits after decimal point) (1 point)

(If the student cannot find the concentration of $Na_2S_2O_3$, use the concentration of 0.0700 mol dm^{-3} for further calculations.)

Part b

Determination of Ksp of $Ca(IO_3)_2$

1. You are provided with the filtrate of the filtered saturated solution of $Ca(IO_3)_2$. (Solution B)
2. Pipette 5.00 cm^3 of the filtrate into an Erlenmeyer flask. Add 10 cm^3 of 10% (w/v) KI and 10 cm^3 of 1 mol dm^{-3} HCl into a flask.
3. Titrate with $Na_2S_2O_3$ solution until the solution has turned pale yellow. Add 2 cm^3 0.1% (w/v) starch solution. The solution should turn dark blue. Titrate carefully to the colorless endpoint. Record the volume of $Na_2S_2O_3$ solution.

b1) Record volume of $Na_2S_2O_3$ solution.

(You do not need to fill in the entire table)

	Titration no.		
	1	2	3
Initial reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Final reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Consumed volume of $Na_2S_2O_3$ solution, cm^3			

Accepted volume, cm^3; V2 = 13.20 ± 0.20 (6 points)

b2) Calculate the concentration of the IO_3^- solution.

$$\frac{(C_{S2O32-} \times V_{S2O32-}) \times 1}{V_{IO3-} \times 6} = C_{IO3-}$$

$$\frac{(0.0497 \times 13.20) \times 1}{5.00 \times 6} = 0.0219$$

Concentration of IO_3^-, mol dm^{-3}: …0.0219………..(answer in 4 digits after decimal point)

(1 point)

b3) Calculate value of Ksp for **$Ca(IO_3)_2$.**

$$C_{Ca^{2+}} = \frac{C_{IO_3^-}}{2}$$

$$= \frac{0.0219}{2} = 0.0110$$

Concentration of Ca^{2+}, mol dm^{-3}: ………0.0110……………………

$$Ksp = [Ca^{2+}][IO_3^-]^2$$

$$Ksp = (0.0110) \times (0.0219)^2$$

$$= 5.28 \times 10^{-6}$$

Ksp for $Ca(IO_3)_2$ = ……5.28×10^{-6}……………(answer in 3 significant figures) (2 points)

(If the student cannot find Ksp, use the value of 7×10^{-7} for further calculations.)

Part c

Determination of concentration of unknown dilute KIO_3 solution

1. You are provided with the filtrate of the filtered saturated solution of $Ca(IO_3)_2$ dissolved in the unknown dilute KIO_3 (provided as solution C).
2. Pipette 5.00 cm^3 of the filtrate solution into an erlenmeyer flask. Add 10 cm^3 of 10% (w/v) KI and 10 cm^3 of 1 mol dm^{-3} HCl into a flask.
3. Titrate with $Na_2S_2O_3$ solution until the solution has turned pale yellow. Add 2 cm^3 0.1% (w/v) starch solution. The solution should turn dark blue. Titrate carefully to the colorless endpoint. Record the volume of $Na_2S_2O_3$ solution.

c1) Record volume of $Na_2S_2O_3$ solution

(You do not need to fill in the entire table)

	Titration no.		
	1	2	3
Initial reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Final reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Consumed volume of $Na_2S_2O_3$ solution, cm^3			

Accepted volume, cm^3; V3 = 14.43 ± 0.20 (6 points)

c2) Calculate the concentration of the IO_3^- in solution C.

$$\frac{(C_{S2O32-} \times V_{S2O32-}) \times 1}{V_{IO3-} \times 6} = C_{IO3-}$$

$$\frac{(0.0497 \times 14.43) \times 1}{5.00 \times 6} = 0.0239$$

Concentration of IO_3^-, mol dm^{-3}: …0.0239………(answer in 4 digits after decimal point)

(1 point)

c3) Calculate the concentration of the unknown dilute KIO_3 sample.

$$\frac{Ksp}{[IO_3^-]^2} = \frac{5.28 \times 10^{-6}}{(0.0239)^2} = [Ca^{2+}]$$

$$= 0.00924$$

Concentration of Ca^{2+}, mol dm^{-3}: ………0.00924 ……………………………….

$$[KIO_3]_{sample} = [IO_3^-]_{in\ soln.C} - [IO_3^-]_{solubilized\ Ca(IO3)2}$$

$$= 0.0239 - (2 \times [Ca^{2+}])$$

$$= 0.0239 - (2 \times 0.00924)$$

Concentration of IO_3^-, mol dm^{-3}: …0.0542.. (answer in 4 digits after decimal point)

(3 point)

Titolazione permanganometrica

(o altre ossidimetriche)

Titolazione permanganometrica

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

A sample contains two of the following cations: Ag^+, Pb^{2+}, Fe^{2+}, Cr^{3+}, Co^{2+}, Al^{3+}, Mn^{2+}, and one of the following anions: SO_4^{2-}, Cl^-, NO_3^-.

Prove the cations and anions in the sample by means of the following reagents:
2 N-HCl, concentrated H_2SO_4, 2 N-H_2SO_4, 2 N-HNO_3, 2 N-CH_3COOH, NaOH, NH_4OH, H_2O_2, Na_2CO_3, KNO_3/Na_2CO_3, NH_4SCN, $Na_2B_4O_7$, NaF, C_2H_5OH, $BaCl_2$, $AgNO_3$, NH_4Cl, $(NH_4)_2Fe(SO_4)_2$, alizarin B.

Write the results into the attached table in the following way:

a) into the column "Reagent" write the formula of the reagent which was needed to prove whether the cation or anion is present or absent in the sample;

b) into the column "+/–" mark the presence or absence of an ion, proved in the sample, by the sign "+" and "–" , respectively.

PROBLEM 2 (practical)

A solution contains sodium oxalate and oxalic acid.

Determine how many milligrams of sodium oxalate and oxalic acid are contained in the solution under investigation.

The following solutions are at your disposal: $KMnO_4$ (c = 0.01972 mol dm^{-3}), NaOH (c = 0.1019 mol dm^{-3}), concentrated H_2SO_4, and a solution of phenolphthalein.

PROBLEM 2 (practical)

Determine the mass of potassium permanganate in the solution you are given. You are provided with hydrochloric acid of a given concentration, a potassium hydroxide solution of an unknown concentration, an oxalic acid solution of an unknown concentration, and a sulphuric acid solution (2 N).

Equipment and reagents:

A burette for titration, indicators (methyl orange, lithmus, phenolphthalein), pipettes (volumes 10, and 15 or 20 cm^3), 2 volumetric flasks (250 cm^3), 2 titration flasks (100 – 150 cm^3).

PROBLEM 3 (practical)

Titrimetric determination of potassium peroxodisulfate ($K_2S_2O_8$)

A) *Principle*

To the sample ($K_2S_2O_8$) a measured amount of a Fe(II) solution is added in an excess. The excess of the Fe(II) is determined using a standard $KMnO_4$ solution.

B) *Procedures*

1) Determination of the concentration of the Fe(II) solution, $[Fe(NH_4)_2(SO_4)_2]$

To a titration vessel, 25.0 cm^3 Fe(II) solution, 10 cm^3 H_3PO_4 (ca. 3.7 mol dm^{-3}) and 10 cm^3 H_2SO_4 (ca. 1 mol dm^{-3}) are added and titrated with the $KMnO_4$ solution to a pink colouration. The concentration of $KMnO_4$ in the solution is exactly 0.02 mol dm^{-3}. Two titrations are carried out and the consumption of the $KMnO_4$ solution is recorded. The mean value (= V_1) is to be given.

2) Determination of peroxodisulfate in the same solution

   a) The dissolved sample is diluted with distilled water to 100 cm^3 in a standard flask and mixed.

   b) 25.0 cm^3 of this solution are transferred to a titration vessel and mixed with 10 cm^3 H_3PO_4 (ca. 3.7 mol dm^{-3}), 10 cm^3 H_2SO_4 (ca. 1 mol dm^{-3}) and 25.0 cm^3 of the Fe(II) solution. The mixture is allowed to stand for 5 minutes and titrated with the $KMnO_4$ solution (0.02 mol dm^{-3}) to a pink colourization. Two titrations are carried out and the consumption of the $KMnO_4$ solution is recorded. The mean value (= V_2) is to be given.

C) *Calculation and evaluation*

I) Reaction equations: To be given:

Partial equations with electron balance

Overall equations

1) Reaction of peroxodisulfate with Fe(II):

Partial:

a) $S_2O_8^{2-}$ . . . .

b) Fe^{2+} . . . .

c) Overall reaction:

2) Reaction of Fe(II) with permanganate:

Partial:

a) Fe^{2+} . . . .

b) MnO_4^- . . . .

c) Overall reaction:

II) The concentration of the Fe(II) solution

1) Give the consumption of the $KMnO_4$ solution (cm^3) for 25.0 cm^3 of the Fe(II) solution (= V_1); See Procedure 1.

2) Calculate the concentration of the Fe(II) solution in mol dm^{-3}.

III) Determination of $K_2S_2O_8$

1) Give the consumption of the $KMnO_4$ solution in the back-titration of the excess Fe(II) solution in cm^3 (= V_2); See Procedure 2.

2) How many mg $K_2S_2O_8$:

3) Calculate the concentration of $K_2S_2O_8$ in the sample solution in mol dm^{-3}.

SOLUTION

I/1/a $S_2O_8^{2-} + 2\,e^- \rightarrow 2\,SO_4^{2-}$

b) $Fe^{2+} \rightarrow Fe^{3+} + e^-$ /. 2

c) $S_2O_8^{2-} + 2\,Fe^{2+} \rightarrow 2\,SO_4^{2-} + 2\,Fe^{3+}$

I/2/a $Fe^{2+} \rightarrow Fe^{3+} + e^-$ /. 2

$MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$

$5\,Fe^{2+} + MnO_4^- \rightarrow 5\,Fe^{3+} + Mn2^+ + 4\,H_2O$

II/1 V_1 cm^3 $KMnO_4$ (0.02 mol dm^{-3}) / 25 cm^3 Fe(II)

2. $$c(Fe^{2+}) = \frac{V_1 \times 0.02 \times 5}{25} = \ldots\ldots\text{ mol/l}$$

III/1 V_2 cm^3 $KMnO_4$ solution (0.02 mol dm^{-3}) for the back titration

2.

$$\alpha)\quad \frac{(V_1 - V_2)\times 0.02\times 5}{1000}\times\frac{270.33}{2} = \ldots\ldots\ldots \text{ mg } K_2S_2O_8$$

$$\beta)\quad \frac{25\times c(\text{Fe}^{2+}) - V_2\times 0.02\times 5}{1000}\times\frac{270.33}{2} = \ldots\ldots\ldots \text{ mg } K_2S_2O_8$$

3.

$$\alpha)\quad \frac{(V_1 - V_2)\times 0.02\times 5}{1000}\times\frac{40}{2} = \ldots\ldots\ldots \text{ mol } K_2S_2O_8\,/\,\text{dm}^3$$

$$\beta)\quad \frac{25\times c(\text{Fe}^{2+}) - V_2\times 0.02\times 5}{1000}\times\frac{40}{2} = \ldots\ldots\ldots \text{ mol / dm}^3$$

PROBLEM 2 (practical)

A solution in a graduated flask contains a mixture of oxalic acid and ammonium oxalate.

One of the bottles denoted X, Y, and Z contains a solution of a calibration substance with reducing character at a concentration of 0.1000 mol dm^{-3}.

You are required to solve the following tasks:

a) Determine the quantity of oxalic acid and of ammonium oxalate in the solution in the graduated flask. (The result will be given in grams.)

b) Write the formula for the substance with reducing character and the equations of the chemical reactions which led to its determination.

In order to carry out the analyses the following solutions are available:

HCl (c = 0.1000 mol dm^{-3}), NaOH (c = 2 mol dm^{-3}), $KMnO_4$ (c = 0.02 mol dm^{-3}), 25 % H_2SO_4, HNO_3 (c = 2 mol dm^{-3}), 5 % $BaCl_2$, 5 % $AgNO_3$, 5 % $Hg_2(NO_3)_2$, phenolphthalein 0.1 %, methyl red 1 %.

c) Describe the procedure used in the individual steps, indicators employed and partial results.

$M_r(H_2C_2O_4) = 90.04$

$M_r((NH_4)_2C_2O_4) = 124.11$

SOLUTION

ANSWER SHEET:

A$_1$ – Identification of the solution with the reducing substance X, Y, Z: $Fe(NH_4)_2(SO_4)_2$

A$_2$ – Identification reactions for the ions of the substance

- $Fe^{2+} + 2\ NaOH \rightarrow Fe(OH)_2 + 2\ Na^+$
- $NH_4^+ + NaOH \rightarrow NH_3\uparrow + H_2O + Na^+$
- $4\ NH_3 + 2\ Hg_2(NO_3)_2 + H_2O \rightarrow O(Hg)_2NH_2.NO_3 + 3\ NH_4OH$
- $SO_4^{2-} + BaCl_2 \rightarrow BaSO_4 + 2\ Cl^-$

B$_1$– Preparation of the 0.1 M NaOH solution

. . . . cm^3 in 200.0 cm^3

B_2 – Concentration of the NaOH in its solution: . . . . M

Indicator used: . . . .

C – Concentration of $KMnO_4$ in its solution . . . . M

D_1 – Mass of oxalic acid in the initial solution . . . . g

Indicator used . . . .

D_2 – Mass of ammonium oxalate in the initial solution . . . . g

Solution

A_1 – 1-2 cm^3 of solution X, Y and Z are put into three test tubes. 6 N H_2SO_4 and a drop of $KMnO_4$ solution are added. The solution which loses colour is the one with reducing character.

A_2 – Establishment of the formula:

. . . . + NaOH – greenish white precipitate $\Rightarrow$ Fe^{2+}

. . . . + NaOH at the upper end of the test-tube, filter paper with a drop of $Hg_2(NO_3)_2$, black spot $\Rightarrow$ NH_4^+

. . . . + $BaCl_2$ – white precipitate $\Rightarrow$ SO_4^{2-}

. . . . + $AgNO_3$ + HNO_3 $\Rightarrow$ Cl^- is absent

Accordingly the substance used is $Fe(NH_4)_2(SO_4)_2$.

The chemical reactions:

$Fe^{2+} + 2\ Na^+ + 2\ OH^- \rightarrow Fe(OH)_2 + 2\ Na^+$

$NH_4^+ + Na^+ + OH^- \rightarrow NH_3 + H_2O + Na^+$

$4\ NH_3 + 2\ Hg_2(NO_3)_2 \rightarrow O(Hg)_2NH_2 . NO_3 + 2\ Hg + 3\ NH_4NO_3$

$SO_4^{2-} + Ba^{2+} + 2\ Cl^- \rightarrow BaSO_4 + 2\ Cl^-$

B_1 – 5 cm^3 2 M solution $\Rightarrow$ 100 cm^3 0.1 M solution

B_2 – *V* cm^3 0.1000 N HCl + 0.1 N NaOH in the presence of phenolphthalein.

C – *V* cm^3 solution X + 10.0 cm^3 H_2SO_4 + H_2O is titrated at elevated temperature with $KMnO_4$.

D_1 – The solution which is to be analyzed is filled to the mark; *V* cm^3 of this solution is titrated with NaOH in the presence of methyl red. The quantity of oxalic acid (moles and g) is calculated.

D_2 – *V* cm^3 solution to be analyzed + 10.0 cm^3 6 N H_2SO_4 + H_2O are heated and titrated with $KMnO_4$ solution.

The total amount of oxalate is calculated (in mol).

The difference gives the amount of ammonium oxalate (moles and g).

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 °C, 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 °C 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

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

n(oxalate) from dissolved calcium oxalate precipitate:

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

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

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

In original Ca/Mg solution:

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

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 sufficient 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 °C 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.

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.

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.

Practical Problem 3 **13 %** of the total	**Code:**		Task	1	2	3	4	5	6	7	8	9	10	Total
	Examiner		Mark	0	25	2	25	3	4	3	2	5	2	**71**
			Grade											

Practical Problem 3. Analysis of a hydrated zinc iron(II) oxalate double salt

Zinc iron(II) oxalate double salt is a common precursor in the synthesis of zinc ferrite which is widely used in many types of electronic devices due to its interesting magnetic properties. However, such double salts may exist with different compositions and different amount of water depending on how the sample was synthesized.

You will analyze a pure sample of hydrated zinc iron(II) oxalate double salt (**Z**) in order to determine its empirical formula.

Procedure

The concentration of the standard $KMnO_4$ is posted on the lab walls.

Bring a clean 250 mL beaker to the lab assistant who will be waiting by the balance. You will receive a pure sample of **Z** for analysis. Accurately weigh between 0.7-0.8 g of the pure sample **Z** onto the weighing paper (***m***, grams). This should then be immediately quantitatively transferred into your 250 mL beaker for analysis, and its mass recorded in table below.

***Task 3.1:* Record the mass of the sample of pure Z taken.**

Mass of sample, *m* (gram)	**Lab assistant's signature**
------------------	---------------------

Analysis of Z

- Using the 100 mL graduated measuring cylinder, measure *ca.* 30 mL of 30 wt% H_2SO_4 solution and add it into the 250-mL beaker containing your accurately weighed pure sample of **Z**. To speed up the dissolving of your sample you may use the hotplate stirrer to warm up the mixture, **but be careful not to boil** it. *You should not use the digital thermometer as the acid may damage it.* After the solid has dissolved, remove the beaker from the hotplate stirrer and cool it to close to room temperature. After the solution has cooled, quantitatively transfer it into the 100 mL volumetric flask. Add distilled water up to the 100 mL–mark. We will now call this solution **C.**

- Use an appropriately labeled beaker to transfer the standardized **$KMnO_4$** solution into the burette graduated with **brown** marks.
- Use another appropriately labeled beaker to transfer the standardize **EDTA** solution into the burette graduated with **blue** marks.

Titration with $KMnO_4$

a) Using the 5 mL graduated pipette add 5.00 mL of the solution **C** into a 250 mL conical flask.

b) To this conical flask add about 2 mL of 30 wt% H_2SO_4 solution, about 3 mL of 3.0 M H_3PO_4 solution, and about 10 mL of distilled water. Heat the mixture on the hot plate stirrer until hot, **but be careful not to boil** it.

c) Titrate the hot solution with the standardized $KMnO_4$ solution, recording your burette readings in the table below. At the end point of the titration, the pink color of the solution appears. Repeat the titration as desired and report your accepted volume of $KMnO_4$ solution consumed (V_1 mL) in the table.

<u>Task 3.2</u>: Record volumes of standardized $KMnO_4$ solution consumed

(You DO NOT need to fill in the entire table)

	Titration No			
	1	**2**	**3**	**4**
Initial reading of the burette of $KMnO_4$, mL				
Final reading of the burette of $KMnO_4$, mL				
Consumed volume of $KMnO_4$, mL				

Accepted volume, V_1 = ________ mL

***Task 3.3*: Can aqueous HCl or HNO_3 be used instead of H_2SO_4 for the dissolving of sample Z and the subsequent analyses?**

HCl	**YES** ☐	**NO** ☐
HNO_3	**YES** ☐	**NO** ☐

Titration with EDTA

- Clean both the 250 mL beakers ready for the next part of the experiment. Pipette 10.00 mL of solution **C** into a 250 mL beaker. Heat and stir the solution on the hotplate stirrer, **but be careful not to boil** it. Add *ca.* 15 mL of 20 wt% NaOH solution to the beaker and keep it on the hotplate for *ca. 3-5* min in order to complete the precipitation of iron hydroxide, and to convert all Zn^{2+} ions into the ionic complex $[Zn(OH)_4]^{2-}$.
- Using a glass funnel and the large quantitative filter paper, filter the hot suspension directly into the 250 mL conical flask. **From this point take care with the volumes as you will be preparing a standard solution of exactly 100 mL from the filtrate**. As it is filtering, prepare some warm distilled water in a 250 mL beaker (*ca.* 50 mL). Wash the precipitate on the filter paper (at least 5 times) with small portions (*ca.* 5 mL) of the warm distilled water. Cool the filtrate down and then quantitatively transfer it into the 100 mL volumetric flask via a glass funnel. Add distilled water to make up to the 100 mL mark. This will now be referred to as solution **D**.
- Pipette 10.00 mL of solution **D** into a 250 mL conical flask. Add *ca.*10 mL ammonia buffer solution ($pH = 9 – 10$) and a small quantity of the ETOO indicator using the glass spatula spoon. Mix well to obtain a purple solution. Titrate the solution with the standardized 2.00×10^{-3} M EDTA solution, recording your burette readings in table below. At the end point, the color of the solution turns blue. Repeat the titration as desired and report your accepted volume of EDTA solution consumed (V_2 mL) in the table.

***Task 3.4*: Record the volumes of EDTA solution consumed**

(You DO NOT need to fill in the entire table)

	Titration No			
	1	**2**	**3**	**4**
Initial reading of the burette of EDTA, mL				
Final reading of the burette of EDTA, mL				
Consumed volume of EDTA, mL				

Accepted volume, **V_2** = ________ **mL**

Determination of the empirical formula of Z

***Task 3.5:* Calculate the number of moles of Zn^{2+}, $n_{Zn^{2+}}$, present in 100 mL of solution C.**

$n_{Zn^{2+}}$ (mol): ……………

***Task 3.6:* Give the ionic equations for the reduction-oxidation reactions taking place in the titration with $KMnO_4$.**

<u>Task 3.7:</u> Calculate the number of moles of Fe^{2+}, $n_{Fe^{2+}}$, present in 100 mL of solution C. **[YOU WILL NEED THE PRECISE CONCENTRATION OF KMnO$_4$ POSTED ON THE WALLS IN YOUR LAB]**

V$_1$, mL = ……………………………………….

$n_{Fe^{2+}}$ (mol): …………………………

<u>Task 3.8:</u> Calculate the number of moles of C$_2$O$_4^{2-}$ anion, $n_{C_2O_4^{2-}}$, in 100 mL of solution C.

$n_{C_2O_4^{2-}}$ = ……………………………………………..

Task 3.9: ***Calculate the number of moles of water,*** n_{H_2O}***, in the original sample of Z taken for analysis.***

***Task 3.10**: Give the empirical formula of Z:*

TASK 2. Analysis of the solution of a chromium – vanadium alloy (12 points)

Quest. #	Q1	Q2	Q3a	Q3b	Q4a	Q4b	Q5a	Q5b	Q6	Total
Marks	32	32	1	1	3	2	4	10	5	90

Antiferromagnetic materials show a good prospect in the development of memory devices for ultra-high-density data storage, the world's smallest magnetic memory bit using only 12 atoms being one of prime examples. Vanadium – chromium alloys exhibit antiferromagnetic properties at subzero temperatures. It is obvious that composition of alloys used in various hi-tech applications should be accurately controlled.

In this task, you will analyze an aqueous solution simulating the product of digestion of vanadium – chromium alloy sample. The task consists of two parts:

- **I.** Oxidation of vanadyl (VO^{2+}) to vanadate (VO_3^-) in the test solution using potassium permanganate, followed by determination **of vanadium** (note that chromium (III) is not oxidized under these conditions).
- **II.** Oxidation of the test solution with ammonium persulfate, followed by titrimetric determination of the **total content of vanadium and chromium** with Mohr's salt (Ammonium iron(II) sulfate).

Procedure

Note!

- ***The amount of vanadium and chromium should be calculated and reported in mg per 100 mL of the test solution.***
- ***Start doing this task with Part A, since you will need time to oxidize the test solution to be analyzed in Part C.***
- ***The 10.00-mL volumetric pipette has two graduation lines. You should pipette a volume between the two lines.***

Part A. Preparation of the solution for determination of vanadium and chromium total content

1. Transfer a 10.00-mL aliquot of your **test solution** into the 150-mL beaker and add 20 mL of 1M sulfuric acid using the 25-mL graduated cylinder.
2. Add 6–8 drops of the 0.3% solution of silver nitrate (the catalyst) and heat the mixture on the hotplate to 70–80°C (position 3), until condensate on the beaker wall appears.

3. Add 20 mL of the 10% ammonium persulfate solution to the heated mixture using the 100-mL graduated cylinder.
4. Continue heating and observe the appearance of **yellow** color, indicating the formation of dichromate.

Note! ***You can perform the determination of vanadium (Part B, 1 – 6), while the mixture is being heated.***

5. Keep heating the mixture for 10-15 min (position 3) after appearance of the yellow color to decompose the excess of ammonium persulfate (the decomposition is over when you see no small bubbles in the solution).
6. Cool the solution **to ambient temperature**.
7. Transfer **quantitatively** the solution from the 150-mL beaker into the **100-mL volumetric flask**, dilute to the mark with distilled water, stopper the flask and mix thoroughly.

Part B. Titrimetric determination of Vanadium

1. Transfer a 5.00-mL aliquot of the test solution into an Erlenmeyer flask using the graduated pipette.

Note! ***The 5.00-mL graduated pipette is self-draining.***

2. Carefully add 0.03 M potassium permanganate solution dropwise, shaking the flask after adding each drop until light pink color appears. Make sure that the light pink color is stable. Remove the excess of potassium permanganate by adding 0.03 M oxalic acid solution dropwise. Shake the flask after each drop until the light pink color changes to **pale blue**. Let the solution stand for about 1 min to make sure that the pink color has disappeared completely.
3. Transfer 10 mL of the 1M H_2SO_4 solution into the Erlenmeyer flask using the 25-mL graduated cylinder.
4. Add 2–3 (**not more!**) drops of the indicator into the Erlenmeyer flask and shake it vigorously. Let the flask stand for 2–3 min and observe the **purple** color appearance.
5. Fill the burette with the Mohr's salt solution. Use the 100-mL plastic beaker labeled "Waste" to drain the excess of Mohr's salt solution from the burette, record the initial reading.
6. Titrate the solution in the Erlenmeyer flask with the Mohr's salt solution until the color changes to **pure light green** through brownish-grey one.
7. Take the final reading of the burette. Repeat as necessary.

Q1. Fill in Table 2.

Table 2. Determination of vanadium

Titration №	1	2	3			
Initial reading of the burette, mL						
Final reading of the burette, mL						
Consumed volume, mL						

Accepted volume, V_1 _____mL

Part C. Titrimetric determination of vanadium and chromium total content in the test solution

1. Wash the 10.00-mL volumetric pipette with distilled water, rinse with the solution prepared in 100-mL volumetric flask (obtained in part A).
2. Pipette a 10.00-mL aliquot into an Erlenmeyer flask, add 10 mL of 1M H_2SO_4 solution using the 25-mL graduated cylinder.
3. Add 3–4 drops of the indicator. Vigorously shake the flask and let it stand for 3–4 min. Observe appearance of **red** color.
4. Fill the burette with the Mohr's salt solution. Use the 100-mL plastic beaker labeled "Waste" to drain the excess of Mohr's salt solution from the burette, record the initial reading.
5. Titrate the solution in the flask with the Mohr's salt solution until the color changes to **light yellow-green**.
6. Take the final reading of the burette. Repeat as necessary.

Q2. Fill in Table 3.

Table 3. Determination of vanadium and chromium total content

Titration No	1	2	3			
Initial reading of the burette, mL						
Final reading of the burette, mL						
Consumed volume, mL						

Accepted volume, V_2 _____mL

Part D. Questions and Data Analysis

Q3. Write down the balanced chemical equations for the reactions that take place upon**:**

a) oxidation of the test solution with **potassium permanganate**

b) titration of vanadate with Mohr's salt

a)	
b)	= $VOSO_4$

Q4. Write down the balanced chemical equations for the reactions that take place upon**:**

a) oxidation of the test solution with **ammonium persulfate**

b) titration of the oxidized test solution with Mohr's salt

a)
b)

Q5. Calculate the a) V(IV) and b) Cr(III) concentrations in the test solution. Calculate the amount of the metals in mg **per 100 mL of test solution**.

a) Your work: Vanadium:
b) Your work: Chromium:

Q6. This protocol can not be applied to the determination of vanadium and chromium in steels, if the steel was digested by conc. HCl. Give equations of two reactions to explain the reasons behind.

TASK 2. Analysis of the solution of a chromium – vanadium alloy (12 points)

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II. Oxidation of the test solution with ammonium persulfate, followed by titrimetric determination of the **total content of vanadium and chromium** with Mohr's salt (Ammonium iron(II) sulfate).

Procedure

Note!

- ***The amount of vanadium and chromium should be calculated and reported in mg per 100 mL of the test solution.***
- ***Start doing this task with Part A, since you will need time to oxidize the test solution to be analyzed in Part C.***
- ***The 10.00-mL volumetric pipette has two graduation lines. You should pipette a volume between the two lines.***

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2. Add 6–8 drops of the 0.3% solution of silver nitrate (the catalyst) and heat the mixture on the hotplate to 70–80°C (position 3), until condensate on the beaker wall appears.

3. Add 20 mL of the 10% ammonium persulfate solution to the heated mixture using the 100-mL graduated cylinder.
4. Continue heating and observe the appearance of **yellow** color, indicating the formation of dichromate.

Note! ***You can perform the determination of vanadium (Part B, 1 – 6), while the mixture is being heated.***

5. Keep heating the mixture for 10-15 min (position 3) after appearance of the yellow color to decompose the excess of ammonium persulfate (the decomposition is over when you see no small bubbles in the solution).
6. Cool the solution **to ambient temperature**.
7. Transfer **quantitatively** the solution from the 150-mL beaker into the **100-mL volumetric flask**, dilute to the mark with distilled water, stopper the flask and mix thoroughly.

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3. Transfer 10 mL of the 1M H_2SO_4 solution into the Erlenmeyer flask using the 25-mL graduated cylinder.
4. Add 2–3 (**not more!**) drops of the indicator into the Erlenmeyer flask and shake it vigorously. Let the flask stand for 2–3 min and observe the **purple** color appearance.
5. Fill the burette with the Mohr’s salt solution. Use the 100-mL plastic beaker labeled “Waste” to drain the excess of Mohr’s salt solution from the burette, record the initial reading.
6. Titrate the solution in the Erlenmeyer flask with the Mohr’s salt solution until the color changes to **pure light green** through brownish-grey one.
7. Take the final reading of the burette. Repeat as necessary.

Q1. Fill in Table 2.

Table 2. Determination of vanadium

Titration №	1	2	3			
Initial reading of the burette, mL						
Final reading of the burette, mL						
Consumed volume, mL						

Accepted volume, V_1 _____mL

Part C. Titrimetric determination of vanadium and chromium total content in the test solution

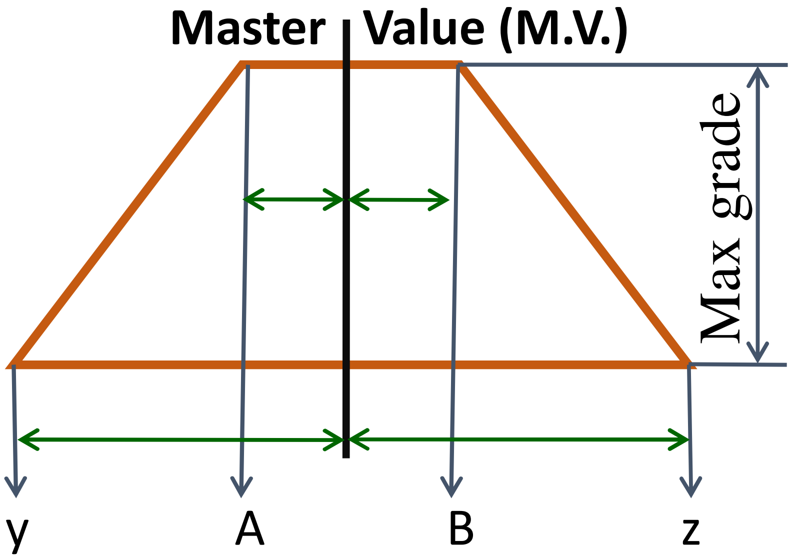
1. Wash the 10.00-mL volumetric pipette with distilled water, rinse with the solution prepared in 100-mL volumetric flask (obtained in part A).
2. Pipette a 10.00-mL aliquot into an Erlenmeyer flask, add 10 mL of 1M H_2SO_4 solution using the 25-mL graduated cylinder.
3. Add 3–4 drops of the indicator. Vigorously shake the flask and let it stand for 3–4 min. Observe appearance of **red** color.
4. Fill the burette with the Mohr's salt solution. Use the 100-mL plastic beaker labeled "Waste" to drain the excess of Mohr's salt solution from the burette, record the initial reading.
5. Titrate the solution in the flask with the Mohr's salt solution until the color changes to **light yellow-green**.
6. Take the final reading of the burette. Repeat as necessary.

Q2. Fill in Table 3.

Table 3. Determination of vanadium and chromium total content

Titration No	1	2	3			
Initial reading of the burette, mL						
Final reading of the burette, mL						
Consumed volume, mL						

Accepted volume, V_2 _____mL



If A< Value < B, then Grade = *Maxgrade*

If Value < y, then Grade = 0, If Value > z, then Grade = 0

If y < Value < A, then Grade = $Maxgrade * \frac{Value-y}{A-y}$

If B < Value < z, then Grade = $Maxgrade * \frac{z-Value}{z-B}$

For Parts B and C (max marks 32 for each titration)

Parameter	Part B	Part C
A	M.V.-2.5%	M.V.-3.5%
B	M.V.+2.5%	M.V.+3.5%
y	M.V.-7.5%	M.V.-10%
z	M.V.+7.5%	M.V.+10%

Part D. Questions and Data Analysis

Q3. Write down the balanced chemical equations for the reactions that take place upon**:**

a) oxidation of the test solution with **potassium permanganate**

b) titration of vanadate with Mohr's salt

a) $2KMnO_4 + 10VOSO_4 + 12H_2O = 2MnSO_4 + 10HVO_3 + K_2SO_4 + 7H_2SO_4$ 1 mark

b) $2HVO_3 + 2FeSO_4 + 3H_2SO_4 = 2VOSO_4 + Fe_2(SO_4)_3 + 4H_2O$ 1 mark

Q4. Write down the balanced chemical equations for the reactions that take place upon**:**

a) oxidation of the test solution with **ammonium persulfate**

b) titration of the oxidized test solution with Mohr's salt

a) $Cr_2(SO_4)_3 + 3(NH_4)_2S_2O_8 + 7H_2O = H_2Cr_2O_7 + 3(NH_4)_2SO_4 + 6H_2SO_4$ 1.5 mark

$2VOSO_4 + (NH_4)_2S_2O_8 + 4H_2O = 2HVO_3 + (NH_4)_2SO_4 + 3H_2SO_4$ 1.5 mark

b) $H_2Cr_2O_7 + 6FeSO_4 + 6H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$ 1.5 mark

$2HVO_3 + 2FeSO_4 + 3H_2SO_4 = 2VOSO_4 + Fe_2(SO_4)_3 + 4H_2O$ 0.5 mark

Q5. Calculate the a) V(IV) and b) Cr(III) concentrations in the test solution. Calculate the amount of the metals in mg **per 100 mL of test solution**.

a) Your work: Vanadium:

a) $C(VO^{2+}) = \frac{V_1(Fe^{2+}) * C(Fe^{2+}) * 1000}{1000 * V_{3,1}}$, mol L^{-1} 3 marks

b) $m(V) = 0{,}1 * C(VO^{2+}) * M(V) * 1000$, mg 1 mark

b) Your work: Chromium:

a) $n(Fe^{2+} on\ Cr_2O_7^{2-}) = \frac{V_2(Fe^{2+}) * C(Fe^{2+})}{1000} - 2 * \frac{V_1(Fe^{2+}) * C(Fe^{2+})}{1000} * \frac{10}{100}$, mol L^{-1}
4 marks

b) $n(Cr_2O_7^{2-}) = \frac{1}{6} n(Fe^{2+}\ on\ Cr_2O_7^{2-})$, mol L^{-1} 2 marks

c) $C(Cr^{3+}) = 2 * \frac{n(Cr_2O_7^{2-}) * 100}{10} * \frac{1000}{100}$, mol L^{-1} 2 marks

d) $m(Cr) = 0{,}1 * C(Cr^{3+}) * M(Cr) * 1000$, mg 2 marks

Q6. This protocol can not be applied to the determination of vanadium and chromium in steels, if the steel was digested by conc. HCl. Give equations of two reactions to explain the reasons behind.

$Fe + 2HCl \rightarrow FeCl_2 + H_2\uparrow$

$2FeSO_4 + (NH_4)_2S_2O_8 \rightarrow Fe_2(SO_4)_3 + (NH_4)_2SO_4$

$2Cl^- + S_2O_8^{2-} \rightarrow Cl_2 + 2SO_4^{2-}$

(decrease of the amount of ammonium persulfate due to its reaction with excess of iron(II) in steels)

2.5 marks

$Ag^+ + Cl^- \rightarrow AgCl\downarrow$; $AgCl + Cl^- \rightarrow AgCl_2^-$

(reaction between the catalyst and chloride)

2.5 marks

Titolazione argentometrica

IChO

International Chemistry Olympiad

PROBLEM 2 (practical)

Analysis of the Nickel Salt:

For the analysis of the salt, only one sample solution is prepared. The determination of the components is achieved by titrating each time 25 ml of the sample solution in duplicate.

For the determination of the ammonia and chlorine content a back titration is carried out. For that purpose a certain amount of reagent is added in excess. The total amount of reagent, available for the sample, is determined by following the same procedure for 25 ml of a blank solution. This titration should not be carried out in duplicate.

Prepare the following solutions:

A) Sample solution:

Pipette 25.0 ml of 1.6 M nitric acid into a volumetric flask of 250 ml. Add a sample of about 1.2 g of the amminenickel(II) chloride and dilute with water to a volume of 250 ml.

B) Blank solution:

Pipette 25.0 ml of the same 1.6 M nitric acid and dilute it with water to a volume of 250 ml.

Note:

1) For the chlorine determination use conical (Erlenmeyer) flasks with a ground glass stopper.
2) The nitric acid contains a small amount of hydrochloric acid. The total acid content is 1.6 M.

a) *Determination of the ammonia content*

Titrate the solutions with a standard solution of NaOH (about 0.1 M). Indicator: methylred, 0.1 % solution in ethanol.

Calculate the percentage of ammonia in the salt.

b) *Determination of the nickel content*

Add about 100 ml of water, 2 ml of ammonia solution (25 %) and 5 drops of murexide solution to the nickel solution, which now should have a yellow colour. Titrate the solution with a standard solution of EDTA (about 0.025 M) until a sharp colour change from yellow to violet is observed. Calculate the percentage of nickel in the salt.

c) *Determination of the chlorine content*

Execute the titration as quickly as possible after the addition of the reagent!

Add to each solution 25 ml of 0.1 M silver nitrate solution. Add about 5 ml of toluene, shake vigorously, add indicator and titrate with the standard solution of ammonium thiocyanate (-rhodanide, about 0.05 M) until a permanent colour change to red is observed. At the end of the titration, shake vigorously again. The red coloration should persist.

Indicator: 1 ml of a saturated solution of iron(III) sulphate.

Calculate the percentage of chlorine in the salt.

Data: Relative atomic masses: H = 1, Cl = 35.5, Ni = 58.7, N = 14.

Questions:

Calculate from the results obtained the molar ratio of the components to two decimal points and enter this on the report form in the format: Ni : Cl : NH_3 = 1.00 : x : y.

PROBLEM 2 (Practical)

Volumetric Determination of Bromide by Back-titration with Thiocyanate after Precipitation with Silver Ions in Excess

Moments worth considering:

- The candidates must consider the number of significant figures that will be reasonable in the results.
- The candidates must be able to carry out the whole analysis by using the delivered portions of silver nitrate and potassium thiocyanate. Supplementation of these two solutions will not be available.
- Only *one* 25 cm^3 pipette will be at disposal for each candidate.

Principle

Bromide is precipitated as silver bromide after a known amount of silver ions has been added in excess.

$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$ (faint yellow-green)

The excess of silver ions is titrated with thiocyanate with a known concentration, after a previous standardization of the thiocyanate solution.

During the titration of the following reaction takes place resulting in the precipitation of silver thiocyanate:

$Ag^+(aq) + SCN^-(aq) \rightarrow AgSCN(s)$ (white)

Fe(III) is added as indicator producing a red-coloured ion at the equivalence point:

$Fe^{3+}(aq) + SCN^-(aq) \rightarrow FeSCN^{2+}(aq)$ (red)

a) *Procedures*

Every candidate has got a 0.5 dm^3 brown bottle with screw cap, containing the potassium thiocyanate solution (about 0.08 M) and also a 0.25 dm^3 brown bottle with screw cap, containing the silver nitrate solution. The concentration of this solution is 0.1000 M. The exact concentration of the KSCN solution is to be determined by the candidates.

i) *Determination of bromide in the unknown sample solution*

Fill the 250 cm^3 volumetric flask containing the bromide sample solution to the mark with water. Transfer three 25.00 cm^3 portions (pipette) of the sample solution to three Erlenmeyer flasks. Add about 5 cm^3 of 6 M nitric acid (measuring cylinder) to each flask. Transfer 25.00 cm^3 (pipette) of the accurately known silver solution and about 1 cm^3 of iron(III) indicator (ind.) (measuring cylinder) to each solution.

Titrate the contents of the three aliquots with the potassium thiocyanate solution. The end-point of the titration is detected when the solution (including the precipitate) becomes permanently *very faint* brownish. It is important to shake the contents vigorously near the end-point and rinse the walls of the flask with water. The colour should be stable for at least one minute.

ii) *Standardization of the potassium thiocyanate solution*

Transfer 25.00 cm^3 (pipette) of the silver nitrate solution to an Erlenmeyer flask, add about 5 cm^3 of 6 M nitric acid and about 1 cm^3 of the iron(III) indicator solution and about 25 cm^3 of water (use measuring cylinders for these solutions). Titrate the contents with the thiocyanate solution and determine the end-point according to the instruction given in the "Determination" procedure.

Atomic mass: $A_r(\text{Br}) = 79.90$

b) *Exercise*

At the equivalent point the solution is saturated with respect to both AgBr and AgSCN. Find the molar concentration of free (unprecipitated) Br^- in this solution:

$$K_{sp}(\text{AgBr}) = 5.00\times10^{-13} \qquad K_{sp}(\text{AgSCN}) = 1.00\times10^{-12}$$

Ignore the effect of *pH* and Fe(III) species.

Note:

On the answer sheet, not only the required final results shall be given, but also examplifications of how the calculations are carried out.

PROBLEM 2 (Practical)

When potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$ is added to a solution containing zinc ions, an insoluble precipitate forms immediately. Your task is to find out the composition of the stoichiometric precipitate that contains no water of crystallization.

The precipitation reaction is quantitative and so quick that it can be used in a titration. The end point can be detected using redox indication, but first the concentration of the potassium hexacyanoferrate(II) solution has to be determined.

Preparation of $K_4[Fe(CN)_6]$ solution and determination of its exact concentration

Dissolve the solid $K_4[Fe(CN)_6].3H_2O$ (M = 422.41 g/mol) sample in the small Erlenmeyer flask and quantitatively transfer it into the 100.00 cm^3 volumetric flask. Take 10.00 cm^3 portions of the hexacyanoferrate(II) solution. Add 20 cm^3 1 mol/dm^3 sulfuric acid and two drops of the ferroin indicator solution to each sample before titration. Titrate with the 0.05136 mol/dm^3 Ce^{4+} solution. Repeat titration as necessary. Cerium(IV) is a strong oxidant under acidic conditions forming Ce(III).

2.1 Report the Ce^{4+} solution volumes consumed.

2.2 Give the equation for the titration reaction. What was the mass of your $K_4[Fe(CN)_6].3H_2O$ sample?

The reaction between zinc ions and potassium hexacyanoferrate(II)

Take 10.00 cm^3 of the hexacyanoferrate(II) solution and add 20 cm^3 1 mol/dm^3 sulfuric acid. Add three drops of indicator solution (diphenyl amine) and two drops of $K_3[Fe(CN)_6]$ solution. The indicator only works if the sample contains some hexacyanoferrate(III), $[Fe(CN)_6]^{3-}$. Titrate slowly with the zinc solution. Continue until a bluish violet colour appears. Repeat titration as necessary.

2.3 Report the zinc solution volumes consumed.

2.4 Interpret the titration answering the questions on the answer sheet.

Mark the correct answer:

The diphenyl amine indicator changes in colour at the end point

☐ a) because the concentration of the Zn^{2+} ions increases.

☐ b) because the concentration of the $[Fe(CN)_6]^{4-}$ ions decreases.

☐ c) because the concentration of the $[Fe(CN)_6]^{3-}$ ions increases.

☐ d) because the indicator is liberated from its complex.

Which form of the indicator is present before the end point?

☐ a) Oxidized

☐ b) Reduced

☐ c) Complexed to a metal ion

At the beginning of the titration the redox potential for the hexacyanoferrate(II) - hexacyanoferrate(III) system is lower than the redox potential of the diphenyl amine indicator.

☐ a) True

☐ b) False

2.5 Determine the formula of the precipitate.

SOLUTION

2.1 Ce^{4+} consumptions:

Full marks if V_1 is within 0.15 cm^3 of the expected value recalculated from the $K_4[Fe(CN)_6]$ mass. Zero marks if deviation is more than 0.50 cm^3. Linear scale is applied in between.

2.2 The titration reaction:

$Ce^{4+} + [Fe(CN)_6]^{4-} = Ce^{3+} + [Fe(CN)_6]^{3-}$

$Ce^{4+} + Fe^{2+} = Ce^{3+} + Fe^{3+}$

2.3 Zinc consumptions:

Full marks (25 pts.) if V_2 is within 0.15 cm^3 of the expected value recalculated from $K_4[Fe(CN)_6]$ mass, zinc concentrations and empirical ratio. Zero marks if the deviation is more than 0.50 cm^3. Linear scale is applied in between.

2.4 Solutions: b), b), a)

2.5 Determine the formula of the precipitate. Show your work.

The mole ratio of the zinc : hexacyanoferrate(II) in the precipitate can be evaluated as:

$$\frac{n(\text{Zn})}{n(\text{Fe(CN)}_6)} = \frac{10\, c(\text{Zn})\, V_2\, M}{m}$$

Values for c(Zn) are distributed according to a certain plan.

The empirical ratio obtained from the experiments is 1.489.

Calculating the zinc/hexacyanoferrate(II) ratio:

Cations are needed to make the precipitate neutral and only potassium is present.

The precipitate is $K_2Zn_3[Fe(CN)_6]_2$.

Any other reasonable calculation giving the same result is accepted.

Hydrogen instead of potassium ($H_2Zn_3[Fe(CN)_6]_2$ or $KHZn_3[Fe(CN)_6]_2$) is also acceptable.

PROBLEM 2 (Practical)

Analysis of a Copper(II) Complex

You are provided with a sample of an inorganic copper(II) complex, the anion of which is made from copper, chlorine, and oxygen. The counter ion is the tetramethyl ammonium cation. There is no water of crystallisation. You are required to determine proportions of copper ions and chloride ions by titration and hence determine the composition of the complex.

Chemicals

- Inorganic complex: three samples of approximately 0.1 g, accurately pre-weighed in vials labelled ‘Sample 1’, ‘Sample 2’, ‘Sample 3’.
- Inorganic complex: three samples of approximately 0.2 g, accurately pre-weighed in vials labelled ‘Sample 4’, ‘Sample 5’ and ‘Sample 6’.
- pH 10 ammonia buffer, 10 cm^3.
- Murexide indicator, solution in H_2O, 10 cm^3.
- EDTA disodium salt, aqueous solution, c = 0.0200 mol dm^{-3}, 150 cm^3.
- Ethanoic acid, 10 cm^3.
- 2,7-Dichlorofluorescein indicator, solution in 7 : 3 EtOH : H_2O), 10 cm^3.
- Dextrin, 2 % solution in H_2O, 25 cm^3.
- Silver nitrate, aqueous solution, c = 0.1000 mol dm^{-3}, 150 cm^3.

Procedure

Titration to determine the proportion of copper ions

(a) You are provided with three accurately pre-weighed samples of copper complex, each of approximately 0.1 g. These are labelled "Sample 1", "Sample 2", "Sample 3", together with the exact mass of the copper complex. Take the first of these, note down the mass of the sample and quantitatively transfer the contents to a 250 cm^3 conical flask using approximately 25 cm^3 of water.

(b) Add pH 10 ammonia buffer solution until the precipitate which forms initially just redissolves (about 10 drops).

(c) Add 10 drops of the murexide indicator.

(d) Titrate with the 0.0200 mol dm^{-3} EDTA solution until the solution turns violet and the colour persists for at least 15 seconds. Record the volume of solution used in the titration.

(e) Repeat if necessary with samples 2 and 3.

Note: You will be marked only on a single value you report in the answer booklet. This may either be an average value, or a single value you feel most confident in.

2.1 Calculate the volume of EDTA solution needed to react completely with 0.100 g of complex.

2.2 Give an equation for the titration reaction.

2.3 Calculate the percentage by mass of copper in the sample.

You will need to wash out your burette before you start the titration for the determination of chloride ions. Any remaining EDTA solution may be disposed of into the waste containers labelled ‘EDTA’.

Titration to determine the proportion of chloride ions present

(f) You are provided with three accurately pre-weighed samples of copper complex each of approximately 0.2 g. These are labelled "Sample 4", "Sample 5", "Sample 6", together with the exact mass of the copper complex. Take the first of these, note down the mass of the sample and quantitatively transfer the contents to a 250 cm^3 conical flask using approximately 25 cm^3 of water.

(g) Add 5 drops of ethanoic acid, followed by 10 drops of dichlorofluorescein indicator and 5 cm^3 dextrin (2 % suspension in water). Shake the bottle well before adding the dextrin suspension.

(h) Titrate with the 0.1000 mol dm^{-3} silver nitrate solution, swirling constantly until the white suspension turns pink and the colour does not disappear after swirling.

(i) Repeat if necessary.

Note: You will be marked only on a single value you report in the answer booklet. This may either be an average value, or the value you feel most confident in.

2.4 Calculate the volume of silver nitrate solution needed to react completely with 0.200 g of complex.

2.5 Give an equation for the titration reaction.

2.6 Calculate the percentage by mass of chloride ions in the sample.

The percentage of carbon, hydrogen and nitrogen in the complex was determined by combustion analysis and found to be as follows:

Carbon: 20.87 %; Hydrogen: 5.17 %; Nitrogen: 5.96 %.

2.7 Mark in the answer booklet, which element in the complex has the greatest percentage error in the determination of its proportion.

Cu Cl O C H N

2.8 Determine the formula of the copper complex. Show your working.

SOLUTION

2.1 Full marks if answer is $V_{\text{corr.}} \pm 0.1\ \text{cm}^3$. Zero marks if answer is less than ($V_{\text{corr.}} - 0.5\ \text{cm}^3$) or greater than ($V_{\text{corr.}} + 0.5\ \text{cm}^3$), linear point scale is applied in between.

2.2 $Cu^{2+} + EDTA^{4-} \rightarrow [Cu(EDTA)]^{2-}$

2.3 $n(\text{EDTA}) = 0.0200\ \text{mol dm}^{-3} \times V(\text{EDTA})\ (\text{in dm}^3) = (0.0200\ \text{mol dm}^{-3} \times V)\ \text{mol}$

$n(\text{Cu}^{2+}) = (0.0200\ \text{mol dm}^{-3} \times V)\ \text{mol}$

$m(\text{Cu}) = M(\text{Cu}) \times n(\text{Cu}) = 63.55\ \text{g mol}^{-1} \times (0.0200\ \text{mol dm}^{-3} \times V)\ \text{mol}$

$$\%\ \text{Cu} = \frac{m(\text{Cu})}{m(\text{sample})} \times 100$$

2.4 Full marks if answer is $V_{\text{corr.}} \pm 0.1\ \text{cm}^3$.

Zero marks if answer is less than ($V_{\text{corr.}} - 0.5\ \text{cm}^3$) or greater than ($V_{\text{corr.}} + 0.5\ \text{cm}^3$), linear point scale is applied in between.

2.5 $Ag^+ + Cl^- \rightarrow AgCl$

2.6 $n(\text{Ag}^+) = 0.100\ \text{mol dm}^{-3} \times V(\text{Ag}^+)\ (\text{in dm}^3) = (0.100\ \text{mol dm}^{-3} \times V)\ \text{mol}$

$n(\text{Cl}^-) = (0.100\ \text{mol dm}^{-3} \times V)\ \text{mol}$

$m(\text{Cl}) = M(\text{Cl}) \times n(\text{Cl}) = 35.45\ \text{g mol}^{-1} \times (0.100\ \text{mol dm}^{-3} \times V)\ \text{mol}$

$$\%\ \text{Cl} = \frac{m(\text{Cl})}{m(\text{sample})} \times 100$$

2.7 If the percentage of oxygen is calculated by subtracting all the others from 100, it has all the errors from the determination of the other elements combined. In practice this leads to a large error which affects the subsequent calculation of the formula unless this point is appreciated.

Cu Cl [✓ O] C H N

2.8 Full marks if the formula is correctly calculated from the student data and the large error in oxygen is taken into account (either by using one of the proportions of the other elements to determine the elemental ratios, or by a consideration of charge balance).

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.

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.

Instructions

- You have a 15 minute reading time before you start work. Begin reading only when the START command is given.
- Follow the safety rules announced in the preparatory tasks. You get one warning for violations. On the second warning you will get disqualified.
- Wear your lab coat and safety goggles while in the lab. Ask your lab assistant for the gloves of your size when you need them.
- Use only the pen, marker pen and calculator provided. Do not write with the marker on paper; use it only to label glass or plastic labware.
- Make sure that your student code is on every answer sheet.
- All answers must be written in the appropriate boxes on the answer sheet. Anything written elsewhere will not be graded. Use the reverse of the exam sheets if you need scratch paper.
- You have no access to sinks in the lab. You are provided with a sufficient quantity of labware. Only a few items need to be used again. Wash these carefully with appropriate solvent into the waste container. Use the brush if needed. Distilled water and paper tissues are freely available.
- Liquid waste is to be put into the container labeled “LIQUID WASTE”. Do not put rubbish (tissues, plastic, etc.) in this container, but into the waste baskets in the lab.
- Chemicals and labware are not supposed to be refilled or replaced. Each such incident (other than the first in the entire exam, which you will be allowed) will result in the loss of 1 point from your 40 practical points.
- Raise your hand if you have a safety question or you need a restroom break or drinking water.
- When you have finished the examination, put your answer sheet into the envelope provided and leave it on the table. Do not seal the envelope.
- You must stop your work immediately when the STOP command is given. A delay in doing this may lead to cancellation of your exam. Do not leave your place until permitted by the lab assistants. You can keep the task text.
- The official English version of this examination is available on request only for clarification.

Instructions specific for Part II

- The working time for Part II (Task 2 and 3) is 200 minutes.
- Start Part II with Task 2. When you are ready to start with Task 3, tell the lab assistant, and you will receive the chemicals and labware for Task 3. Reagents for Task 2 will be taken away from you at this point.
- Part II of the exam (Task 2-3) contains 10 pages, its answer sheets have 7 pages.
- Ask the lab assistants when you need your alcohol lamp lighted. Heat only glass test tubes. Close the alcohol lamp with the cap when finished.

Labware

Item	Quantity
General equipment for all tasks, for each student, on the table	
Test tube rack (60 holes)	1
Paper tissue	5
Permanent marker	1
Glass stirring rod, 20 cm	1
Polypropylene funnel, diam. 3.5 cm	1
Soft plastic cups	3
Strong plastic cup	1
Caps for polystyrene test tubes	22
Tasks 2 and 3, for each student, on the table	
Container with a screw cap for waste,3 dm^3, labeled “Liquid Waste, Tests 2&3”	1
Task 2, for each student, on the table	
Storage box labeled “Task 2”	1
Laboratory stand with double burette clamp	1
Burette, 25.00 cm^3	2
Graduated pipette, 10.0 cm^3	1
Graduated pipette, 1.00 cm^3	1
Bulb (Mohr) pipette, 10.00 cm^3	1
Erlenmeyer flask, 100 cm^3	2
Graduated cylinder, 10.0 cm^3	2
Brush	1
Polypropylene funnel, 5.5 cm	1
Task 2, for each student, in the storage box “Task 2”	
Polystyrene test tubes, 10 cm^3	8
Pipette filler	1
Pasteur pipettes for indicators	2
Task 3, for each student, get from the lab assistants	
Storage box labeled “Task 3”	1
Task 3, for each student, in the storage box “Task 3”	
Polystyrene test tubes, 10 cm^3	20
Alcohol lamp	1
Test tube holders, wooden	1
Glass test tubes	10
Pasteur pipettes	10
Strong plastic cup	1

Chemicals

Name	State	Conc.	Q-ty	Placed in	Labeled
Task 2, for each student, on the table					
Nitric acid	Aqueous solution	2 M	-*	Glass bottle with dropper cap, 250 cm^3	HNO_3
Task 2, for each student, in the storage box "Task 2"					
Water sample solution	Aqueous solution	To be determined	100 cm^3	Glass bottle with screw cap, 100 cm^3	Water sample
Sodium fluoride	Aqueous solution	9 mg/dm^3 in fluoride	50 cm^3	Glass bottle with screw cap, 50 cm^3	F^-, 9 mg/dm^3
Zirconyl Alizarin indicator	Acidic aqueous solutions	0.055% $ZrOCl_2$, 0.028% Alizarin Red S	10 cm^3	Glass bottle with screw cap, 25 cm^3	Zirconyl Alizarin
Sodium chloride	Aqueous solution	0.0500 M	50 cm^3	Glass bottle with screw cap, 50 cm^3	NaCl, 0.0500 M
Ammonium iron(III) sulfate dodecahydrate	Aqueous acidic solution	20 g/dm^3	10 cm^3	Glass bottle, 15 cm^3	Fe^{3+} ind.
Silver nitrate	Aqueous solution	To be determined	200 cm^3	Amber glass bottle, 250 cm^3	$AgNO_3$
Ammonium thiocyanate	Aqueous solution	See exact concentration on the label	100 cm^3	Glass bottle with screw cap, 100 cm^3	NH_4SCN, X.XXXX M
Potassium chromate	Aqueous solution	10%	5 cm^3	Glass bottle, 15 cm^3	K_2CrO_4
Task 3, for each student, on the table					
Ethanol	Liquid	95 %	150 cm^3	Glass bottle with dropper cup, 250 cm^3	C_2H_5OH
Task 3, for each student, in the storage box "Task 3"					
Organic unknowns 1 to 8	Liquid	-	0.5 cm^3	Syringes, 2 cm^3	1 to 8
Potassium permanganate	Aqueous solution	0.13 %	5 cm^3	Amber glass bottle, 50 cm^3	$KMnO_4$
Ammonium cerium(IV) nitrate reagent	2.0 M HNO_3 aqueous solution	28.6 %	5 cm^3	HDPE bottle, 30 cm^3	Ce(IV)
Acetonitrile	Liquid	-	45 cm^3	Glass bottle, 50 cm^3	CH_3CN

Name	**State**	**Conc.**	**Q-ty**	**Placed in**	**Labeled**
2,4-Dinitrophenylhydrazine reagent	Sulfuric acid solution in aqueous ethanol	3 %	20 cm^3	HDPE bottle, 30 cm^3	DNPH
Iron(III) chloride	0.5 M HCl aqueous solution	2.5 %	1 cm^3	HDPE bottle, 30 cm^3	$FeCl_3$
Hydroxylamine hydrochloride	Ethanolic solution	0.5 M	10 cm^3	HDPE bottle, 30 cm^3	$NH_2OH \times HCl$
Sodium hydroxide	Aqueous solution	6 M	5 cm^3	HDPE bottle, 30 cm^3	NaOH
Hydrochloric acid	Aqueous solution	1 M	25 cm^3	HDPE bottle, 30 cm^3	HCl

*In the quantity left after doing Task 1.

Periodic table with relative atomic masses

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

Task 2

Determination of fluoride and chloride content in mineral water

Georgia is world famous for its splendid mineral waters. Many of these are used to cure various diseases. Manufacturers have to carefully control the ionic composition of waters, fluoride and chloride being among the most important ions.

Visual colorimetric detection of fluoride

The method of fluoride determination is based on the decrease in the color intensity of zirconium(IV)-Alizarin Red S complex in the presence of fluoride ions due to formation of a more stable colorless complex. The equilibrium is achieved in about 20 minutes after the reagent addition. The fluoride concentration is determined visually by comparing the color developed in the sample with those in the calibration solutions.

Transfer 9.0 cm^3 of mineral water from the sample into the plastic test tube labeled “X”.

Calculate how much of the 9.0 mg/dm^3 standard fluoride solution you will need to prepare a set of calibration solutions with the following fluoride ion content: 0.0; 1.0; 2.0; 3.5; 5.0; 6.5; 8.0 mg/dm^3 (calculate for 9.0 cm^3 of each solution).

Using the 1.0 cm^3 and 10.0 cm^3 graduated pipettes, add the calculated amounts of the standard fluoride solution to the test-tubes, then add 1.0 cm^3 of Zirconyl Alizarin indicator into each test tube, and bring the volume in each calibration test tube to the 10.0 cm^3 mark with distilled water (the mark is shown in the figure with the arrow).

2.1.1. Report the fluoride volumes used in your dilutions.

Mix the obtained solutions in the test tubes. Set the tube rack aside for at least 20 minutes.

2.1.2. Compare the color of the sample and the calibration solutions looking on them from the top down and from the front. Select the concentration of the standard that is closest to the fluoride concentration of the water sample.

Note: the rack with the test tubes will be photographed by the lab staff after the whole exam is finished.

Standardization of silver nitrate solution by the Mohr method

Transfer 10.0 cm^3 of the standard 0.0500 mol/dm^3 NaCl solution into an Erlenmeyer flask using the bulb (Mohr) pipette. Add approximately 20 cm^3 of distilled water and 10 drops of 10% aqueous K_2CrO_4 solution.

Fill a burette with the silver nitrate solution. Titrate the contents of the flask with the silver nitrate solution while vigorously mixing the solution containing the precipitate formed. The final titrant drops are added slowly with vigorous swirling of the flask. The titration is complete when the faint color change visible on titrant addition does not disappear in the pure yellow suspension. Take the final burette reading. Repeat the titration as necessary.

2.2.1. Report your volumes on the answer sheet.

2.2.2. Write balanced chemical equations for the titration of NaCl with $AgNO_3$ and for the end-point indication reaction.

2.2.3. Calculate the concentration of the $AgNO_3$ solution from your measurement.

2.2.4. The Mohr titration method requires a neutral medium. Write down equations for the interfering reactions that take place at lower and at higher pH.

Chloride determination by the Volhard method

Wash the bulb (Mohr) pipette with distilled water. Wash the Erlenmeyer flasks first with a small portion of the ammonia solution left over from Task 1 to help removing the silver salt precipitate and then with distilled water. (In case you used up all the ammonia solution in the first task, you can get a refill without penalty.)

Transfer a 10.0 cm^3 aliquot of the mineral water from the sample into an Erlenmeyer flask using the bulb (Mohr) pipette. Add 5 cm^3 of 2 mol/dm^3 nitric acid using a graduated cylinder. Add 20.00 cm^3 of the silver nitrate solution from the burette and mix well the suspension. Add appr. 2 cm^3 of the indicator (Fe^{3+}) solution with the Pasteur pipette.

Fill the second burette with the standard ammonium thiocyanate solution (see the exact concentration on the label). Titrate the suspension with this solution while vigorously swirling. At the end point one drop produces a faint brown color that is stable even after intense mixing. Take the final burette reading. Repeat the titration as necessary.

Note. The AgCl precipitate exchanges Cl^- ions with SCN^- ions from the solution. If you titrate too slowly or with breaks, the brown color disappears with time, and too much titrant is spent for the titration. Therefore when approaching the endpoint you should add the titrant at a *constant* slow rate swirling the flask *constantly* so that the suspension would stay white. The appearance of faint brown color will mean reaching the endpoint.

2.3.1. Report your volumes on the answer sheet.

2.3.2. Write down balanced chemical equations for the back titration with NH_4SCN and that for the end-point indication reaction.

2.3.3. Calculate the chloride concentration (in mg/dm^3) in the water sample from your measurements.

2.3.4. If Br^-, I^-, and F^- ions are present in the sample in addition to chloride, the concentration of which ion(s) will contribute to the result of the Volhard titration?

2.3.5. When trying to determine the concentration of Cl^- in the presence of other halides, an analyst added some potassium iodate and sulfuric acid to the sample and boiled the solution. Afterwards he reduced the excess of iodate to iodine by boiling the sample with phosphorous acid H_3PO_3. What interfering anions were removed by this operation? Write the chemical equations for the reactions of these ions with iodate.

Task 2 14% of the total

2.1.1	2.1.2	2.2.1	2.2.2	2.2.3	2.2.4	2.3.1	2.3.2	2.3.3	2.3.4	2.3.5	Sum
2	15	30	2	2	2	30	2	4	2	4	95

2.1.1. Report the fluoride volumes used in your dilutions.

F^- content (mg/dm^3)	0.0	1.0	2.0	3.5	5.0	6.5	8.0
Calculated volume of F^- solution (cm^3)							

2p

2.1.2. Circle the concentration of the standard that is closest to the fluoride concentration of the water sample.

15p, 5p for adjacent values.

F^- content (mg/dm^3)	0.0	1.0	2.0	3.5	5.0	6.5	8.0

2.2.1. Report your titration volumes.

Titration no.	1	2				
Initial burette reading, cm^3						
Final burette reading, cm^3						
Volume spent, cm^3						

Your accepted volume, V_1: cm^3

30p on a sliding scale

2.2.2. Write a balanced chemical equation for the titration of NaCl with $AgNO_3$ and that for the end-point indication reaction.

Titration reaction:

$Cl^- + Ag^+ \longrightarrow AgCl\downarrow$

Indicati

$CrO_4^{2-} + 2\ Ag^+ \longrightarrow Ag_2CrO_4\downarrow$

2p

2.2.3. Calculate the concentration of the $AgNO_3$ solution from your measurement.

Your work:

$c(Ag^+) = c(Cl^-)10.0\ cm^3\ /\ V_1$

2 p

$c(Ag^+)$:

2.2.4. The Mohr titration method requires a neutral medium. Write equations for the interfering reactions that take place at lower and at higher pH.

Low pH:

$2\ CrO_4^{2-} + 2\ H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$ (dichromic or chromic acids also accepted),

or $Ag_2CrO_4 + H^+ \rightarrow 2Ag^+ + HCrO_4^-$

High pH:

$2\ Ag^+ + 2\ OH^- \longrightarrow Ag_2O + H_2O$

2p

2.3.1. Report your volumes on the answer sheet.

Titration no.	1	2				
Initial burette reading, cm^3						
Final burette reading, cm^3						
Volume spent, cm^3						

Your accepted volume, V_2: cm^3

30p on a sliding scale

2.3.2. Write a balanced chemical equation for the back titration with NH_4SCN and that for the end-point indication reaction.

Titration reaction:

$Ag^+ + SCN^- \longrightarrow AgSCN\downarrow$

Indicati

$SCN^- + Fe^{3+} \longrightarrow Fe(SCN)^{2+}$ or analogous reaction

2p

2.3.3. Calculate the chloride concentration (in mg/dm^3) in the water sample from your measurements.

Your work:

$c(Cl^-) = [20.00\ cm^3\ c(Ag^+) - V_2\ c(SCN^-)]\ M(Cl) / 10.00\ cm^3$

4p, 3p if in different unit

$c(Cl^-)$: mg/dm^3

2.3.4. If Br^-, I^-, and F^- ions are present in the sample in addition to chloride, the concentration of which ion(s) will contribute to the result of the Volhard titration? Tick the appropriate box(es).

☐ Br^- ☐ I^- ☐ F^- ☐ none

Br^-, I^-

2p, 1p if 1 mistake committed

2.3.5. When trying to determine the concentration of Cl^- in the presence of other halogens, an analyst added some potassium iodate and sulfuric acid to the sample and boiled the solution. Afterwards he reduced the excess of iodate to iodine by boiling the sample with phosphorous acid H_3PO_3. What interfering anions were removed by this operation?

☐ Br^- ☐ I^- ☐ F^- ☐ none

Br^-, I^-

2p

Write the reaction equations of these ions with iodate.

$5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

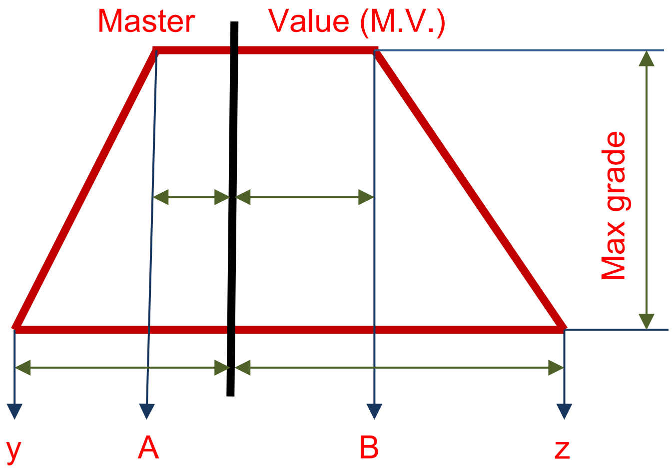
$10Br^- + 2IO_3^- + 12H^+ \rightarrow 5Br_2 + I_2 + 6H_2O$ (IBr also accepted)

2p

Replacements:

Item	Quantity	Lab assistant's signature	Student's signature

Grading scheme for the titration results



If A< Value < B, then Grade = Max grade
If Value < y, then Grade = 0, If Value > z, then Grade = 0
If y < Value < A, then Grade = Max grade × (Value – y)/(A – y)
If B < Value < z, then Grade = Max grade × (z – Value)/(z – B)

Question	**M.V., mL**	**A, mL**	**B, mL**	**y, mL**	**z, mL**	**Max grade**
2.2.1.	**10.0**	**9.9**	**10.15**	**9.8**	**10.4**	30p
2.3.1.	**Theoretical values**	**–0.1**	**+0.3**	**–0.3**	**+0.8**	30p

Spettrofotometria UV-Vis

PROBLEM 2 (practical)

The spectrophotometric determination of the concentration, acid constant K_{a2} and pK_{a2} of H_2X

Apparatus:

7 volumetric flasks (100 cm^3), 2 beakers (50 cm^3), 1 capillary pipette (Pasteur), 1 pipette (10 cm^3; graduated in intervals of 0.1 cm^3), 1 washing bottle, 1 glass rod, 1 container for waste materials, funnel.

Reagents:

Compound NaHX, aqueous stock solution of Na_2X (0.00100 mol dm^{-3}), aqueous solution of sodium perchlorate (1.00 mol dm^{-3}), aqueous solution of HCl (0.1 mol dm^{-3}), aqueous solution of NaOH (0.1 mol dm^{-3}).

Procedure:

a) Weigh accurately 183.5 ± 0.5 mg of NaHX and dissolve it in water in a volumetric flask and dilute up to the 100 cm^3 mark. Pipette 15.0 cm^3 of this solution into another 100 cm^3 volumetric flask and fill up to the mark with water to obtain the stock solution of NaHX. If you do not use your own material, you will get the NaHX from the service desk.

b) Prepare 5 solutions, numbered 1-5, in the remaining five 100 cm^3 volumetric flasks. These solutions have to fulfil the following requirements:

- The total concentration of ($[X^{2-}] + [HX^-]$) in each solution must be exactly 0.000100 mol dm^{-3}.
- The concentration of sodium perchlorate in each solution must be 0.100 mol dm^{-3} to maintain constant ionic strength. The solutions are prepared by pipetting into each volumetric flask 1-5 the accurate volumes of the NaHX and Na_2X stock solutions, adding a required volume of sodium perchlorate solution and filling up to the mark with water.

- Solution 1 is prepared by pipetting the required amount of the stock solution of NaHX. Add ca. 3 cm^3 of HCl (aq) with the pipette to ensure that the anion is completely in the form HX^-, before adding the sodium perchlorate solution.

- Solution 5 is prepared by pipetting the required amount of the stock solution of Na_2X which is provided for you. Add ca. 3 cm^3 of the NaOH(aq) to ensure that the anion is completely in the form X^{2-}, before adding the sodium perchlorate solution.

- The three remaining solutions 2-4 are prepared by pipetting the stock solutions of NaHX and Na_2X in the following ratios before adding the sodium perchlorate solution:

Solution No.	Ratio NaHX(aq) : Na_2X(aq)
2	7 : 3
3	1 : 1
4	3 : 7

c) Take the five volumetric flasks to the service centre where their UV-vis spectra will be recorded in the region 300-500 nm for you. In another service centre the accurate pH of each solution will be recorded. You may observe the measurements.

d) From the plot of absorbance vs. wavelength, select the wavelength most appropriate for the determination of pK_{a2} of H_2X, and measure the corresponding absorbance of each solution.

e) Calculate the pK_{a2} of H_2X from the pH-absorbance data when the ionic strength I = 0.1 and the temperature is assumed to be ambient (25 °C). Note that:

$$K_{a2} = \frac{[H^+][X^-]}{[HX^-]} = \frac{c_{H^+} \times c_{X^{2-}}}{c_{HX^-}}$$

$$K_{a2} = \frac{(A\ A_{HX^-})[H^+]}{(A_{X^{2-}} - A)} \quad or \quad A = A_{X^{2-}} - (AA_{HX^-})\frac{[H^+]}{K_{a2}}$$

$$pf_{H^+} = \frac{0.509 \times \sqrt{I}}{1 + \sqrt{I}}$$

f) Which of your prepared solutions shows the largest buffer capacity? Calculate this buffer capacity, *P*, by any suitable method. You may use the equations given:

$$P = 2.3 \times \left([OH^-] + [H^+] + \frac{K_a [H^+] C}{(K_a + [H^+])^2} \right)$$

$$P = 2.3\times\left(\frac{K_w}{[\mathrm{H}^+]} + [\mathrm{H}^+] + \frac{[\mathrm{X}^{2-}]\,[\mathrm{HX}^-]}{C}\right)$$

C is the total concentration of the acid.

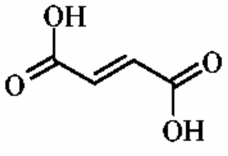
$K_w = 2.0\times10^{-14}$ at $I = 0.1$ and 25 °C.

PROBLEM 3 (Practical)

Determination of Iron in Iron Pills

Introduction

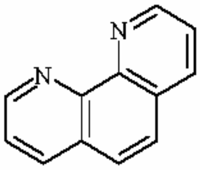
Iron is an essential component of hemoglobin, transporting oxygen in the blood to all parts of the body. It also plays a vital role in many metabolic reactions. Iron deficiency can cause anaemia resulting from low levels of hemoglobin in the blood. Iron deficiency is the most widespread mineral nutritional deficiency worldwide. One way to reduce iron shortage is by treatment with iron pills. The active ingredient in the iron pill to be examined, is iron(II) present as iron(II) fumarate. Besides this organic iron(II) compound the pill contains other compounds such as binding agents. The structure of fumaric acid is:



Fumaric acid

Iron(II) and 1,10-phenanthroline form an orange/red coloured complex $[(C_{12}H_8N_2)_3Fe]^{2+}$. The absorbance of this complex, determined at 510 nm in a buffer solution (pH=8) is a measure for the iron content of the iron pill. Since 1,10-phenanthroline only binds to iron(II) and iron(II) is readily oxidized to iron(III), hydroxylammonium chloride is added to reduce all iron(III) to iron(II). A simplified reaction scheme is:

$2\ NH_2OH + 4\ Fe^{3+} \rightarrow N_2O + 4\ H^+ + H_2O + 4\ Fe^{2+}$



1,10-Phenanthroline

Procedure

The weight of the iron pill is determined with an accuracy of 1 mg using a balance. The pill is carefully pulverized in a mortar and transferred quantitatively into a 100 cm^3 beaker with the aid of a small amount of distilled water. Hydrochloric acid (5 cm^3, 4 M) is added. The content of the beaker is heated up to approximately 60 °C on a hotplate. The solution turns a yellow colour.

The beaker is then placed in an ultrasonic bath for at least 5 minutes. The beaker is kept in place by styrofoam. The suspension is filtered by suction using a Hirsch funnel containing a small layer of moistened hi-flow filter aid pressed onto the filter. The hi-flow filter aid is washed with ample distilled water. The filtrate is carefully transferred into a volumetric flask (250 cm^3) and the final volume adjusted by adding distilled water and with regular mixing. An amount of 10 cm^3 is pipetted from this solution and transferred into a volumetric flask of 100 cm^3. Again the volume is adjusted with distilled water while mixing the content of the flask.

From this solution, 10 cm^3 is pipetted and transferred into a volumetric flask of 100 cm^3. Subsequently, 1,10-phenanthroline solution (10 cm^3) and hydroxylammonium chloride solution (1 cm^3) are added. Then the volume is adjusted with buffer solution (pH 8).

The absorbance of this solution is measured with a spectrophotometer at 510 nm against water as a blank in a 1.000 cm cell.

Calculate the amount of iron in the iron pill on basis of the known molar absorptivity (extinction coefficient, ε) of the iron(II)phenanthroline complex at 510 nm. The molar absorptivity of the iron(II)phenanthroline complex at 510 nm is 11100 M^{-1}cm^{-1}.

Important

In order to eliminate deviations in absorbance typically connected to the spectrophotometer used, a correction factor is denoted on the spectrophotometer you will be using for your experiment. The absorbance observed must be multiplied by this factor in order to obtain the correct absorbance of the solution of the iron complex.

SOLUTION

The competitors were expected to show the following data, tables, graphs or calculations:

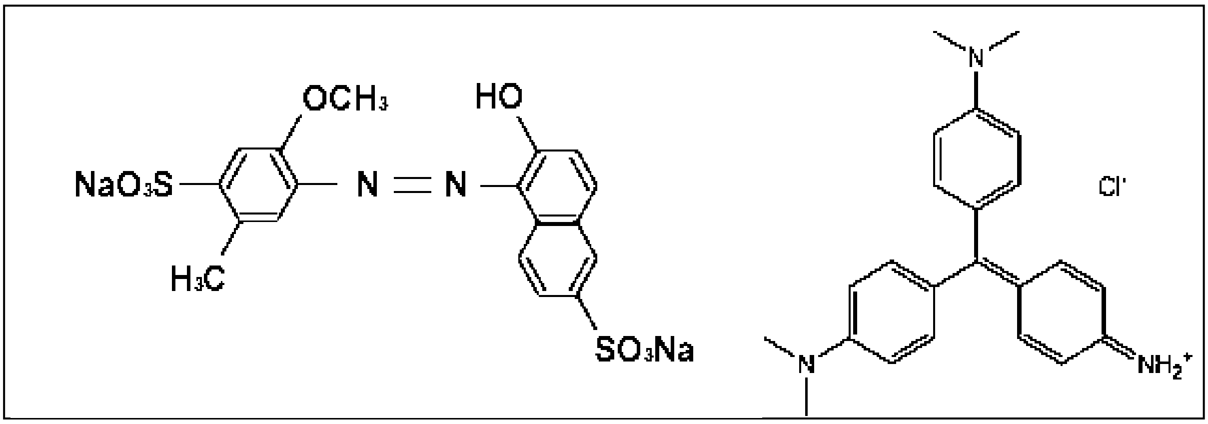
1. Weight of the iron pill in mg.
2. Reading of the spectrophotometer and corrected absorbance.
3. Calculation of the concentration of iron(II)phenanthroline complex in the cell in mmol dm^{-3}.
4. Calculation of the total amount of iron(II) in the pill in mg.
5. Calculation of the iron content of the pill in weight %.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Reverse-phase Chromatography: Spectrophotometric Analysis

Chromatographic separation followed by spectrophotometric analysis is one of the most widely practiced analytical techniques in chemical laboratories around the world. For example, organic compounds in a complex mixture are often analyzed by reverse-phase liquid chromatography with spectrophotometric detection. In reverse-phase chromatography, hydrophobic interactions between the stationary phase material (usually octadecyl group) and the non-polar moiety of the analyte is utilized. The chromatogram can be simplified and the compound of interest selectively determined by proper choice of the detector wavelength. In this part of the Practical Test, spectrophotometric analysis of dyes, with and without separation, will be performed.



Food Red No. 40 Methyl Violet 2B

1.1 Spectrophotometric Analysis of R and B in a Mixed Solution

a) Measure absorbance of both Solutions R (3.02×10^{-5} M) and B (1.25×10^{-5} M) (Fig. A & B). Fill in the Table in the Answer Sheet with your measurements. Draw absorption spectra for the red dye in red ink and for the blue dye in blue ink (Fig. 1.1).

b) Repeat absorbance measurements for Solution MD. Solution MD is a mixture of Solution R and B in a certain ratio. Add the spectrum in black ink to Fig. 1.1.

c) Based on the Beer-Lambert law, determine the molar concentration of both dyes in Solution MD using the data in the Table. Do not determine the fraction of one dye by subtracting the fraction of another dye from 1.

1.2 Chromatographic Separation Followed by Spectrophotometric Analysis

a) Elute the cartridge with about 10 cm^3 of Solution E using 10 cm^3 syringe (Fig. C).

b) Load 1.00 cm^3 of solution MD onto the cartridge (Fig. D).

c) Using 1 cm^3 syringe, elute with Solution E (Fig. E). Collect the solution eluting through the outlet in a 10 cm^3 volumetric flask. Repeat until the red compound is completely eluted and collected.

d) Fill the flask to the 10 cm^3 mark with Solution E and mix. Call this Solution F.

e) Obtain the absorption spectrum of solution F as in Experiment 1.1. Dilution takes place during elution. Therefore, multiply the measured absorbance by 10 when drawing the spectrum for Solution F. Draw spectrum with broken line in Fig. 1.1 in red ink.

f) Dilute Solution R as necessary and construct a calibration curve, at a wavelength of your choice, for analysis of the red dye (R) in Solution F. Draw a calibration curve in the answer sheet (X-axis, concentration; Y-axis, absorbance, Fig. 1.2). Indicate the wavelength used. The calibration curve must have three points in addition to the origin. Mark the position of Solution F on the calibration curve.

g) Report the concentration of R in the original Solution MD.

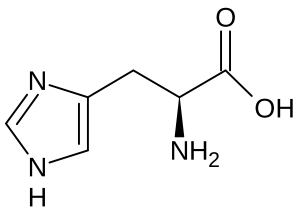
h) Compare this concentration with the value you obtained in Experiment 1-1 and report the recovery (amount eluted/amount loaded) associated with chromatography.

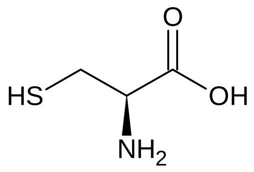
PRACTICAL PROBLEMS

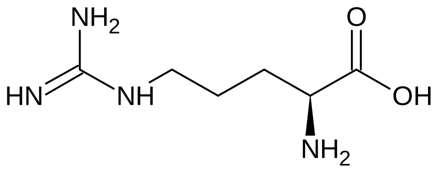
PROBLEM 1 (Practical)

Ion-exchange chromatography of amino acids

Ion-exchange chromatography is an important analytical and preparative method, which allows fractioning of charged substances. Interaction of ionic groups of the substances with counterions attached to the resin is behind the method. In this task you will have to carry out separation of a given mixture of three amino acids followed by quantitative assay of individual amino acids eluted from the column by using specific chromogenic reactions. Since queues of students are possible at spectrophotometers, we strongly suggest you starting the exam with Problem 1.


His


Cys


Arg

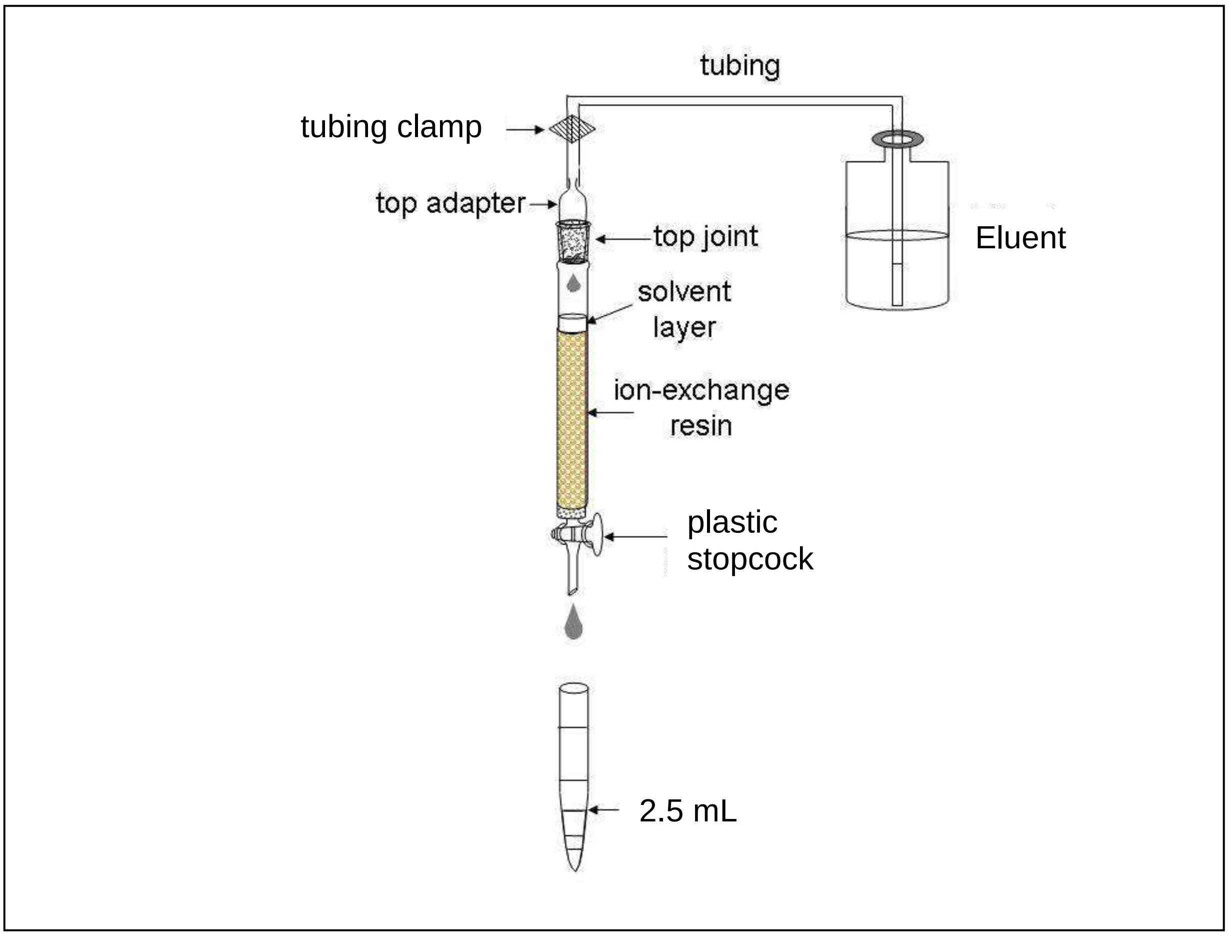
Three amino acids (see the structures above) are present in the mixture. These are histidine, cysteine, and arginine. Cross-linked sulfonated polystyrene is used as a cation-exchange resin (see the picture of the system below). At the beginning of the experiment the column is equilibrated with Eluent 1 (*pH* 4.9).

Procedure

Chromatography. Step 1

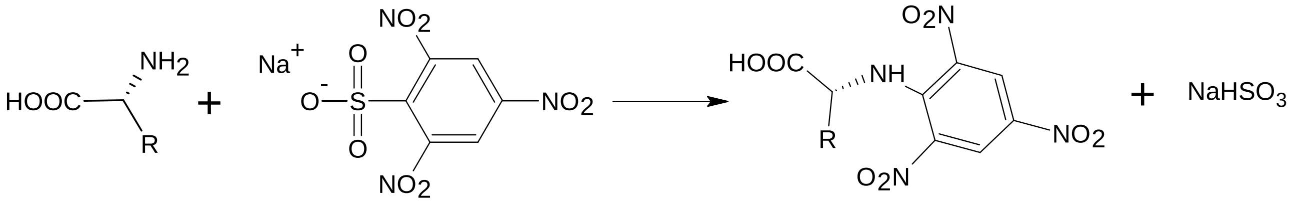
Apply the given solution of a mixture of amino acids to the column. First, open the stopcock to allow the solvent in the column draining into the Erlenmeyer flask labelled "Waste" so that the solvent is level with the top of packing material, still preventing the resin surface from drying off. Close the stopcock and carefully add the analyzed solution to the top of the column by using a syringe. Open the stopcock and let the sample soak inside the gel (drain the solvent into the "Waste" flask). Close the stopcock and add about 1 cm^3 of Eluent 1 (corresponds to ~ 1 cm of liquid in the column) by carefully releasing the tubing clamp. Attach the top joint tightly, fixing the column with one hand and the adaptor with the other (be sure that the joint is fitted closely to the column). Replace the "Waste" flask at the stand with the test tubes in the rack. Release the tubing clamp and open the stopcock to let the eluent flow down through the column. Proceed with elution. (Always pen the stopcock to start elution and close the stopcock to stop it).

Collect the fractions in the test tubes up to the volume of 2.5 cm^3 (as shown in the Picture). If needed, label them with marker. After collecting each 4 to 8 fractions stop elution and carry out qualitative analysis of the collected samples.



Qualitative analysis of samples

Qualitative assay of amino acids is based on the reaction of their α-amino groups with sodium 2,4,6–trinitrobenzene sulfonate (TNBS):



The assay is carried out in the wells of a polystyrene plate, each well corresponding to a definite test tube. Before starting the assay, mix 1 cm^3 of TNBS solution with 10 cm^3 of carbonate buffer solution and place 0.1 cm^3 of the resulting mixture into half of the plate wells (from A1 to H5). Then add 0.1 cm^3 of the analyzed fraction into a well. Start with A1 well and continue with B1, C1, etc (move top to bottom and left to right). If an amino acid is present in the analyzed fraction, intense yellow coloration will develop in the corresponding well within 3 min. Use the coloration in the first well as the reference. To reliably estimate the coloration, place the plate on the white sheet of paper.

Note: all aliquots of 0.1 cm^3 should be added by using the pipettor. We expect you to use one tip for all fractions of a single peak.

1.1 a Draw the profile of coloration intensity (qualitatively) on the plate sketch in the Answer Sheet. Use the following symbols: (-) – no coloration, 1 – weak coloration, 2 – moderate coloration and 3 – intense coloration. Keep drawing the profile during the whole chromatography process.

Continue collecting fractions and analyzing them until you get at least two wells with coloration as in A1 well, which will indicate that the first amino acid has left the column completely (end of the first peak).

Chromatography. Step 2

As soon as you are finished with collecting the first peak, change to Eluent 2. To do so, close the stopcock, fix the tubing clamp (Important!), disconnect the tubing leading to the bottle with Eluent 1 and connect the tubing leading to the bottle with Eluent 2. Attach the top joint tightly.

1.1 b Indicate when the eluents have been changed by drawing lines between the corresponding wells on the plate sketch.

Continue elution, collecting fractions and carrying out qualitative analysis of samples as described above.

Chromatography. Step 3

As soon as you are finished with collecting the second peak, change to Eluent 3 as described in Step 2. Continue chromatography until the third amino acid leaves the column completely.

Stop chromatography by closing the stopcock and fixing the clamp.

Based on the results of qualitative analysis, choose the fractions which contain the amino acids.

1.1 Write down in the Answer Sheet the labels of wells corresponding to the chosen fractions.

1.2 Combine the fractions from each peak and measure the volumes of combined fractions using a measuring cylinder. Report the volumes of combined fractions excluding amounts used for the qualitative analysis. Write down the obtained results in the Answer Sheet.

Pour combined fractions in the amber glass vials labelled “Peak 1”, “Peak 2”, “Peak 3”. Prepare samples for quantitative spectrophotometric analysis as described below.

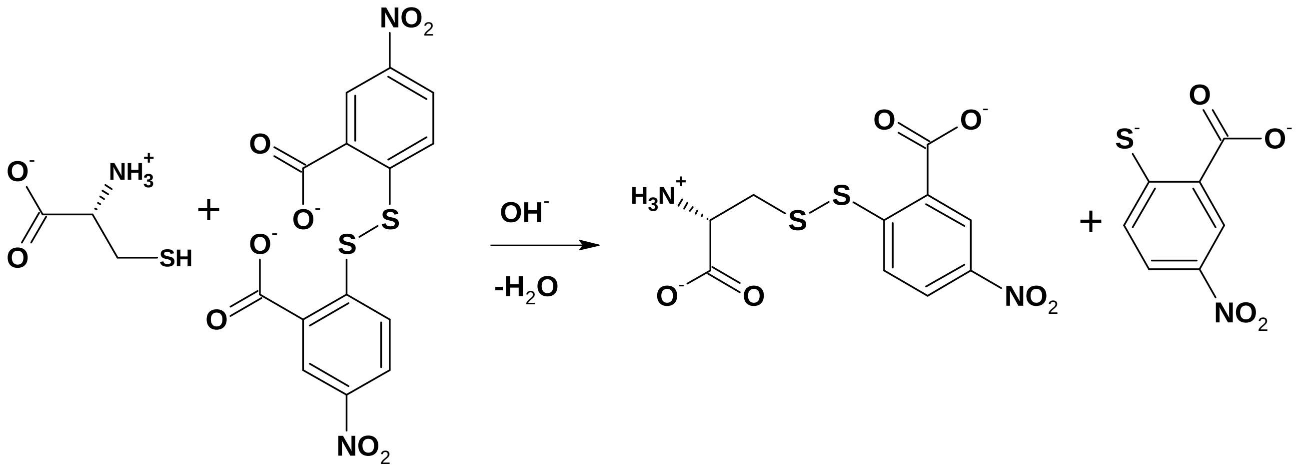
When finished with Practical exam, close the vials and leave them on the table. The combined fractions will be subsequently analyzed by lab staff.

Spectrophotometric analysis

For each probe, you should submit two cells to the operator. Prepare the probes as follows.

Important! When storing, always put cell in the cell holder! All cells have 2 ribbed and 2 working vertical surfaces. While operating with cells, do not touch working surfaces, otherwise you may get incorrect values of absorbance.

Assay 1 (peak 1). Cysteine concentration is determined by the Ellmann reaction:



Test tube A_1 (Reference).

Place 0.1 cm^3 of Eluent 1 from plastic microtube into a test tube and add 2.9 cm^3 of Ellmann reagent (DTNB).

Test tube B_1 (Sample).

Place 0.1 cm^3 of the analyzed solution into a test tube and add 2.9 cm^3 of Ellmann reagent (DTNB).

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cells labelled A_1 (for reference) and B_1 (for sample).

Assay 2 (peak 2). Determination of histidine concentration is based on the ability of imidazole moiety to react with diazonium compounds (Pauli reaction).

Test tube A_2 (Reference).

Place 2.8 cm^3 of Tris-HCl buffer solution into a test tube, add 0.1 cm^3 of Eluent 2 from plastic microtube and 0.1 cm^3 of Pauli reagent.

Test tube B_2 (Sample).

Place 2.8 cm^3 of Tris-HCl buffer solution into a test tube, add 0.1 cm^3 of the analyzed solution and 0.1 cm^3 of Pauli reagent.

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cells labelled A_2 (for reference) and B_2 (for sample).

Assay 3 (peak 3). Determination of arginine concentration is based on the ability of guanidinium moiety to react with some phenols under alkaline and oxidative conditions

(Sakaguchi reaction).

Test tube A_3 (Reference).

Place 0.1 cm^3 of Eluent 3 into a test tube and add 1.5 cm^3 of 10 % NaOH solution, 1 cm^3 of 8-hydroxyquinoline solution and 0.5 cm^3 of sodium hypobromite solution.

Test tube B_3 (Sample).

Place 0.1 cm^3 of the analyzed solution into a test tube and add 1.5 cm^3 of 10 % NaOH solution, 1 cm^3 8-hydroxyquinoline solution and 0.5 cm^3 of sodium hypobromite solution.

Shake the test tubes vigorously for 2 min (**Important!**) and observe formation of orange colour. Add 0.2 cm^3 of 8 M urea solution to each test tube, mix the contents and transfer about 3 cm^3 of each mixture to the corresponding cells labelled A_3 (for reference) and B_3 (for sample).

All mixtures should be analyzed by spectrophotometry not earlier than 10 min and not later than 2 h after preparation. Submit the set of 6 cells to the spectrophotometer operator. In case of a queue at the spectrophotometer, ask the operator to put your student code on the list at the signboard. You will be invited by the operator in due time. Meanwhile, you can answer the theoretical question and start fulfilling Problem No 2.

In case your sample(s) have not been subjected to studies within the proper time interval (which is quite improbable), prepare the sample(s) afresh.

Get the print-offs with the spectra of your samples and check it. Sign the print-offs and get the operator's signature.

1.3 Determine absorbance at the corresponding wavelengths and calculate the content (in mg) of each amino acid in the mixture you were given. The optical length is 1.0 cm. Complete the Answer Sheets taking into account that one mole of each amino acid gives one mole of the corresponding product.

Reference data:

The values of extinction coefficients:	Molar masses of the amino acids.
Product of Ellmann reaction: 13600 M^{-1}cm^{-1} at 410 nm	Cysteine: 121 g mol^{-1}
Product of Pauli reaction: 6400 M^{-1}cm^{-1} at 470 nm	Histidine: 155 g mol^{-1}
Product of Sakaguchi reaction: 7700 M^{-1}cm^{-1} at 500 nm	Arginine: 174 g mol^{-1}

1.4 Draw three resonance structures of the species responsible for mixture coloration as a result of Ellmann reaction.

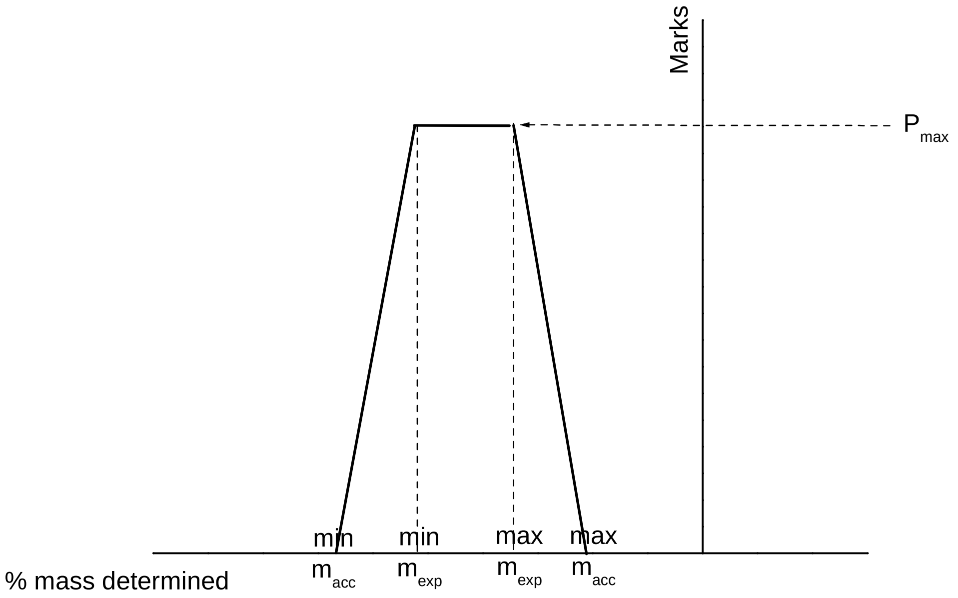
SOLUTION

1.2 – 1.3

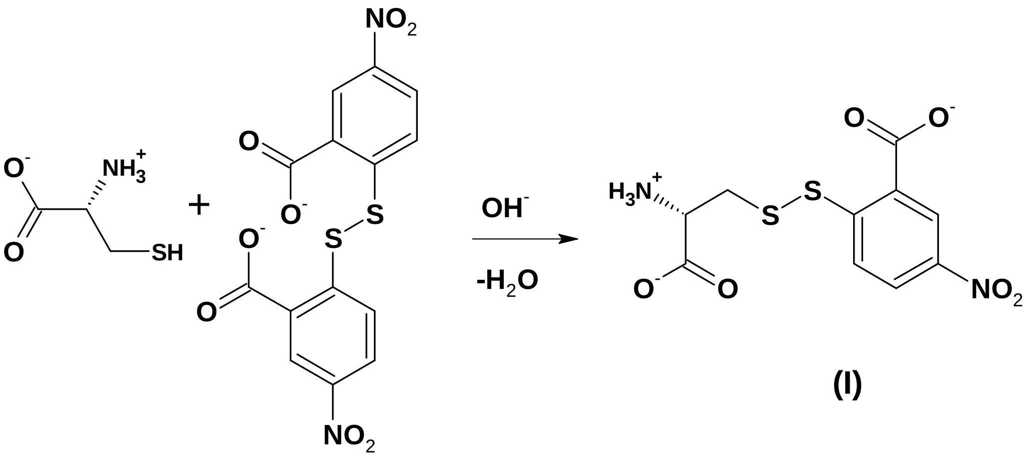
Content of an amino acid = $\dfrac{A_\lambda n\ V\ M}{\varepsilon\, l}$,

A_λ is the absorbance of the sample calculated from the spectra, l is the optical length (1.0 cm), n is the dilution factor determined as a ratio of the aliquot of analyzing solution (0.1 cm^3) and the final volume of the sample in the cells, V is the volume of the combined fraction from the corresponding peak, and M is the molar mass of the amino acid.

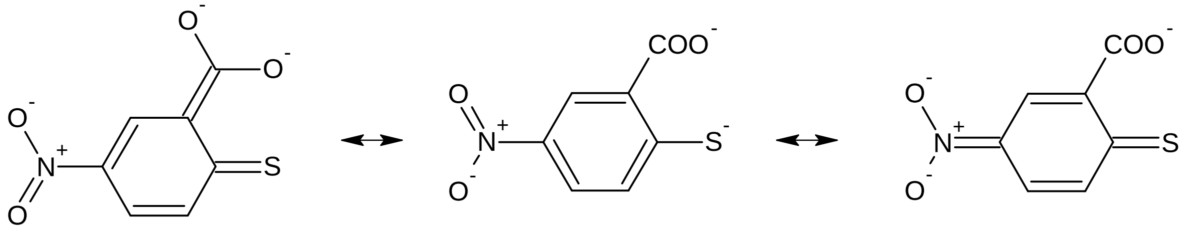
Content of each amino acid is determined by using the following plot (values recalculated from volumes reported by students and absorbance values recorded by spectrophotometer).



1.4 As it is given in the task text, mixed disulfide and 2-thio-5-nitrobenzoic acid are formed in the reaction.



Under slightly alkaline conditions, thiol group of (**II**) dissociates, and thiophenolate-anion is formed. Resonance structures can be realized for this compound:



The electronic structure of asymmetrical disulfide (**I**) does not differ considerably from that of the original Ellmann reagent. Therefore, it can be concluded that the compound responsible for coloration is thiophenolate-anion (a form containing C=S bond).

PROBLEM 2 (Practical)

Determination of Fe(II) and Fe(III) by visual colorimetry

In this experiment, you are required to determine Fe(II) and Fe(III) in a given sample solution which simulates a dissolved magnetite ore by visual colorimetric analysis involving a colour reaction between Fe(II) and 2,2'-bipyridine (bpy) to form an intensely red complex, $Fe(bpy)_3^{2+}$.

The amount of $Fe(bpy)_3^{2+}$ complex can be quantified by visual colorimetric measurement using Nessler tubes. This is a quite simple technique that was employed before photoelectric instruments were generally available, but an accuracy of less than ± 5% can be achieved. In this technique, a pair of Nessler tubes is used; one is filled with a reference solution, and the other is filled with a solution to be tested. The depths of colours of the two solutions are balanced by adjusting the heights of liquid columns of the solutions.

When the colours look the same, the concentration can be calculated from that of the reference solution with a known concentration and the height of the column of each solution based on the Lambert-Beer law:

$$A = \varepsilon c\, l$$

where A is the absorbance, c is the concentration, l is the pass length and ε is the molar absorption coefficient. First, you will learn to employ this technique by conducting measurements **A** and **B**, and then you will determine the concentrations of Fe(II) and Fe(III) with measurements **C** and **D**.

Chemicals

- Sample solution
- Standard $Fe(bpy)_3^{2+}$ solution 1 containing 2.0 mg of iron in 1 dm^3 of the solution.
- Standard $Fe(bpy)_3^{2+}$ solution 2 containing 3.0 mg of iron in 1 dm^3 of the solution.
- Acetate buffer solution, pH 4.6, 1 : 1 mixture of acetic acid and sodium acetate.
- Disodium hydrogen phosphate solution, c = 0.1 mol dm^{-3}.
- 2,2'-bipyridine aqueous solution, w = 0.2 %.
- Sodium thioglycolate.

Procedures

(1) Add 5 cm^3 of acetate buffer solution, 5 cm^3 of disodium hydrogen phosphate solution (to mask Fe(III)), 5 cm^3 of 2,2'-bipyridine solution and 10.00 cm^3 of sample solution into a 50 cm^3 volumetric flask using appropriate pipettes for each and dilute the resulting solution with water to the 50 cm^3 mark. Then stopper the flask and mix the solution well. Allow it to stand for at least 20 min to fully develop colour. This solution is named "sample 1."

(2) Add 5 cm^3 of acetate buffer solution, 5 cm^3 of 2,2'-bipyridine solution and 5.00 cm^3 of sample solution into a 50 cm^3 volumetric flask. Then add 20 mg of sodium thioglycolate powder (in excess) to reduce Fe(III) to Fe(II). Dilute the solution with water to the 50 cm^3 mark, stopper the flask and mix the solution well. Allow it to stand for at least 20 min. This solution is named "sample 2."

(3) Perform visual colorimetric measurements A – D based on the "Instructions for visual colorimetric measurement" shown below.

Instructions for visual colorimetric measurement

Set a pair of Nessler tubes on a Nessler tube rack placed on an LED light box (do not remove it from the bag at any time) and turn on the light (see Fig. 2.1). Pour the provided "standard $Fe(bpy)_3^{2+}$ solution 1" into one tube to an appropriate height (70 – 90 mm is recommended) from the bottom (etched marks on the tube indicate fixed heights from the bottom in mm) and use this as a reference for measurements **A** – **D**. Pour the solution to be measured into the other tube, and then compare its depth of colour with that of the reference solution by looking downward through the solutions toward the LED light box.

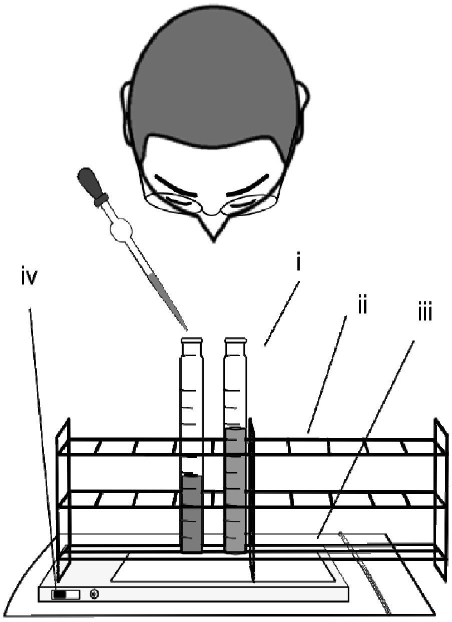


Fig. 2.1
Visual colorimetric measurement:
i: Nessler tube;
Ii: Nessler tube rack; iii: LED light box in a zipper storage bag;
Iv: power switch.

Adjust the height of the liquid column of the test solution by adding or removing the solution with a graduated pipette until the depth of colour in the two tubes is identical. Estimate your reading to at least 1 mm.

Note that the depths of colour in a certain range may be recognized as identical to human eyes. The appropriate value for the height of the test solution, *h*, should be determined by taking the range into the consideration. For example, if you adjust the height of the liquid column of the test solution only by increasing (or decreasing) the volume, you could reach a lower (or higher) value than the true one. A possible way to estimate the true value is to take an average between the values of lower and higher limits.

Measurement A:

Perform a measurement using “standard $Fe(bpy)_3^{2+}$ solution 1” as both the reference and the test solutions. In this measurement, pour the reference solution into a Nessler tube to achieve an appropriate height, and then pour the test solution into the other Nessler tube until the colours of the two solutions match each other. (When the colours match, the heights should ideally be the same.) Then add more test solution until you recognize that the colours have become different from each other. Report both the lower and higher limits of the height of the liquid column of test solution with the same depth of colour as the reference solution.

2.1 Report your results for measurement A using the table provided on the answer sheet.

Measurement B:

Perform a measurement of “standard $Fe(bpy)_3^{2+}$ solution 2” as a test solution using “standard $Fe(bpy)_3^{2+}$ solution 1” as a reference.

2.2 Report your results for measurement B using the table provided on the answer sheet.

Measurement C:

2.3 Perform the measurement of sample 1.

Report your results for measurement C using the table provided on the answer sheet.

Measurement D:

2.4 Perform the measurement of sample 2.

Report your results for measurement D using the table provided on the answer sheet.

2.5 Express the concentration, *c*, of the test solution, using the concentration of the reference solution, *c'*, and the heights of each liquid column, *h* and *h'*.

2.6 Calculate the concentrations of Fe(II) and Fe(III) in the original sample solution in mg dm^{-3}.

SOLUTION

2.1– 2.4

The competitors were requested to summarize their results in four tables for measurements A, B, C, and D, respectively. It was necessary to record the height, *h*', (in mm) of the standard solution and the height, *h*, of the test solution.

A distribution graph was proposed and applied for evaluations of the competitors' results.

2.5 $c = \dfrac{c' \, h'}{h}$

2.6 For Fe^{2+}:

$$c(\mathrm{Fe^{2+}}) = \frac{2.0\ \mathrm{mg\ dm^{-3}} \times h'_\mathrm{C} \times 50\ \mathrm{cm^3}}{h_\mathrm{C} \times 10\ \mathrm{cm^3}}$$

$c(\mathrm{Fe^{2+}})$: concentration, (mg dm^{-3}), of Fe^{2+} in the sample solution,

h_C: experimental height, (mm), of the liquid column of the test solution in the measurements C,

h'_C: experimental height, (mm), of the liquid column of the standard solution in the measurements C.

For Fe^{3+}:

$$c(\mathrm{Fe^{3+}}) = \frac{2.0\ \mathrm{mg\ dm^{-3}} \times h'_\mathrm{D} \times 50\ \mathrm{cm^3}}{h_\mathrm{D} \times 5\ \mathrm{cm^3}} - c(\mathrm{Fe^{3+}})$$

$c(\mathrm{Fe^{3+}})$: concentration, (mg dm^{-3}), of Fe^{3+} in the sample solution,

h_D: experimental height, (mm), of the liquid column of the test solution in the measurements D,

h'_D: experimental height, (mm), of the liquid column of the standard solution in the measurements D.

Concentrations of Fe^{2+} and Fe^{3+} used for particular original sample solutions:

	c(Fe^{2+}) / mg dm^{-3}	c(Fe^{3+}) / mg dm^{-3}
Sample 1	8.16	18.0
Sample 2	8.60	19.0
Sample 3	9.08	17.7

Chemicals and Equipment (Task 1A).

I. Chemical and materials (the actual labeling for each is given in bold font)

	Hazard Statements[a]
Instrument check solution, 80 cm^3 in a plastic bottle	
2.00×10^{-4} mol dm^{-3} **Methyl orange indicator solution,** 30 cm^3 in a wide mouth glass bottle	H301
1.00×10^{-3} mol dm^{-3} **Bromothymol blue indicator solution,** 30 cm^3 in a wide mouth glass bottle	
Methyl red indicator solution, 10 cm^3 in a wide mouth glass bottle	H225-H319-H371
1 mol dm^{-3} **HCl**, 30 cm^3 in a plastic bottle	H290-H314-H335
1 mol dm^{-3} **NaOH**, 30 cm^3 in a plastic bottle	H290-H314
buffer **solution A,** 110 cm^3 in a plastic bottle	
Unknown solution X, 50 cm^3 in a plastic bottle	
Unknown solution Y, 50 cm^3 in a plastic bottle	
Unknown solution Z, 50 cm^3 in a plastic bottle	

[a]**See page** 34 **for definition of Health Statements**

II. Equipment and labwares

Shared Equipment	**Quantity**
UV-Visible spectrophotometer	1 per 2 students
Personal Labwares	**Quantity**
Beaker, 25 cm^3	2
Volumetric flask, 25.00 cm^3	9
Measuring pipette, 2.00 cm^3	2
Measuring cylinder, 10.0 cm^3	3
Pasteur pipette	6
Rubber bulb for Pasteur pipette	6
Pipette filler bulb (3-way)	1
Pipette tray	1
Test tube (13 x 100 mm)	6
Test tube rack	1
Plastic cuvette, optical path length = 1.00 cm	1
Waste bottle, 1 dm^3	1
Sticker label set in a zipped bag	1

Task 1A 13%	a		b			c		Total
	a1	a2	b1	b2	b3	c1	c2	
Total	12	2	6	1	1	2	2	26
Score								

Accounted For 13% of Total Score

Task 1A: Acid-base indicator and its application for pH measurement

Acid-base indicators are weak acids (or bases) that exhibit different colors when they are present in solution as their acidic form (HIn, color 1) or as their basic form (In^-, color 2). They undergo the following reaction in dilute aqueous solution.

$$HIn \rightleftharpoons H^+ + In^-$$

As the pH of a solution containing the indicator changes, the equilibrium shown above will be driven either towards reactants (HIn), or products (In^-) causing the solution color to change depending on the concentration of each form present. In strongly acidic solution, most of the indicator will be present in the HIn form (color 1) and in strongly basic solutions, most of the indicator will be in the In^- form (color 2). At intermediate pH values, the solution color will be a mix of color 1 (absorption at wavelength 1) and color 2 (absorption at wavelength 2), depending on the relative amounts of HIn and In^- present.

By monitoring the absorbance values at two wavelengths, the concentrations of HIn and In^- can be calculated by using the following expressions.

$$\begin{aligned} A^{\lambda 1}_{total} &= A^{\lambda 1}_{HIn} + A^{\lambda 1}_{In-} \\ &= \varepsilon^{\lambda 1}_{HIn}\, b[HIn] + \varepsilon^{\lambda 1}_{In-} b[In^-] \\ A^{\lambda 2}_{total} &= A^{\lambda 2}_{HIn} + A^{\lambda 2}_{In-} \\ &= \varepsilon^{\lambda 2}_{HIn}\, b[HIn] + \varepsilon^{\lambda 2}_{In-} b[In^-] \end{aligned}$$

where b is pathlength of solution and ε is the molar absorptivity.

At a certain pH value, the relative amounts of HIn and In^- in solution are related to the acid dissociation constant (K_a) of the indicator, as shown in the following equation.

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

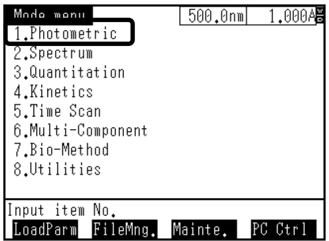
Therefore, for a given pH value, acid dissociation constant (K_a) of the indicator can be calculated when the relative amounts of HIn and In^- in solution are known.

Experimental Set-up

Instructions for using a spectrophotometer

1. Set a spectrophometer to measure the absorbance at the desired wavelength following the procedure shown in the diagram.
2. Wipe the outside of a cuvette containing distilled water and insert the cuvette into the sample compartment.
3. Adjust the zero absorbance using water.
4. Remove the cuvette, replace water in the cuvette by sample solution to be analyzed. Make sure to tap out any bubbles and wipe the outside of the cuvette before placing the cuvette into the sample compartment.
5. Read the absorbance value of the sample.

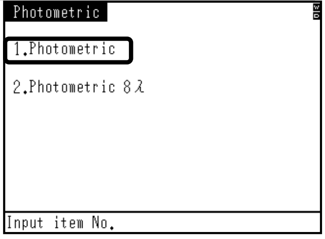
Note: When changing the wavelength, make sure to adjust zero absorbance using "water".



Step 1: Press 1

Press 1 icon on the keypad to select Photometric mode

Note: If the main menu as shown in the left picture is not displayed on the screen, press [return] on the keypad.



Step 2: Press 1

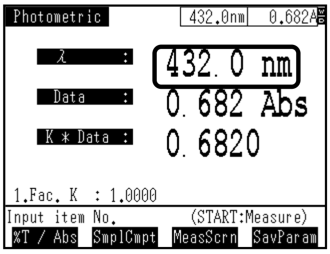
Press 1 icon on the keypad to select Photometric mode single wavelength mode

Step 3: Set the wavelength

Press **[GO TO WL]** on the keypad to set the wavelength

Press number on the keypad

Note: For example, if the desired wavelength is 432, press 4 3 2 on the keypad.



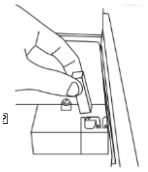
Press **[ENTER]** on the keypad

<u>[GO TO WL]</u> → <u>4 3 2</u> → <u>[ENTER]</u>

Note: If the Abs is not displayed on the screen, press [F1] on the keypad to switch between %T and Abs

Rinse with DI water

Fill the solution around ¾ of the cuvette height and wipe with paper



Step 4: Get the absorbance value

Place cuvette containing water in the sample compartment and press [AUTO ZERO] on the keypad.

Place cuvette containing sample solution in the sample compartment to measure the absorbance

Repeat Step 3-4 to measure the absorbance at another wavelength

General Information

In 0.1 mol dm^{-3} HCl, indicators are in the acidic form (HIn) only.

In 0.1 mol dm^{-3} NaOH, indicators are in the basic form (In^-) only.

There will be no mark for the answer in the dotted line box.

NOTE:

Students are suggested to check the spectrophotometer before use by measuring the absorbance values of the instrument check solution at two different wavelengths, i.e., 430 and 620 nm.

Spectrophotometer No. ________ is used throughout the experiment.

Record the absorbance values of the instrument check solution

	A (at 430 nm)	A (at 620 nm)
Measured value	________________	________________
Guided value	0.220 – 0.260	0.450 – 0.510

In case that the measured values are within the guided values, students can proceed with further experiments. If not, students can ask for assistance.

Part a

Absorbance measurement of an acid-base indicator (methyl orange) in strong acid and strong base

1. Pipette 1.50 cm^3 of 2.00×10^{-4} mol dm^{-3} **methyl orange indicator** solution into a 25.00-cm^3 volumetric flask, add 2.5 cm^3 of 1 mol dm^{-3} HCl into the flask and make up to the volume using distilled water. Record the absorbance at 470 and 520 nm.
2. Pipette 2.00 cm^3 of 2.00×10^{-4} mol dm^{-3} **methyl orange indicator** solution into a 25.00-cm^3 volumetric flask, add 2.5 cm^3 of 1 mol dm^{-3} NaOH into the flask and make up to the volume using distilled water. Record the absorbance at 470 and 520 nm.
3. Calculate the molar absorptivities at 470 and 520 nm of acidic and basic forms of **methyl orange**.

a1) Record the absorbance values of methyl orange in acid and basic solutions

(You do not need to fill the entire table.)

methyl orange in acidic form	A (at 470 nm)	A (at 520 nm)
Replicate 1		
Replicate 2		
Replicate 3		
Accepted value (3 digits after decimal point)	______	______

methyl orange in basic form	A (at 470 nm)	A (at 520 nm)
Replicate 1		
Replicate 2		
Replicate 3		
Accepted value (3 digits after decimal point)	______	______

a2) Calculate the molar absorptivities of the acidic form and basic form of methyl orange (unit, $dm^3\ mol^{-1}\ cm^{-1}$)

Blank area for calculation

The molar absorptivities of methyl orange are as follows: (unit, $dm^3 \ mol^{-1} \ cm^{-1}$)

	acidic form (HIn)		basic form (In^-)	
methyl orange	ε^{470}_{HIn}	ε^{520}_{HIn}	ε^{470}_{In-}	ε^{520}_{In-}
	__________	__________	__________	__________

Part b

Absorbance measurement of an acid-base indicator (bromothymol blue) in buffer solution

Bromothymol blue is an acid-base indicator which shows yellow color when it is present as an acidic form (HIn) and it shows blue color when it is present as a basic form (In^-). The absorption maximum of the bromothymol blue in the acidic form is at 430 nm and that in the basic form is at 620 nm. The molar absorptivities of bromothymol blue in the acidic form are 16,600 $dm^3 mol^{-1} cm^{-1}$ at 430 nm and 0 $dm^3 \ mol^{-1} \ cm^{-1}$ at 620 nm. The molar absorptivities of bromothymol blue in the basic form are 3,460 $dm^3 \ mol^{-1} \ cm^{-1}$ at 430 nm and 38,000 $dm^3 \ mol^{-1} \ cm^{-1}$ at 620 nm.

1. Pipette 1.00 cm^3 of 1.00×10^{-3} mol dm^{-3} **bromothymol blue indicator** solution into a 25.00-cm^3 volumetric flask, and make up to the volume using solution A. (Note: solution A is a buffer solution pH = 7.00)
2. Record the absorbance at 430 and 620 nm.
3. Calculate the concentrations of the acidic form and basic form of **bromothymol blue indicator** solution in the volumetric flask.
4. Calculate the acid dissociation constant of **bromothymol blue**.

b1) Record the absorbance values of bromothymol blue in buffer solution

(You do not need to fill the entire table.)

bromothymol blue in buffer solution	A (at 430 nm)	A (at 620 nm)
Replicate 1		
Replicate 2		
Replicate 3		
Accepted value (3 digits after decimal point)	__________	__________

b2) Calculate the concentrations of the acidic form and basic form of bromothymol blue indicator in the resulting solution

Blank area for calculation

The concentrations of the acidic form and basic form of bromothymol blue in the resulting solution are as follows:

[HIn], mol dm^{-3}	[In^{-}], mol dm^{-3}
____________________ (3 significant figures)	____________________ (3 significant figures)

b3) Calculate the acid dissociation constant of bromothymol blue from this experiment.

Blank area for calculation

The acid dissociation constant of bromothymol blue from this experiment is as follows:

The acid dissociation constant = ____________________________ (3 significant figures)

Part c

Determination of solution pH by using acid-base indicator (methyl red)

Methyl red is an acid-base indicator which shows reddish-pink color when it is present as an acidic form (HIn) and it shows yellow color when it is present as a basic form (In^-). The molar absorptivities of methyl red in the acidic form are 9,810 $dm^3\ mol^{-1}\ cm^{-1}$ at 470 nm and 21,500 $dm^3\ mol^{-1}\ cm^{-1}$ at 520 nm. The molar absorptivities of methyl red in the basic form are 12,500 $dm^3\ mol^{-1}\ cm^{-1}$ at 470 nm and 1,330 $dm^3\ mol^{-1}\ cm^{-1}$ at 520 nm. The pKa of methyl red is 4.95.

Note: There is no need to accurately measure the volumes used in this part, as it does not affect the accuracy of the results obtained.

1. Fill a test tube to one quarter with solution of unknown pH X. Add three drops of **methyl red** into the solution and mix thoroughly. Record the color.
2. Fill a test tube to one quarter with solution of unknown pH Y. Add three drops of **methyl red** into the solution and mix thoroughly. Record the color.
3. Fill a test tube to one quarter with solution of unknown pH Z. Add three drops of **methyl red** into the solution and mix thoroughly. Record the color.

Record the color change of indicator in sample solutions (no mark)

indicator	Color observed		
	in sample X	in sample Y	in sample Z
Methyl red			

c1) Select one solution from the three sample solutions, of which the pH can be determined spectrophotometrically by using methyl red as an indicator.

☐ Sample X ☐ Sample Y ☐ Sample Z

4. Use a measuring cylinder to transfer 10 cm^3 of the selected unknown solution into a beaker. Add three drops of **methyl red** indicator into the solution and mix thoroughly. Record the absorbance at 470 and 520 nm.
5. Calculate the concentration ratio of basic form and acidic form of **methyl red** in the solution.
6. Calculate the pH of the selected unknown solution.

Record the absorbance values of the resulting solution

selected unknown solution	A (at 470 nm)	A (at 520 nm)

c2) Calculate the concentration ratio of the basic form and acidic form of methyl red indicator in an unknown solution and the pH value of the unknown solution

Blank area for calculation

The concentration ratio of the basic form and acidic form of methyl red indicator in an unknown solution and the pH value of the unknown solution are as follows:

sample	$[In^-]$ / [HIn]	pH
	____________ (2 digits after decimal point)	____________ (2 digits after decimal point)

General Instructions.

General Information

In 0.1 mol dm^{-3} HCl, indicators are in the acidic form (HIn) only.

In 0.1 mol dm^{-3} NaOH, indicators are in the basic form (In^-) only.

There will be no mark for the answer in the dotted line box.

NOTE:

Students are suggested to check the spectrophotometer before use by measuring the absorbance values of the instrument check solution at two different wavelengths, i.e., 430 and 620 nm.

Spectrophotometer No. ________ is used throughout the experiment.

Record the absorbance values of the instrument check solution

	A (at 430 nm)	A (at 620 nm)
Measured value	________________	________________
Guided value	0.220 – 0.260	0.450 – 0.510

In case that the measured values are within the guided values, students can proceed with further experiments. If not, students can ask for assistance.

Part a

Absorbance measurement of an acid-base indicator (methyl orange) in strong acid and strong base

1. Pipette 1.50 cm^3 of 2.00×10^{-4} mol dm^{-3} **methyl orange indicator** solution into a 25.00-cm^3 volumetric flask, add 2.5 cm^3 of 1 mol dm^{-3} HCl into the flask and make up to the volume using distilled water. Record the absorbance at 470 and 520 nm.
2. Pipette 2.00 cm^3 of 2.00×10^{-4} mol dm^{-3} **methyl orange indicator** solution into a 25.00-cm^3 volumetric flask, add 2.5 cm^3 of 1 mol dm^{-3} NaOH into the flask and make up to the volume using distilled water. Record the absorbance at 470 and 520 nm.
3. Calculate the molar absorptivities at 470 and 520 nm of acidic and basic forms of **methyl orange**.

a1) Record the absorbance values of methyl orange in acid and basic solutions

(You do not need to fill the entire table.)

methyl orange in acidic form	A (at 470 nm)	A (at 520 nm)
Replicate 1		
Replicate 2		
Replicate 3		
Accepted value (3 digits after decimal point)	0.318 (SD = 0.009)	0.538 (SD = 0.011)

methyl orange in basic form	A (at 470 nm)	A (at 520 nm)
Replicate 1		
Replicate 2		
Replicate 3		
Accepted value (3 digits after decimal point)	0.425 (SD = 0.009)	0.141 (SD = 0.004)

a2) Calculate the molar absorptivities of the acidic form and basic form of methyl orange (unit, dm^3 mol^{-1} cm^{-1})

Blank area for calculation

The molar absorptivities of methyl orange are as follows: (unit, $dm^3\ mol^{-1}\ cm^{-1}$)

	acidic form (HIn)		basic form (In^-)	
methyl orange	ε^{470}_{HIn}	ε^{520}_{HIn}	ε^{470}_{In-}	ε^{520}_{In-}
	________	________	________	________

Part b

Absorbance measurement of an acid-base indicator (bromothymol blue) in buffer solution

Bromothymol blue is an acid-base indicator which shows yellow color when it is present as an acidic form (HIn) and it shows blue color when it is present as a basic form (In^-). The absorption maximum of the bromothymol blue in the acidic form is at 430 nm and that in the basic form is at 620 nm. The molar absorptivities of bromothymol blue in the acidic form are 16,600 $dm^3 mol^{-1} cm^{-1}$ at 430 nm and 0 $dm^3\ mol^{-1}\ cm^{-1}$ at 620 nm. The molar absorptivities of bromothymol blue in the basic form are 3,460 $dm^3\ mol^{-1}\ cm^{-1}$ at 430 nm and 38,000 $dm^3\ mol^{-1}\ cm^{-1}$ at 620 nm.

1. Pipette 1.00 cm^3 of 1.00×10^{-3} mol dm^{-3} **bromothymol blue indicator** solution into a 25.00-cm^3 volumetric flask, and make up to the volume using solution A. (Note: solution A is a buffer solution pH = 7.00)
2. Record the absorbance at 430 and 620 nm.
3. Calculate the concentrations of the acidic form and basic form of **bromothymol blue indicator** solution in the volumetric flask.
4. Calculate the acid dissociation constant of **bromothymol blue**.

b1) Record the absorbance values of bromothymol blue in buffer solution

(You do not need to fill the entire table.)

bromothymol blue in buffer solution	A (at 430 nm)	A (at 620 nm)
Replicate 1		
Replicate 2		
Replicate 3		
Accepted value (3 digits after decimal point)	0.489 (SD = 0.006)	0.734 (SD = 0.014)

b2) Calculate the concentrations of the acidic form and basic form of bromothymol blue indicator in the resulting solution

Blank area for calculation

The concentrations of the acidic form and basic form of bromothymol blue in the resulting solution are as follows:

[HIn], mol dm^{-3}	[In^{-}], mol dm^{-3}
______________________ (3 significant figures)	______________________ (3 significant figures)

b3) Calculate the acid dissociation constant of bromothymol blue from this experiment.

Blank area for calculation

The acid dissociation constant of bromothymol blue from this experiment is as follows:

The acid dissociation constant = ______________________________ (3 significant figures)

Part c

Determination of solution pH by using acid-base indicator (methyl red)

Methyl red is an acid-base indicator which shows reddish-pink color when it is present as an acidic form (HIn) and it shows yellow color when it is present as a basic form (In^-). The molar absorptivities of methyl red in the acidic form are 9,810 dm^3 mol^{-1} cm^{-1} at 470 nm and 21,500 dm^3 mol^{-1} cm^{-1} at 520 nm. The molar absorptivities of methyl red in the basic form are 12,500 dm^3 mol^{-1} cm^{-1} at 470 nm and 1,330 dm^3 mol^{-1} cm^{-1} at 520 nm. The pKa of methyl red is 4.95.

Note: There is no need to accurately measure the volumes used in this part, as it does not affect the accuracy of the results obtained.

1. Fill a test tube to one quarter with solution of unknown pH X. Add three drops of **methyl red** into the solution and mix thoroughly. Record the color.
2. Fill a test tube to one quarter with solution of unknown pH Y. Add three drops of **methyl red** into the solution and mix thoroughly. Record the color.
3. Fill a test tube to one quarter with solution of unknown pH Z. Add three drops of **methyl red** into the solution and mix thoroughly. Record the color.

Record the color change of indicator in sample solutions (no mark)

indicator	Color observed		
	in sample X	in sample Y	in sample Z
Methyl red			

c1) Select one solution from the three sample solutions, of which the pH can be determined spectrophotometrically by using methyl red as an indicator.

☑ Sample X ☐ Sample Y ☐ Sample Z

4. Use a measuring cylinder to transfer 10 cm^3 of the selected unknown solution into a beaker. Add three drops of **methyl red** indicator into the solution and mix thoroughly. Record the absorbance at 470 and 520 nm.
5. Calculate the concentration ratio of basic form and acidic form of **methyl red** in the solution.
6. Calculate the pH of the selected unknown solution.

Record the absorbance values of the resulting solution

selected unknown solution	A (at 470 nm)	A (at 520 nm)

c2) Calculate the concentration ratio of the basic form and acidic form of methyl red indicator in an unknown solution and the pH value of the unknown solution

Blank area for calculation

The concentration ratio of the basic form and acidic form of methyl red indicator in an unknown solution and the pH value of the unknown solution are as follows:

sample	$[In^-] / [HIn]$	pH
	____________ (2 digits after decimal point)	____________ (2 digits after decimal point)

Cinetica

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

You will follow the concentration change of one of the reactants by the method of comparative visual colorimetry. From data obtained experimentally plot graphically the change of the reactant concentration in dependence on time.

Procedure:

1. *Making of the comparative colorimetric scale of bromine solution*

Measure with a syringe into 10 identical test-tubes the following quantities of bromine water (0.01-molar): into the first one – 10.0 cm^3; 2nd – 9.0 cm^3; 3rd – 8.0 cm^3, ... 9th – 2.0 cm^3; into the tenth one – 1.0 cm^3. Then add to all the test-tubes (except the first one) distilled water to reach a total volume of 10.0 cm^3 in each. Seal the test-tubes with stoppers and mix the solutions. Put the test-tubes in a stand with a white background. Finally calculate the concentration (in mol dm^{-3}) of bromine in the solutions in all test-tubes.

2. *Reaction of bromine solution with formic acid*

Carry out the reaction by mixing 100.0 cm^3 of bromine solution with 1.0 cm^3 of 1.00-molar solution of formic acid. Immediately after mixing transfer 10.0 cm^3 of the resulting solution to the test-tube identical with that used for colorimetric scale. By comparing the colour shade of the reaction mixture (in one-minute intervals) with that of the solutions in the scale, investigate changes of bromine concentration in dependence on time.

Put the data in a table containing time (t) and concentration of Br_2.

Task:

Plot the bromine concentration in dependence on time a read the half-time of the reaction from the diagram.

Questions:

1.1 Write the equation for the reaction of bromine with formic acid assuming that the reactants are in stoichiometric amounts.

1.2 In analytical chemistry a volumetric solution of bromine can be prepared by dissolving a mixture of bromate and bromide in acid medium. Explain this mode of preparation by means of a chemical equation in ionic form.

SOLUTION

Questions:

1.1 $HCOOH (aq) + Br_2 (aq) \rightarrow CO_2 (g) + 2 H^+ (aq) + 2 Br^- (aq)$

1.2 $BrO_3^- + 5 Br^- + 6 H^+ \rightarrow 3 Br_2 + 3 H_2O$

PROBLEM 2 (practical)

The values of standard reduction potentials are given for the following redox systems:

$2\ S_2O_3^{2-} / S_4O_6^{2-}$ $E_1^0 = 0.17$ V

$2\ I^- / I_2$ $E_2^0 = 0.535$ V

$2\ SO_4^{2-} / S_2O_8^{2-}$ $E_3^0 = 2.05$ V

Problems:

2.1 Set in order the oxidation forms of the above given redox systems from the weakest to the strongest oxidising agent (write into Table 1)

In a similar way order the reduction forms from the weakest to the strongest reducing agent.

2.2 In the bellow given equations mark by arrows the expected possible course (direction) of the chemical reaction (Table 1).

$2\ I^- + S_4O_6^{2-} = I_2 + 2\ S_2O_3^{2-}$

$2\ I^- + S_2O_8^{2-} = I_2 + 2\ SO_4^{2-}$

$2\ S_2O_3^{2-} + S_2O_8^{2-} = S_4O_6^{2-} + 2\ SO_4^{2-}$

2.3 On the assumption that solutions of the same concentration are used, is it possible to tell without making any experiment which of the given reactions would run at a higher rate and which ones at a lower rate?

In order to confirm your hypothesis given under 3, perform the following three qualitative experiments:

Experiment 1

Pour 20.0 cm^3 of a 0.10-molar solution of $Na_2S_2O_3$ into an Erlenmeyer flask and quickly add under intense stirring 1.0 cm^3 of a 0.10-molar iodine solution.

Experiment 2

Measure 20.0 cm^3 of a 0.10-molar solution of $(NH_4)_2S_2O_8$ into an Erlenmeyer flask and quickly add under intense stirring 4.0 cm^3 of a 0.10-molar potassium iodide solution.

Experiment 3

Put 20.0 cm^3 of a 0.10-molar solution of $(NH_4)_2S_2O_8$ into an Erlenmeyer flask and then quickly add under intense stirring 2.0 cm^3 of a 0.10-molar sodium thiosulphate solution.

Since both the reactants and reactant products are colourless, the course of the reaction can be followed indirectly. For that purpose, add to the solution after 1 – 2 minutes two or three drops of a 0.10-molar iodine solution. If the result of your experiment is surprising, perform experiment No 3 again but allow solutions of $Na_2S_2O_3$ and $(NH_4)_2S_2O_8$ to react for 10 minutes.

Order the reactions from experiments No 1 – 3 (into Table 3) according to their increasing reaction rate and then answer the question whether it is possible on the basis of known values of the standard reduction potentials to guess, at least qualitatively, the reaction rate for the reaction mixture containing two pairs of redox systems.

Conclusions made on the above experiments make it possible to investigate the influence of concentration of each of the starting substances on the rate of the reaction between I^- and $S_2O_8^{2-}$ ions.

Perform experiment No 4 according to the following instructions:

Experiment 4

a) Measure successively into a 250 cm^3 Erlenmeyer flask: 25.0 cm^3 of a 0.20-molar potassium iodide solution, 10.0 cm^3 of a 0.01-molar sodium thiosulphate solution, 5.0 cm^3 of a starch paste, and stir the content of the flask.

b) Measure 25.0 cm^3 of a 0.20-molar $(NH_4)_2S_2O_8$ solution into a 100 cm^3 beaker. Pour the content of the beaker quickly into the flask, press a stop-watch and stir the content of the flask. Measure the time till the moment when the solution becomes blue.

Perform analogously experiment No 4 three times over, using the bellow given volumes of the 0.20-molar potassium iodide solution, while the volumes of $Na_2S_2O_3$ and $(NH_4)_2S_2O_8$ solutions as well as that of the starch paste remain unchanged. Moreover, add to the solution the bellow given volumes of a 0.20-molar potassium nitrate solution so that the volume of the resulting solution is always the same. Explain the use of potassium nitrate in this case.

4 (ii): 15.0 cm^3 0.20-molar KI + 10.0 cm^3 0.20-molar KNO_3
4 (iii): 10.0 cm^3 0.20-molar KI + 15.0 cm^3 0.20-molar KNO_3
4 (iv): 5.0 cm^3 0.20-molar KI + 20.0 cm^3 0.20-molar KNO_3

2.4 List the results of experiments No 1-4 briefly and clearly in the attached Tables.

Write formulas of the corresponding substances above the arrows in Table 1 (as required under 2.1) and mark the expected course of the mentioned chemical reactions by arrows in the equations.

For a qualitative evaluation of reaction rate (Table 2) use terms such as: very rapid, rapid, slow, very slow.

Fill in Table 3 exactly according to the titles of the columns.

2.5 Calculate the reaction rate according to the formula:

$$v = \frac{\Delta c(S_2O_8^{2-})}{\Delta \tau} \text{ (mol dm}^{-3}\text{ s}^{-1}\text{)}$$

$\Delta c(S_2O_8^{2-})$ - concentration change of $S_2O_8^{2-}$ in a time interval.

Plot (on the attached mm-paper) the dependence of reaction rate on the concentration of I^- anions at a constant concentration of $S_2O_8^{2-}$ anions in the solution.

2.6 Making use of the knowledge gained from the preceding experiment and the solutions which are at your disposal, suggest another experiment which would make it possible to investigate the reaction rate dependence on concentration of $S_2O_8^{2-}$ anions at a constant concentration of I^- anions in the solution.

Considering Table 3, fill in Table 4. Mark the columns in the Table, suggest a plan of the experiment and list experimental results as well as the calculated values. Similarly as before, plot the dependence under investigation on a mm-paper.

2.7 Write a general relation for the reaction rate dependence on the concentration of reactants and then using the diagrams attached, calculate the values for the reaction rate constant for both cases and determine their mean value.

SOLUTION

2.1 $S_4O_6^{2-} \qquad\qquad I_2 \qquad\qquad S_2O_8^{2-}$

$\xrightarrow{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$

Increase of oxidising properties of oxidised forms

$SO_4^{2-} \qquad\qquad I^- \qquad\qquad S_2O_3^{2-}$

$\xrightarrow{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$

Increase of reducing properties of reduced forms

2.2 The expected course of the chemical reactions:

$2\, I^- + S_4O_6^{2-} \leftarrow I_2 + 2\, S_2O_3^{2-}$ (a)

$2\, I^- + S_2O_8^{2-} \rightarrow I_2 + 2\, SO_4^{2-}$ (b)

$2\ S_2O_3^{2-} + S_2O_8^{2-} \rightarrow S_4O_6^{2-} + 2\ SO_4^{2-}$ (c)

2.3 The formulation of any hypothesis either supporting or neglecting the possibility of predicting the reaction rate, should be accepted as correct.

Results of experiments Nos 1-3:

1 - reaction (a) is very rapid;

2 - reaction (b) is slow;

3 - reaction (c) is very slow, its course can hardly be observed.

Conclusion: The known differences between the values of standard reduction potentials of two pairs of redox systems do not allow to guess even qualitatively the proper relations between the rates of the corresponding reactions.

2.4 You are required to fill in the following data into Table 3:

- volumes of individual solutions,
- the total volume of the solution (65 cm^3),
- calculated values for I^- and $S_2O_8^{2-}$ concentrations,
- reaction time,
- calculated values for the reaction rate.

The addition of 0.20-molar KNO_3 solution is needed to keep the constant ionic strength of the resulting solution.

In plotting the reaction rate in dependence on the values of $[I^-]^2$ (at the constant concentration of $S_2O_8^{2-}$ anions) we get a straight line crossing the beginning of the coordinate system.

Table 4 should be filled in analogously as Table 3 where, moreover, the individual columns should be specified.

Solutions for the experiment are prepared in the same way but the solution of KI (25 cm^3) will form a constant addition, whereas those of $(NH_4)_2S_2O_8$ and $(NH_4)_2SO_4$ will form a changeable addition in the resulting solution and the other conditions are equal. Ammonium sulphate plays the same role in the solution as potassium nitrate in the preceding experiment.

In this case the reaction rate versus the concentration of $S_2O_8^{2-}$ anions is plotted (at a constant concentration of I^- anions) to give also a straight line crossing the beginning of the coordinate system.

2.5 The rate of the reaction:

$v = k\,[S_2O_8^{2-}]\,[I^-]^2$

a) $[I^-]$ = const $\Rightarrow$ $v = k'\,[S_2O_8^{2-}]$

$$k = \frac{k'}{[I^-]^2}$$

k' is the slope of the straight line.

b) $[S_2O_8^{2-}]$ = const $v = k''\,[I^-]^2$

$k'' = k\,[S_2O_8^{2-}]$

$$k = \frac{k''}{[S_2O_8^{2-}]}$$

k'' is the slope of the straight line.

The values of the rate constants obtained from the procedures a) and b) should be theoretically equal. If they partly differ, calculate the mean value of the rate constant.

PROBLEM 4 (Practical)

Kinetics of an S_N1 Reaction

In an aqueous ethanolic solution, *tert*-butyl chloride (2-chloro-2-methylpropane) undergoes an S_N1 nucleophilic substitution reaction leading to the formation of 2-methylpropan-2-ol and hydrochloric acid:

tert-BuCl + H_2O = *tert*-BuOH + HCl

The rate of the reaction is given by

$$\frac{d\,[\text{HCl}]}{d\,t} = k_1\,[\textit{tert}\ \text{BuCl}]$$

The aim of this experiment is to determine the rate constant k_1 at ambient temperature.

Procedure:

1. Using a pipette transfer 2.0 cm^3 of *tert*-butyl chloride (flask 4.1 on the general-use bench) into a clean and dry 250 cm^3 ground neck Erlenmeyer (conical) flask.
2. As soon as possible add 148 cm^3 (measure with the graduated cylinder) of the aqueous ethanol solution standing on the general-use bench (flask 4.2).
3. Stopper the Erlenmeyer flask and stir vigorously using the magnetic stirrer. Start your timer. Note carefully the temperature, T(0), of the solution.
4. After approximately 5, 15, 25, 35, 45, 55 min (determined accurately), transfer 10.0 cm^3 samples using a pipette into 20 cm^3 of a mixture of ice and acetone (propanone).

   Add 2 drops of bromothymol blue and titrate the liberated acid with a solution of Y mol dm^{-3} aqueous sodium hydroxide (Y will be shown on the board).

Questions:

4.1 The concentrations of *tert*-BuCl at time t = 0 and at time t are linked by the following relationship:

$$\ln \frac{[\text{tertBuCl}]_0}{[\text{tertBuCl}]_t} = k_1.t$$

Establish the theoretical expression:

$$\ln \frac{V_\infty}{V_\infty - V} = k_1\, t$$

where *V* stands for the volume of sodium hydroxide used at time *t* and *V*(8) for the corresponding value at *t*(8).

$t_\infty = t(8); \quad V_\infty = V(8)$

4.2 Calculate *V*(8) (density of *tert*-BuCl at 20 °C: 850 kg m^{-3}, molar mass of *tert*-BuCl: 92.5 g mol^{-1}).

4.3 Fill in the table on the answer sheet whose columns will be:

$$t(\text{min}),\ V(\text{cm}^3),\ V_\infty,\ V,\ \frac{V_\infty}{V_\infty - V},\ \ln\frac{V_\infty}{V_\infty - V}$$

Draw the curve

$$\ln\frac{V_\infty}{V_\infty - V} = f(t)$$

4.4 Determine the value of k_1 (give the value of *t*(0)).

SOLUTION

4.1 $\text{t-BuCl} + H_2O \rightarrow \text{t-BuOH} + \text{HCl}$

$t = 0$	$(\text{t-BuCl})_0$	
t	(t-BuCl)	$(\text{t-BuCl})_0 - (\text{t-BuCl})$
$t(8)$		$(\text{t-BuCl})_0$

$$\frac{d(\text{HCl})}{dt} = -\frac{(t - \text{BuCl})}{dt} = k_1\,(t - \text{BuCl})$$

$$\ln\frac{(t - BuCl)_0}{(t - BuCl)} = k_1\, t$$

t:

$$c(\text{HCl}) = c_0(\text{t-BuCl}) - c(\text{t-BuCl}) = \frac{V(\text{NaOH}) \times c(\text{NaOH})}{V(\text{HCl})} = \frac{V \times \text{Y} \times 10^{-2}}{10}$$

t(8)

$$c(\text{HCl}) = c_0(\text{t-BuCl}) = \frac{a\,Y}{10}$$

$$c(\text{t-BuCl}) = \frac{(a - V)\,\text{Y}}{10}$$

$$\ln\frac{c_0(\text{t-BuCl})}{c(\text{t-BuCl})} = \ln\frac{a}{a-V} = k_1\, t$$

4.2 $n_0(\text{t-BuCl}) = \dfrac{1.70}{92.5}$ $M(\text{t-BuCl}) = 92.5 \text{ g mol}^{-1}$

$$\text{Y} \times \text{a} \times 10^{-3} = \frac{10}{150} \times n_0(\text{t-BuCl})$$

$$\text{a}_{(\text{ml})} = \frac{170}{\text{Y} \times 10^{-3} \times 15 \times 92.5}$$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

A Kinetic Study of the Acid Catalyzed Reaction Between Acetone and Iodine in Aqueous Solution

The reaction between acetone and iodine in aqueous solution is catalyzed by H^+.

$$CH_3\text{-}CO\text{-}CH_3\ (aq) + I_2\ (aq) \xrightarrow{H^+} CH_3\text{-}CO\text{-}CH_2I\ (aq) + H^+(aq) + I^-(aq)$$

In this experiment, the kinetics of the iodination is measured to determine the rate law of the reaction. The rate equation for the loss of I_2(aq) has been shown to have the form

$$\text{Rate} = -\frac{d[I_2]}{dt} = k\,[CH_3COCH_3]^x\,[I_2]^y\,[H^+]^z$$

where H^+ ions are the catalyst.

In order to determine the rate constant k and the kinetic orders x, y and z, the initial rate of reaction is measured.

$$\text{Initial rate} = k\,[CH_3COCH_3]_0^x\,[I_2]_0^y\,[H^+]_0^z$$

where $[\ ]_0$ are the initial concentrations of acetone, I_2 and H^+, respectively.

If the initial rates are measured for various initial concentrations of the reactants then the order with respect to each reactant can be obtained.

The initial rate is obtained by measuring the decrease in the I_2(aq) concentration after a short time interval (7.0 min. in this experiment) after the start of the reaction. Aqueous sodium acetate solution is added to stop the reaction after 7 minutes. The acetate ion reacts immediately with the H^+ to produce acetic acid and so reducing the concentration of H^+. The reaction is thus stopped as there is no catalyst present.

Since the reaction does not come to a complete halt, the solution should be titrated immediately after the addition of the sodium acetate solution.

The remaining iodine I_2 (aq) is determined by titration with sodium thiosulphate, $Na_2S_2O_3$. As the end point of the titration is approached, starch indicator is added and the titration is continued until the blue colour disappears.

Chemicals

1.	Aqueous iodine solution in 0.4 M KI	80 cm^3
2.	0.100 M aq. HCl	50 cm^3
3.	0.50 M aq. CH_3COONa	80 cm^3
4.	Standard 0.02 M $Na_2S_2O_3$(aq) solution (the exact concentration will be announced at the beginning of practical part)	200 cm^3
5.	Aqueous acetone (50% by volume) (Density of pure acetone; 0.787 g cm^{-3}, MW. = 58.08)	50 cm^3
6.	Starch indicator	7 cm^3

Procedure

A. Standardization of Iodine Solution

1. Pipet 5.00 cm^3 of aqueous iodine into a clean 125 cm^3 Erlenmeyer flask.
2. Add 10 cm^3 of distilled water using graduated cylinder.
3. Titrate the iodine with the standard 0.02 M sodium thiosulphate solution until the colour of the solution is pale yellow.
4. Add 3 – 4 drops of starch indicator and continue the titration until the blue colour disappears.
5. Record the initial and the final volumes of the thiosulphate solution and the volume used in the answer sheet.
6. Repeat the titration as necessary (Steps 1 to 5).
7. Give the titre volume for calculation in the answer sheet.
8. Calculate the iodine concentration.

B. A kinetic study of acid catalyzed reaction between acetone and iodine in aqueous solution

1. Label the stoppered flasks as follows: Flask I, II, III and IV.
2. To each respective flask add the following volumes of distilled water, 0.100 M hydrochloric acid and 50 % acetone:

Flask No.	Volume (cm^3)		
	water	0.100 M HCl	50 % acetone
I	5.00	5.00	5.00
II	0.0	5.00	5.00
III	0.0	5.00	10.00
IV	0.0	10.00	5.00

Stopper each flask immediately after addition of the solutions.

3. Measure out 10 cm^3 of 0.50 M aq. CH_3COONa into the graduated cylinder.
4. Set the stop-watch to 0.0000 display.
5. Pipet 5.00 cm^3 of iodine solution into the stoppered Flask No. I.
   Start the stop-watch as soon as the first drop of iodine solution is added.
6. Stopper the flask and swirl continuously.
7. Just before 7.0 min, remove the stopper, at 7.0 min, immediately pour 10 cm^3 of sodium acetate solution (from step 3) into the reaction flask. Shake well.
8. Titrate the remaining iodine with standard thiosulphate solution.
9. Record the volume of the thiosulphate solution.
10. Repeat the above steps (Steps 3 to 9) for Flask II, III and IV but add in step 5 the I_2(aq) solution to each flask as indicated:

Flask II: 10.00 cm^3 I_2 solution
Flask III: 5.00 cm^3 I_2 solution
Flask IV: 5.00 cm^3 I_2 solution

Calculations

B-1. Calculate the initial concentrations (M) of iodine, acetone and HCl solutions in Flasks I to IV, assuming volumes are additive.

B-2. Calculate concentrations of iodine (M) remaining in Flasks I to IV at 7.0 minutes.

B-3. Calculate the initial reaction rate for Flasks I to IV in M s^{-1}.

B-4. The rate of reaction has the form

$$\text{Rate} = -\frac{d[I_2]}{dt} = k\,[CH_3COCH_3]^x\,[I_2]^y\,[H^+]^z$$

Calculate the reaction orders x, y and z from the initial rates and the initial concentrations of acetone, iodine and HCl. The values of x, y and z should be rounded off to the nearest integer and fill in the answer sheet. Write rate equation or rate law.

B-5. Calculate the rate constant, k, for Flasks I to IV with proper unit.

B-6. Give the mean value of the rate constant.

SOLUTION

The competitors were required to perform the following tasks:

In part A: Using the concentration of standard $Na_2S_2O_3$ solution (in bottle) and titration results it was required to calculate the concentration of iodine in the solution. Results were expected to be shown in a table in the answer sheet.

In part B: The following calculations B1 – B5 were required to be shown in the answer sheet:

B-1. *Calculation for initial concentrations (M) in the solution mixtures.*

B-2. *Calculation of the concentration (M) of iodine remaining in flasks I to IV at 7 minutes.*

B-3. *Calculation of initial rate of disappearance of I_2 at 7 minutes in flasks I to IV*.

Rate of disappearance of iodine (M s^{-1}) = $-\dfrac{d[I_2]}{dt} = \dfrac{c(I_2)_{\text{initial}} - c(I_2)_{7\,\text{min}}}{7 \times 60\ s}$

B-4. *Calculation of x, y, and z in the rate equation*:

$$\text{rate} = -\frac{d[I_2]}{dt} = k\,[CH_3COCH_3]^x\,[I_2]^y\,[H^+]^z$$

In comparing the rates in solutions **II** : **I**, **III** : **I**, and **IV** : **I** one can calculate the following values:

$x = 1$; $y = 0$; $z = 1$

The rate equation has the form: rate = $k\,[CH_3COCH_3]\,[H^+]$

B-5. *Calculation of the rate constants for solution mixtures **I** to **IV** and the mean value of the rate constant.*

PROBLEM 3 (Practical)

Determination of the Rate Constant for the Redox Reaction between Ethanol and Chromium (VI)

The oxidation of alcohols by chromium (VI) forms the basis for analysis of breath samples for measuring alcohol content. A dilute solution of $K_2Cr_2O_7$ in the presence of a strong acid (3.6 M HCl here) is a source of $HCrO_4^-$ which is the oxidant involved in the reaction.

In this experiment, the rate of the reaction between $HCrO_4^-$ and CH_3CH_2OH is determined titrimetrically. Under the given experimental conditions, the rate law reduces to

rate = $k[HCrO_4^-]^x$

where **x** is the order of the reaction.

At any given time, $[HCrO_4^-]$ is obtained by iodometric titration.

Procedure

You are given 100 cm^3 of standard $K_2Cr_2O_7$ solution in HCl in a bottle. Transfer all the absolute ethanol given in a vial into this bottle and stopper it. Mix the contents thoroughly, start the stopwatch immediately and regard this as time *t* = 0. Fill the burette with this solution.

After every 10 minutes, start to draw 10 cm^3 of this solution to a clean conical flask containing 4 cm^3 of the given KI solution. The solution will turn brown. Titrate this solution with the given standard $Na_2S_2O_3$ solution until the colour changes to pale greenish yellow. Add 2 cm^3 of starch indicator and continue the titration until the colour changes from blue to pale green. Record the burette reading in the answer sheet. Repeat this procedure at 10 minutes intervals to obtain four readings.

SOLUTION

The results of the titration (volumes) were required to be written on the Answer Sheet.

The other tasks to be solved:

3.1 Write down the possible oxidation products in the reaction of $HCrO_4^-$ and CH_3CH_2OH.

Solution: Acetic acid, CH_3COOH

Acetaldehyde, CH_3CHO

3.2 Write the chemical equation for the reaction between $HCrO_4^-$ and KI:

Solution: $2\ HCrO_4^- + 6\ I^- + 14\ H^+ \rightarrow 3\ \mathbf{I}_2 + 2\ Cr^{3+} + 8\ H_2O$

3.3 Write down the balanced chemical equation involved in the titration.

Solution: $I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

3.4 Give the main steps for the calculation of $HCrO_4^-$ concentration (mol dm^{-3}) for any one titration reading.

3.5 Give **c**oncentrations of $HCrO_4^-$ at different times (in a table attached).

3.6 Plot the graph of log $[HCrO_4^-]$ *vs.* time.

3.7 From the nature of the graph determine the order (**x**) of the reaction with respect to $HCrO_4^-$

3.8 Determine the rate constant for the reaction.

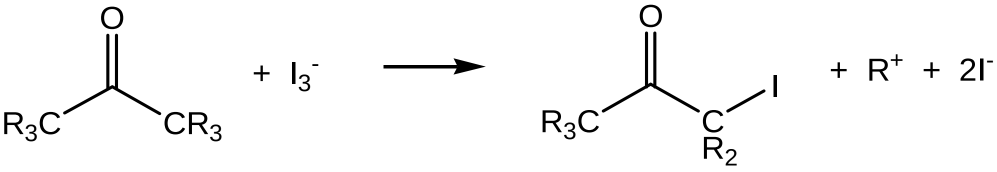
PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Kinetics, Isotope Effect, and Mechanism of Iodination of Acetone

Discoveries about the mechanisms of chemical reactions underlie advances in catalysis and synthesis. One of the most powerful tools for probing reaction mechanisms is the study of kinetics because the ways in which reaction rates vary with reaction conditions follow directly from the mechanism of reaction. A second powerful tool is the study of isotopically substituted molecules. While isotopes impart similar reactivity, there are slight differences in reaction rates as a function of nuclear mass.

In this task you will use both kinetics and isotope effects to provide information about the iodination of acetone in acidic aqueous solution:



R = H or D

The reaction takes place with a rate law

$$\text{Rate} = k\,[\text{acetone}]^m\,[I_3^-]^n\,[H^+]^p$$

where the rate constant k and the integer reaction orders m, n, and p are for you to determine. You will also compare the reactivity of acetone with that of acetone-d_6, where the six atoms of protium (^{1}H) have been replaced by deuterium (^{2}H, D), to determine the isotope effect (k_H / k_D) of the reaction. From these data you will make inferences about the mechanism of this reaction.

Please read the whole description of this task and plan your work before you begin.

Chemicals

- HCl, aqueous solution, c = ~2 mol dm^{-3} ***)**, 50 cm^3
- KI_3, aqueous solution, c = ~0.01 mol dm^{-3} ***)**, 10 cm^3 , labelled "I_2",
- Acetone, $(CH_3)_2CO$, M = 58.08 g mol^{-1}, density = 0.791 g cm^{-3}, 10 cm^3,

- Acetone-d_6, $(CD_3)_2CO$, M = 64.12 g mol^{-1}, density = 0.872 g cm^{-3}, 3.0 cm^3

---

*) The exact concentration is indicated on the label.

Procedure

Reaction rates are dependent on temperature. Record the temperature in the room you are working in (ask the room assistant).

Measure the volumes of hydrochloric acid, distilled water, and potassium triiodide solution (labelled as "I_2") that you choose into the reaction vessel. The initial concentrations of the reagents in the reaction mixtures should be in the ranges given below (you need not explore the full ranges given, but your values should not be significantly outside these ranges):

$[H^+]$: between 0.2 and 1.0 mol dm^{-3}
$[I_3^-]$: between 0.0005 and 0.002 mol dm^{-3}
[acetone]: between 0.5 and 1.5 mol dm^{-3}

To initiate the reaction, add the chosen volume of acetone to the solution containing the other reagents, quickly cap the reaction vessel, start the timer, shake the vial vigorously one time, then put it aside on a white background. Report the volumes of reagents that you use in table 1.1. When setting up and running a reaction do not hold or touch the vial below the level of liquid in it. The progress of the reaction can be monitored visually by watching the disappearance of the yellow-brown colour of the triiodide ion. Record the time required for the colour to disappear. When the reaction is complete, set aside the vessel, and leave it sealed so that you do not expose yourself to iodoacetone vapours.

Repeat as often as desired with different concentrations of reagents. Report the concentrations of the reagents that you use in table 1.3.

Hint: Change one concentration at a time.

Once you have studied the rate of reaction of acetone, you should examine the rate of reaction of acetone-d_6. Note that while you have an ample supply of acetone, you will be given only 3.0 cm^3 of acetone-d_6 because of the greater expense of the isotopically labelled material. Therefore, any refilling of acetone-d_6 will be accompanied by a one point penalty. When you need to use this reagent, raise your hand and the lab supervisor will open the sealed ampoule for you. The reactions of deuterium-substituted compounds are generally slower than those of protium-substituted compounds. You would thus be well advised to use reaction conditions that promote faster reactions when working with $(CD_3)_2CO$.

When you have finished your work:

a) empty the water bottle and place it along with any unused equipment back to the box labelled “Kit #1”,

b) place used pipettes and sealed used vials in designated containers under the hoods,

c) use a container labelled “Broken Glass Disposal” to dispose of all parts of the empty ampoule.

You may clean up your area after the STOP command has been given.

1.1 Record your results for acetone, $(CH_3)_2CO$, in the table below. *You need not fill the entire table.*

Table 1.1

Run #	Volume HCl solution, cm^3	Volume H_2O, cm^3	Volume I_3^- solution, cm^3	Volume $(CH_3)_2CO$, cm^3	Time to disappearance of I_3^-, s
1					
2					
3					
etc.					

1.2 Record your results for acetone-*d*$_6$, $(CD_3)_2CO$, in the table below. *You need not fill the entire table.*

Table 1.2

Run #	Volume HCl solution, cm^3	Volume H_2O, cm^3	Volume I_3^- solution, cm^3	Volume $(CD_3)_2CO$, cm^3	Time to disappearance of I_3^-, s
1d					
2d					
3d					
etc.					

1.3 Use the following tables to calculate concentrations and average rates for the reactions you studied. Assume that the volume of each reaction mixture is equal to the sum of volumes of its constituent solutions. You need not use all of your runs in your calculation of *k* (parts 1.5 and 1.6), but you must indicate which run or runs you used in your calculation by checking the appropriate box in the right-hand column.

Table 1.3

$(CH_3)_2CO$:

Run #	Initial $[H^+]$, mol dm^{-3}	Initial $[I_3^-]$, mol dm^{-3}	Initial $[(CH_3)_2CO]$, mol dm^{-3}	Average rate of disappearance of I_3^-, mol dm^{-3} s^{-1}	Run used in calculating k_H? **Yes** **No**
1					☐ ☐
2					☐ ☐
3					☐ ☐
etc.					

Table 1.4

$(CD_3)_2CO$:

Run #	Initial $[H^+]$, mol dm^{-3}	Initial $[I_3^-]$, mol dm^{-3}	Initial $[(CD_3)_2CO]$, mol dm^{-3}	Average rate of disappearance of I_3^-, mol dm^{-3} s^{-1}	Run used in calculating k_D? **Yes** **No**
1d					☐ ☐
2d					☐ ☐
3d					☐ ☐

1.4 Give the integer reaction order in acetone, triiodide, and hydrogen ion.

$$\text{rate} = -\frac{d[I_3^-]}{dt} = k\,[(CH_3)_2CO]^m\,[I_3^-]^n\,[H^+]^p$$

m =

n =

p =

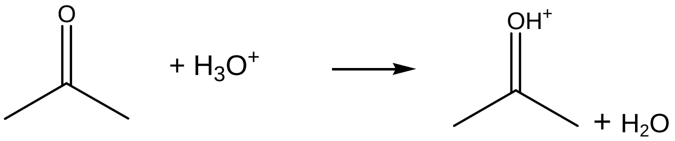
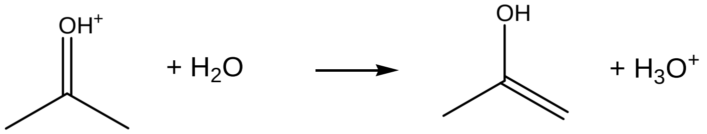
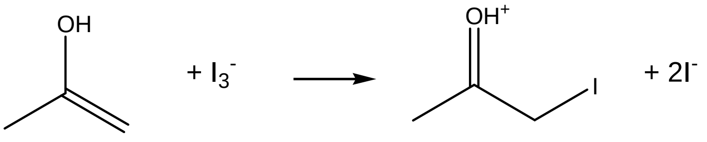
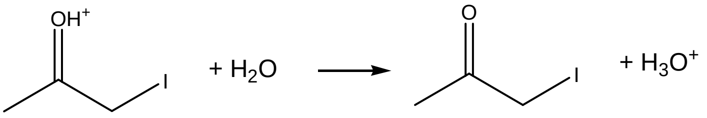
1.5 Calculate the rate constant k_H for the reaction of acetone, $(CH_3)_2CO$, and indicate the units.

1.6 Calculate the rate constant k_D for the reaction of acetone-d_6, $(CD_3)_2CO$, and calculate the value of k_H / k_D (the isotope effect of the reaction).

From the kinetic and isotope effect data you may draw certain conclusions about the reaction mechanism. Shown below is a reasonable mechanism for the iodination of acetone. One reaction is the rate-determining step with all previous steps rapidly achieving an equilibrium that strongly favours the reactants.

1.7 In the box in the **first column** on the right next to each step, place a check mark (✓) if your *experimentally measured rate law* (part **1.4**) is **consistent** with that step being rate-determining and a mark **(X)** if your measured rate law is **inconsistent** with that step being rate-determining.

In the box in the second column on the right next to each step, place a check mark (✓) if your *experimentally measured isotope effect* (part 1.6) is **consistent** with that step being rate-determining and a mark **X** if your measured isotope effect is **inconsistent** with that step being rate-determining.

	Rate determining step consistent with rate law?	Rate determining step consistent with isotope effect?
		
		
		
		

SOLUTION

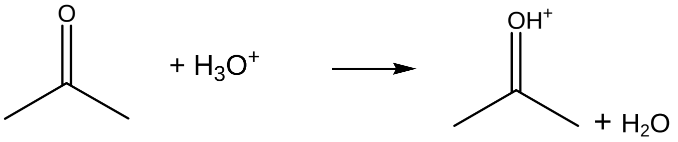
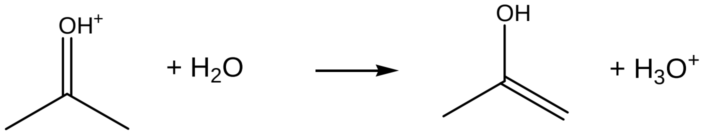
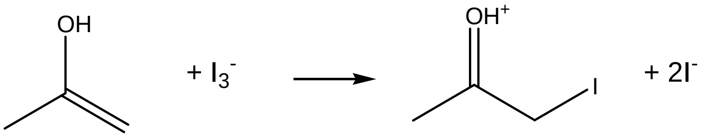
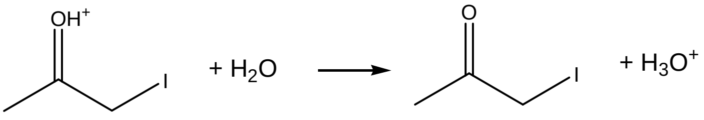
1.4 m = 1; n = 0; p = 1

1.5 $k_H = 2.8 \pm 0.4 \cdot 10^{-5}$ dm^3 mol^{-1} s^{-1}

1.6 $k_D = 4.3 \pm 0.6 \cdot 10^{-6}$ dm^3 mol^{-1} s^{-1}

k_H **/** $k_D = 6.5 \pm 0.4$

1.7

	Rate determining step consistent with rate law?	Rate determining step consistent with isotope effect?
	✓	X
	✓	✓
	X	X
	X	X

PRACTICAL EXAMINATION

Practical Problem 1 **14 %** of the total	Code:		Question	1	2	3	4	5	6	Total
	Examiner		Mark	2	4	50	2	2	10	**70**
			Grade							

Practical Problem 1. The oxidation of iodide by iron(III) ions – a kinetic study based on the thiosulfate clock reaction

Clock reactions are commonly used as demonstrations by chemical educators owing to their visual appeal. Oxidation of iodide by iron(III) ions in a weakly acidic medium is a reaction that can be transformed into a clock reaction. In the presence of thiosulfate and starch, chemical changes in this clock reaction can be presented by the following equations:

$$Fe^{3+}{}_{(aq)} + S_2O_3^{2-}{}_{(aq)} \rightleftharpoons [Fe(S_2O_3)]^{+}{}_{(aq)} \qquad (1)\ \text{fast}$$

$$2Fe^{3+}{}_{(aq)} + 3I^{-}{}_{(aq)} \longrightarrow 2Fe^{2+}{}_{(aq)} + I_3^{-}{}_{(aq)} \qquad (2)\ \text{slow}$$

$$I_3^{-}{}_{(aq)} + 2S_2O_3^{2-}{}_{(aq)} \longrightarrow 3I^{-}{}_{(aq)} + S_4O_6^{2-}{}_{(aq)} \qquad (3)\ \text{fast}$$

$$2I_3^{-}{}_{(aq)} + \text{starch} \longrightarrow \text{starch - }I^{-}_5 + I^{-}{}_{(aq)} \qquad (4)\ \text{fast}$$

Reaction **(1)** is a fast reversible equilibrium which occurs in the reaction mixture giving a reservoir of iron(III) and thiosulfate ions. After being produced in reaction **(2)**, iodine in the form of triiodide ion (I_3^-), is immediately consumed by thiosulfate in reaction **(3)**. Therefore, no iodine accumulates in the presence of thiosulfate. When thiosulfate is totally depleted, the triiodide ion accumulates and it may be detected by use of starch indicator according to reaction **(4)**.

The kinetics of reaction (**2**) is easily investigated using the initial rates method. One has to measure the time elapsed between mixing the two solutions and the sudden color change.

For the oxidation of iodide by iron(III) ions (reaction **2**), the reaction rate can be defined as:

$$v = -\frac{d\left[\mathrm{Fe}^{3+}\right]}{dt} \qquad (5)$$

The initial reaction rate can then be approximated by:

$$v_0 \approx -\frac{\Delta\left[\mathrm{Fe}^{3+}\right]}{\Delta t} \qquad (6)$$

with $\Delta[\mathrm{Fe}^{3+}]$ being the change in the concentration of iron(III) ions in the initial period of the reaction. If Δt is the time measured, then $\Delta[\mathrm{Fe}^{3+}]$ is the change in iron(III) ion concentration from the moment of mixing to the moment of complete thiosulfate consumption (assume that the reaction rate does not depend on thiosulfate concentration). Therefore, from the reactions' stoichiometry it follows:

$$-\Delta\left[\mathrm{Fe}^{3+}\right] = \left[\mathrm{S_2O_3}^{2-}\right]_0 \qquad (7)$$

and consequently:

$$v_0 \approx \frac{\left[\mathrm{S_2O_3}^{2-}\right]_0}{\Delta t} \qquad (8)$$

The initial thiosulfate concentration is constant and significantly lower than that of iron(III) and iodide ions. The above expression enables us to determine the initial reaction rate by measuring the time required for the sudden color change to take place, Δt.

The rate of reaction is first order with respect to $[\mathrm{Fe}^{3+}]$, and you will determine the order with respect to $[\mathrm{I}^-]$. This means the initial reaction rate of reaction can be expressed as:

$$v_0 = k[\mathrm{Fe}^{3+}]_0[\mathrm{I}^-]_0^y \qquad (9)$$

where k is the rate constant and y is the order with respect to $[\mathrm{I}^-]$.

We assume that the reaction rate does not depend on the thiosulfate concentration, and that the reaction between Fe^{3+} and $\mathrm{S_2O_3}^{2-}$ is negligible. You have to observe carefully the color changes during the clock reaction and to determine the reaction order with respect to $[\mathrm{I}^-]$, and the rate constant of clock reaction.

Experimental Set-up

Instructions for using the digital timer (stopwatch)

1. Press the **[MODE]** button until the **00:00:00** icon is displayed.
2. To begin timing, press the **[START/STOP]** button.
3. To stop timing, press the **[START/STOP]** button again.
4. To clear the display, press the **[SPLIT/RESET]** button.

PRECAUTIONS

- To minimize fluctuations in temperature only use the distilled water on your bench (in the wash bottle and in the glass 1 L bottle).
- The heating function of the heating magnetic stirrer must be **TURNED OFF** (as shown in Figure 1 below) and be sure that the stirrer plate is not hot before starting your experiment. Put the insulating plate (labeled I.P.) on top of the stirrer plate for added insulation.
- Start the stopwatch as soon as the solutions #A and #B are mixed. Stop the stopwatch as soon as the solution suddenly turns dark blue.
- Magnetic stirrer bar (take it with the provided tweezers) and beakers should be washed and rinsed with distilled water and wiped dry with paper towel to reuse.

General Procedure

Solution # **A** (containing $Na_2S_2O_3$, KI, KNO_3 and starch) is first placed in the beaker and is stirred using the magnetic bar. The rate of stirring is set at level 8 as indicated in Figure 1. Solution **#B** (containing $Fe(NO_3)_3$ and HNO_3) is quickly added into solution **#A** and ***the stopwatch is simultaneously started. The time is recorded at the moment the solution suddenly turns dark blue***. The temperature of the solution is recorded using the digital thermometer.

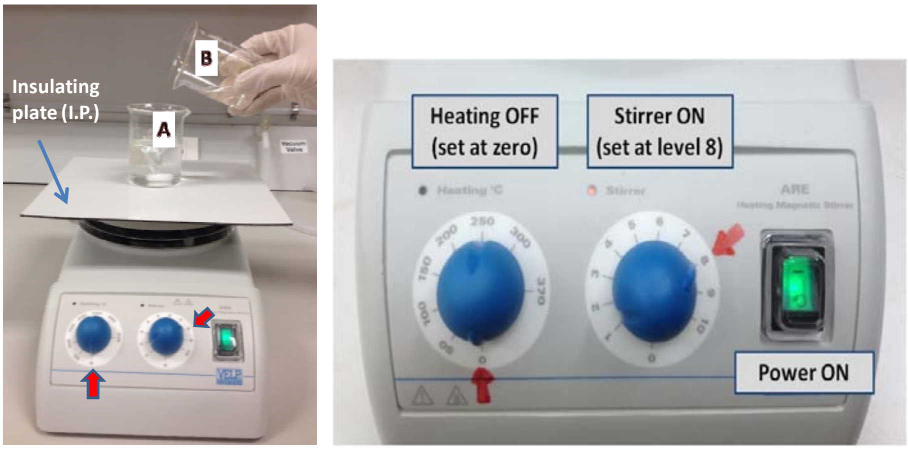


Figure 1. The apparatus employed for kinetic study of the clock reaction.

1. ***Practice run to observe the color changes***

- There is no need to accurately measure the volumes used in this part – just use the marks on the beaker as a guide.
- Pour *ca.* 20 mL of solution # **A1** (*containing KI, $Na_2S_2O_3$, and starch in water*) to a 100-mL graduated beaker containing a magnetic stirrer bar. Place the beaker on top of the insulating plate on the magnetic stirrer.
- Pour *ca.* 20 mL of solution # **B1** (*containing $Fe(NO_3)_3$ and HNO_3 in water*) in another 100 mL graduated beaker.
- Quickly pour the solution # **B1** into solution # **A1** and start stopwatch simultaneously. Stop stopwatch when the color of the mixture changes. There is no need to record this time. Answer the following questions.

***Task 1.1**: Write down the molecular formula of the limiting reactant for the given clock reaction.*

***Task 1.2**: What are the ions or compounds responsible for the colors observed in this experiment? Tick the appropriate box.*

Color	Compound
Purple	☐ Fe^{3+} ☐ $[Fe(S_2O_3)]^+$ ☐ Fe^{2+} ☐ starch-I_5^- ☐ I_3^-
Dark blue	☐ Fe^{3+} ☐ $[Fe(S_2O_3)]^+$ ☐ Fe^{2+} ☐ starch-I_5^- ☐ I_3^-

2. *Determination of the order with respect to $[I^-]$ (y), and the rate constant (k)*

In this section, Δt is determined for different initial concentrations of KI according to the table below. The experiment is repeated as necessary for each concentration of KI.

*<u>Hint:</u> Use 25 mL graduated pipette for solution #**A2-1**, 10 mL graduated pipette for KI, 5 mL graduated pipette for solution #**B2**, and one of the burettes for water (you will need to refill the burette from the wash bottle for each measurement).*

- Prepare 55 mL of solution **# A2** in a 100 mL beaker containing a magnetic stirrer bar and place it on top of the insulating plate on the stirrer. Solution #**A2** contains solution **#A2-1**, KI, and distilled water (see the table below for the volume of each component).
- Add 5 mL of solution **# B2** in another 100 mL beaker.

Quickly pour prepared solution #**B2** into solution #**A2**. Determine the time (Δt) necessary for the color change by a stopwatch. The temperature of the solution is recorded.

<u>Task 1.3</u>: Record the time (Δt) for each run in the table below. (You DO NOT need to fill all three columns for the runs.) For each concentration of KI, record your accepted reaction time ($\Delta t_{accepted}$) and temperature. You will be only graded on your values of $\Delta t_{accepted}$ and $T_{accepted}$.

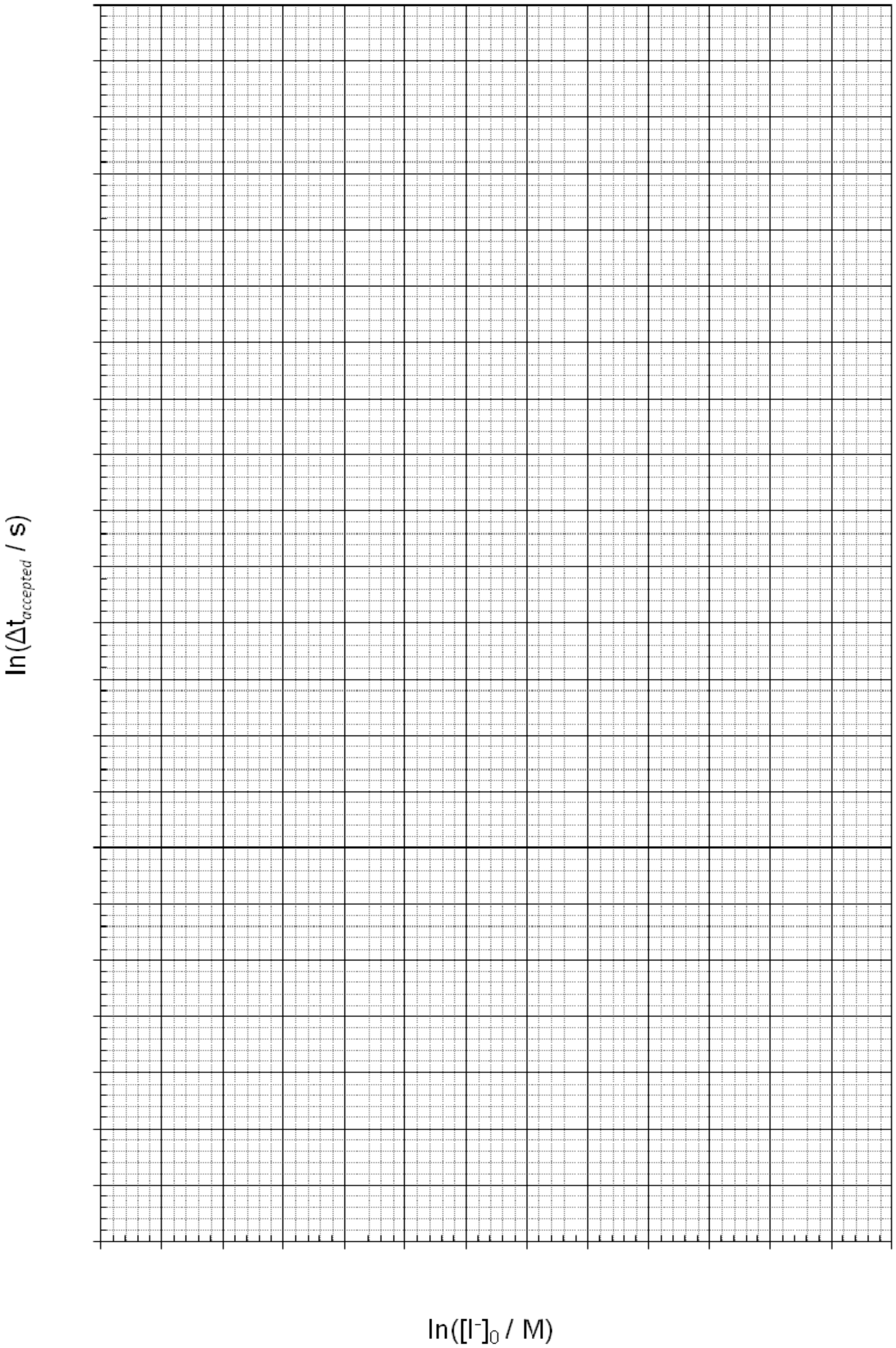
No	**55 mL of solution #A2**			Run 1		Run 2		Run 3		$\Delta t_{accepted}$ (s)	$T_{accepted}$ (°C)
	#A2-1 (mL)	H_2O (mL)	0.100M KI (mL)	Δt (s)	T (°C)	Δt (s)	T (°C)	Δt (s)	T (°C)		
1	20.4	31.6	3.0								
2	20.4	30.1	4.5								
3	20.4	28.6	6.0								
4	20.4	27.4	7.2								
5	20.4	25.6	9.0								

When you are satisfied you have all the necessary data for Problem 1, before continuing further with the analysis, it is strongly recommended that you start the practical procedure for Problem 2 since there is a reaction time of one hour in that Problem.

***Task 1.4*: Fill in the table below and plot the results in the graph.**

Hint: *Make sure your data is graphed as large as possible in the provided space.*

No.	1	2	3	4	5
$\ln([I^-]_0 / M)$	- 5.30	- 4.89	- 4.61	- 4.42	- 4.20
$\Delta t_{accepted}$ (s)					
$\ln(\Delta t_{accepted} / s)$					


ln(Δt_accepted / s)
ln([I⁻]₀ / M)

***Task 1.5*: Draw the best fit line on your graph and use this to determine the order with respect to [I⁻] (y).**

y = ………………………………

***Task 1.6*: Complete the table below and calculate k for each of the concentrations of iodide. Report your accepted value for the rate constant, giving the appropriate unit. Remember that the order with respect to [Fe^{3+}] is equal to one.**

No	$\Delta t_{\text{accepted}}$ (s)	$[\text{Fe}^{3+}]_0$ ($\times 10^{-3}$ M)	$[\text{I}^-]_0$ ($\times 10^{-3}$ M)	$[\text{S}_2\text{O}_3^{2-}]_0$ ($\times 10^{-3}$ M)	***k***
1			5.0		
2			7.5		
3			10.0		
4			12.0		
5			15.0		

k_{accepted} = …………………

TASK 3. Kinetic determination of Diclofenac (DCF) (13 points)

Quest. #	Q1	DCF curves	DCF Control	Reaction order	Total
Marks	10	40	20	10	80

Kinetic methods with spectrophotometric detection for assaying drugs have been intensively developed during the last decade due to a number of obvious advantages, including inherent simplicity, cost-effectiveness, availability in most quality control laboratories, and improved selectivity. In this task you will:

- Perform kinetic determination of Diclofenac (DCF) in a medicine by following the progress of the drug oxidation reaction.
- Determine the reaction order with respect to DCF

Q1. Spectral changes in the course of DCF oxidation with $KMnO_4$ are given in Fig. 4, (1 to 10 reflects the reaction progress). Complete the table below suggesting which wavelengths can be applied for photometric kinetic determination of DCF. In each case, indicate the direction of the absorbance changes (denote increasing with ↑ and decreasing with ↓).

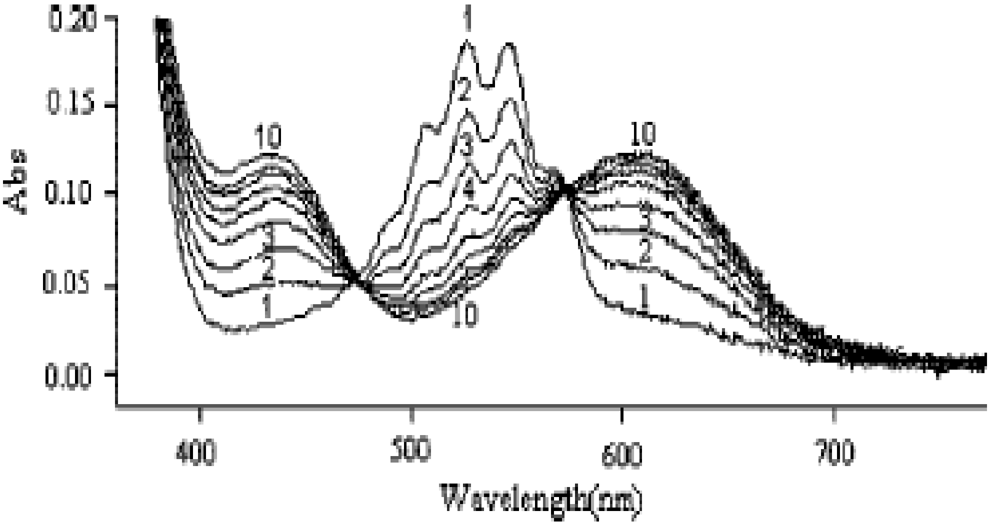


Fig. 4. DCF oxidation with $KMnO_4$

#	Wavelength, nm	Yes or No and direction
1	420	
2	480	
3	520	
4	580	
5	610	

Procedure

Part A. Assembling of laboratory equipment

Assemble the laboratory equipment as shown in Fig. 5. Connect the photometer (1), 525 nm (fixed wavelength) and thermostat (2) to the Netbook via USB slots. Connect the thermostat to the cable labeled "Thermo" to the power supply at your work place via the power adapter. Put the optical cuvette (3) on top of the magnetic stirrer (4), pass the cuvette through the photometer from aside (not possible from top down) and place the thermostat over the cuvette from top down (Fig. 5b).

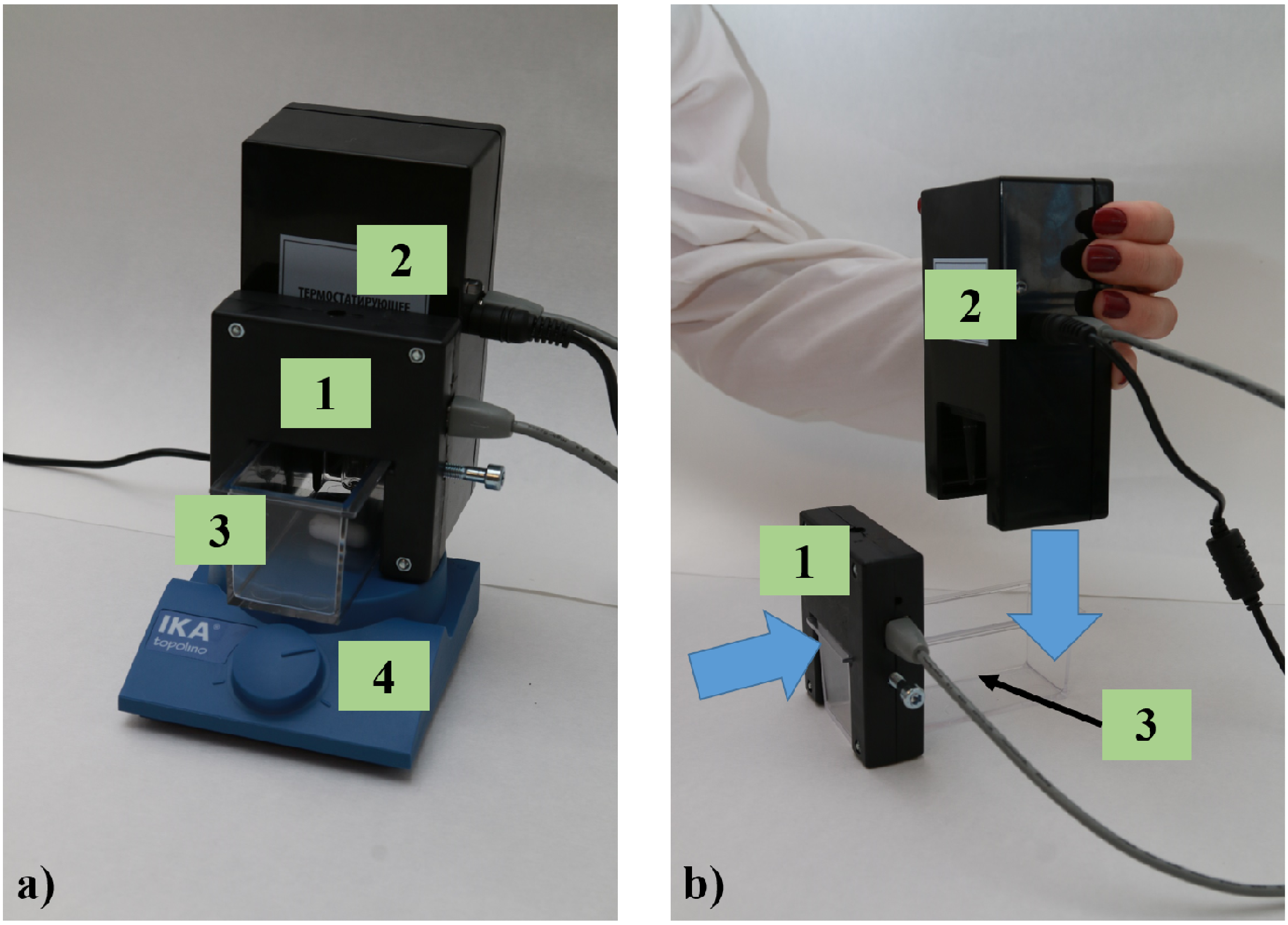


Fig. 5. Laboratory equipment

Hints!

- *Plug in your Netbook to the mains before switching on.*
- *Plug in all the equipment (the photometer and thermostat) before switching on the Netbook. Switch on the mouse.*
- *If only one window (hereafter referred to as Pattern) instead of two appears after launching the software, quit and re-launch the program.*

- ***Do not unplug ANY device from the USB slot while carrying out the measurements. If it still happens, you will see a warning on the screen. Quit and re-launch the program.***
- ***If your Netbook falls asleep, click the «Setup» button in the Measurements window on the absorbance plot pattern when reverting to the measurements.***
- ***In case you see chaotic temperature changes on the screen, stop and re-start the measurement.***

Part B. Plotting of the calibration curve

All measurements needed to plot the calibration curve are carried out at 30 °C with constant $KMnO_4$ and H_2SO_4 initial concentrations. The DCF concentration is varied by using 4 different aliquots (of 0.2, 0.4, 0.6, and 0.8 mL) of the DCF stock solution.

1) Transfer 5 mL of 1M H_2SO_4 solution using the graduated cylinder and 0.2 mL of DCF stock solution using the 2 mL pipette into the 100 mL volumetric flask, dilute to the mark with distilled water, stopper the flask and mix thoroughly.
2) Carry over the flask contents into the cuvette, put the medium-size stir-bar and switch on the magnetic stirrer. Adjust the stirring speed regulator to the mark shown on Fig. 5a to provide for intensive mixing.
3) Launch the «Chemistry-Practicum» software on the Netbook. The software will detect the external devices (sensors) automatically. You will see two plot patterns (that of absorbance/extinction/optical density, D *vs.* t, s; and that of temperature, T °C *vs.* t, s) on the display.
4) Set the following parameters in the Menu bars of the corresponding plot patterns (Fig. 6):

- Click the ➔ icon next to the X button («Fixes X-axis maximum on screen») on the absorbance plot pattern. The entire plot will always fit to the screen;
- Click the Y button («Sets the Y range») on the absorbance plot pattern and set the absorbance range (the ordinate axis) from -0.1 to 1.1.
- Type “2” (instead of “1”) in the box of the measurements interval on the absorbance plot pattern.
- Choose «Precisely» in the «Precisely/Roughly» window on the temperature plot pattern, then click on the «T = X» button and set the required temperature of 30 °C in the pop-up window.
- Calibrate the photometer by clicking the «Setup» button in the Measurements window on the absorbance plot pattern.

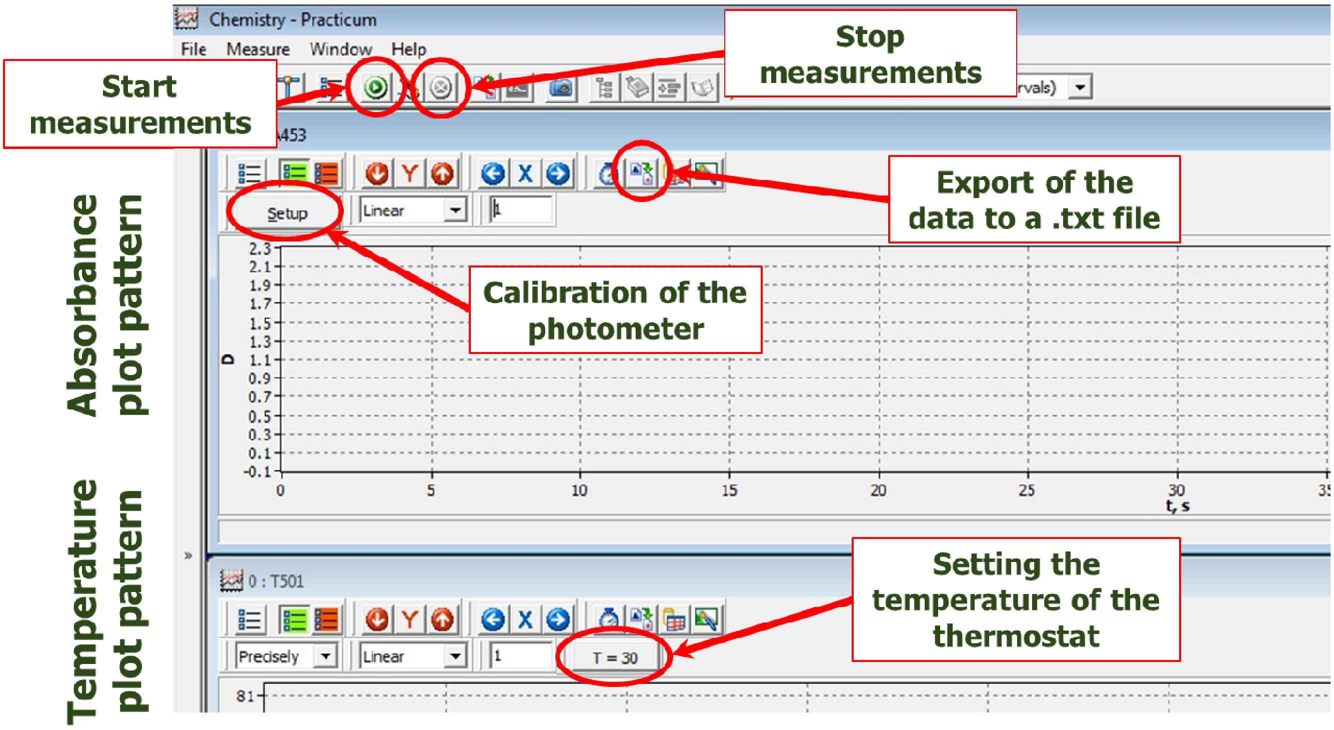


Fig. 6. “Chemistry-Practicum” software interface

Note! ***Setting the parameters (step 4) is needed only prior to the first measurement.***

5) Click the ▶ button («Start measure for chosen sensors») to switch on the thermostat and observe the lamp heating up the solution in the cuvette. Follow the current temperature reported in the line above the plot. Wait until the thermostat lamp switches off, reflecting the set up temperature is attained. Stop the measurements by clicking ⊗ button (is activated and turns to red-orange when the measurement is on).
6) Click any part of the absorbance plot pattern to activate it. Take 2 mL of the $KMnO_4$ solution using the 2 mL pipette. Click the ▶ button («Start measure for chosen sensors») in the Menu bar of the Measurements window and quickly blow out (press the pipette piston) the permanganate solution from the pipette into the cuvette.

Note! ***Make sure the temperature in the cuvette equals 30 °C before adding the $KMnO_4$ solution!***

7) Observe the progress of the kinetic curve on the screen. Continue measurement for 50 s after adding the $KMnO_4$ solution, then terminate the measurement by clicking the «Stop measurements» ⊗ button.

8) Save the data by clicking the 📤 button («Export all the data collected in an external file») in the Menu bar of the absorbance plot pattern, choose the **Desktop** and type the file name “DCF2” (change the name to “DCF4”, or “DCF6”, or “DCF8” in the subsequent experiments).

Note!

- ***Use only the names of the given format!***
- ***Always save the data on your Desktop before starting the next experiment, otherwise the current data set will be lost after the next click on the ▶ button.***
- ***Make sure absorbance plot pattern is active when exporting the data. Otherwise, you will export invalid results. In case no pattern is chosen, you will get a warning.***

9) Empty the cuvette into the Waste bottle, wash thoroughly the cuvette with distilled water. Use black magnet from the outer side of the cuvette to avoid your stir-bar being dropped into the Waste bottle while washing. Wipe carefully the external surfaces of the cuvette with the napkin. Also, use the napkin to dab the thermostat lamp.

10) Repeat the steps 1), 2) 5)-9) with the other volumes of the DCF stock solution.

Part C.

1. Studying of the DCF containing medicine (“Control”)

1) Wash the volumetric flask and prepare the mixture as described above using a 0.4 mL aliquot of the medicine (“Control”) instead of the DCF stock solution.
2) Repeat the steps 1), 2), 5)-9) described in Part B. When saving the data, name the file “DCFmed”.
3) Repeat the measurement of the “Control” as necessary.

2. Experimental data analysis

1) Open the Excel file on your memory stick in Excel. One by one open your saved data files in Notepad by double clicking on them on Desktop. Choose Edit/Select All in the Menu bar, then right click and copy the selected data into the Excel sheet with the corresponding name (the volume of DCF added or “DCFmed”) and choose Edit/Paste in the Menu bar. You will see the experimental data on the Excel sheet (time, s, in column A, and absorbance in column B).

2) Ignore the values before the maximum. Select columns A and B, and plot the data. Use the "Insert Scatter" icon shown on Fig. 7.

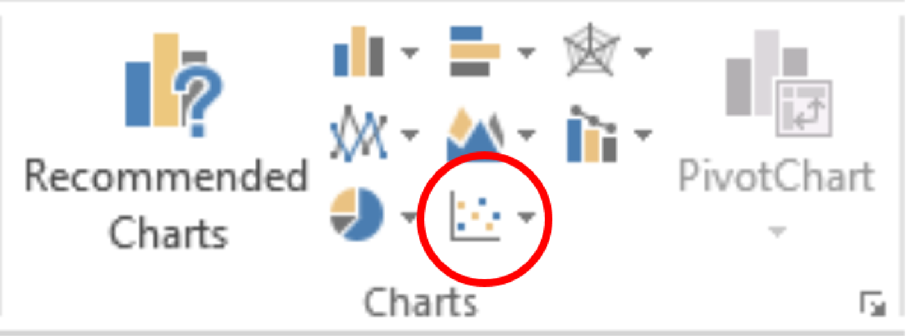


Figure 7. Position of the "Insert Scatter" icon

3) Choose the initial linear section of the remaining curve (15 to 20 data points), apply linear approximation by adding the linear trend line and bring the parameters to the chart area. Make sure that the R^2 value exceeds 0.98. If needed, decrease the number of the experimental data points plotted removing later data points. Still always search for the most wide range of the experimental data providing for the target R^2 value. Determine the value of the initial rate of absorbance change, v_0.

Note! ***You will get zero point for this part of the task if less than 12 values are included in the plotted data range.***

4) Analyze similarly the experimental data obtained with the other DCF concentrations and with the medicine solution "Control" ("DCFmed" file).
5) Calculate the DCF concentrations in the reaction mixtures (in mg/L). Write down the DCF concentrations and initial rates in appropriate cells of the "Results" Excel sheet.
6) Plot the calibration graph on the "Results" sheet and use it to determine the DCF concentration in the analyzed mixture prepared from the medicine ("Control"). Fill in the appropriate cells of the "Results" Excel sheet with the coefficients of linear approximation of the calibration graph. Calculate the DCF concentration in the medicine.
7) Write down the accepted value in the cell F10 of the "Results" sheet.
8) On the "Results" Excel sheet, graphically determine the reaction order with respect to DCF and write down the exact obtained value in the cell I3.
9) Once finished, save your file and invite your Lab assistant to demonstrate that you have got experimental data in the Excel file. Sign and get the Lab assistant's signature.

Note! ***Only the data saved on the memory stick will be considered as the result of the Task.***

Data present in Excel on the memory stick (to be ticked by the Lab assistant)

☐ Yes ☐ No Student ______________ Lab assistant ______________

REPLACEMENTS WITH PENALTY

Item	Quantity	Student’s signature	Lab assistant’s signature

TASK 3. Kinetic determination of Diclofenac (DCF) (13 points)

Quest. #	Q1	DCF curves	DCF Control	Reaction order	Total
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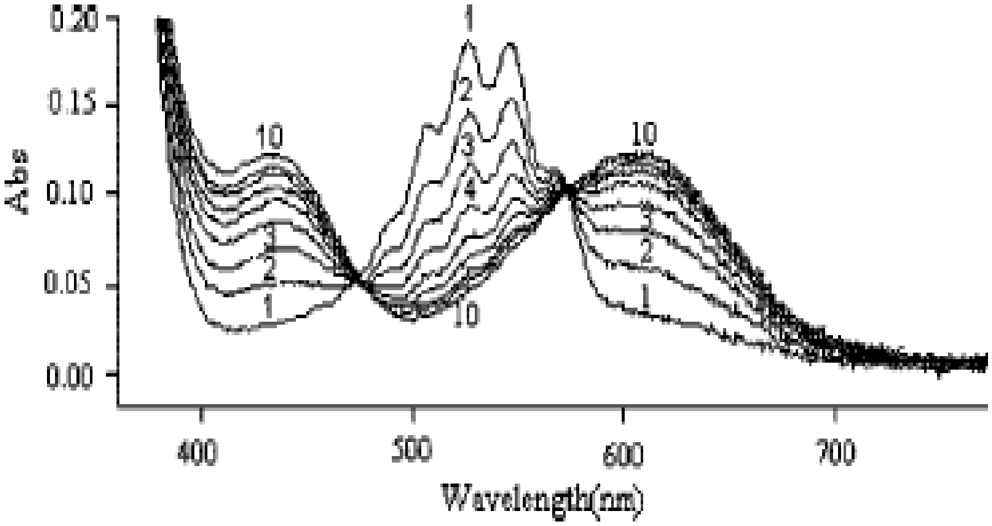

Fig. 4. DCF oxidation with $KMnO_4$

#	Wavelength, nm	Yes or No and direction
1	420	Yes ↑ 2 marks
2	480	No 2 marks
3	520	Yes ↓ 2 marks
4	580	No 2 marks
5	610	Yes ↑ 2 marks

Procedure

Part A. Assembling of laboratory equipment

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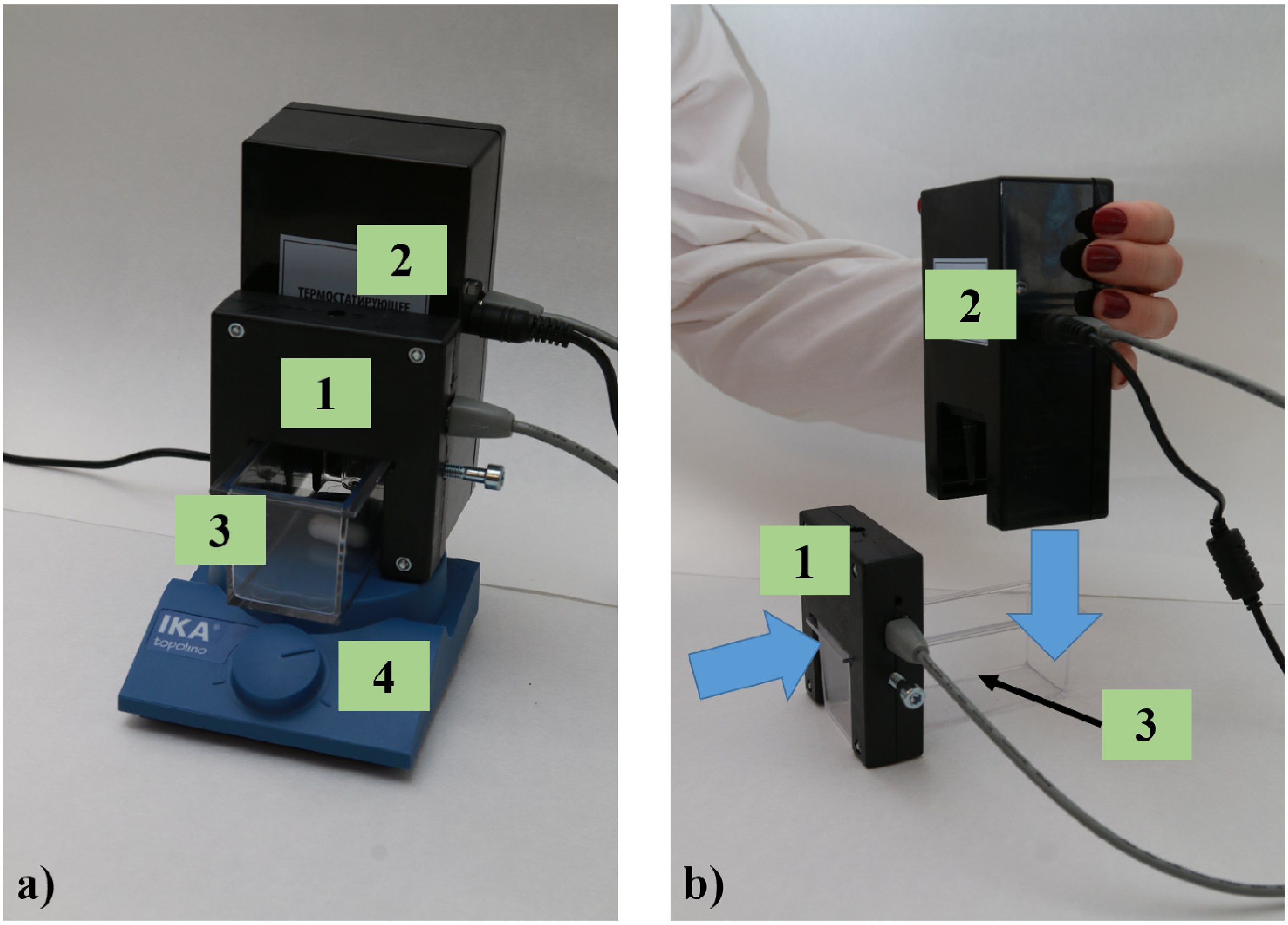

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4) Set the following parameters in the Menu bars of the corresponding plot patterns (Fig. 6):

- Click the ➡ icon next to the X button («Fixes X-axis maximum on screen») on the absorbance plot pattern. The entire plot will always fit to the screen;
- Click the Y button («Sets the Y range») on the absorbance plot pattern and set the absorbance range (the ordinate axis) from -0.1 to 1.1.
- Type “2” (instead of “1”) in the box of the measurements interval on the absorbance plot pattern.
- Choose «Precisely» in the «Precisely/Roughly» window on the temperature plot pattern, then click on the «T = X» button and set the required temperature of 30 °C in the pop-up window.
- Calibrate the photometer by clicking the «Setup» button in the Measurements window on the absorbance plot pattern.

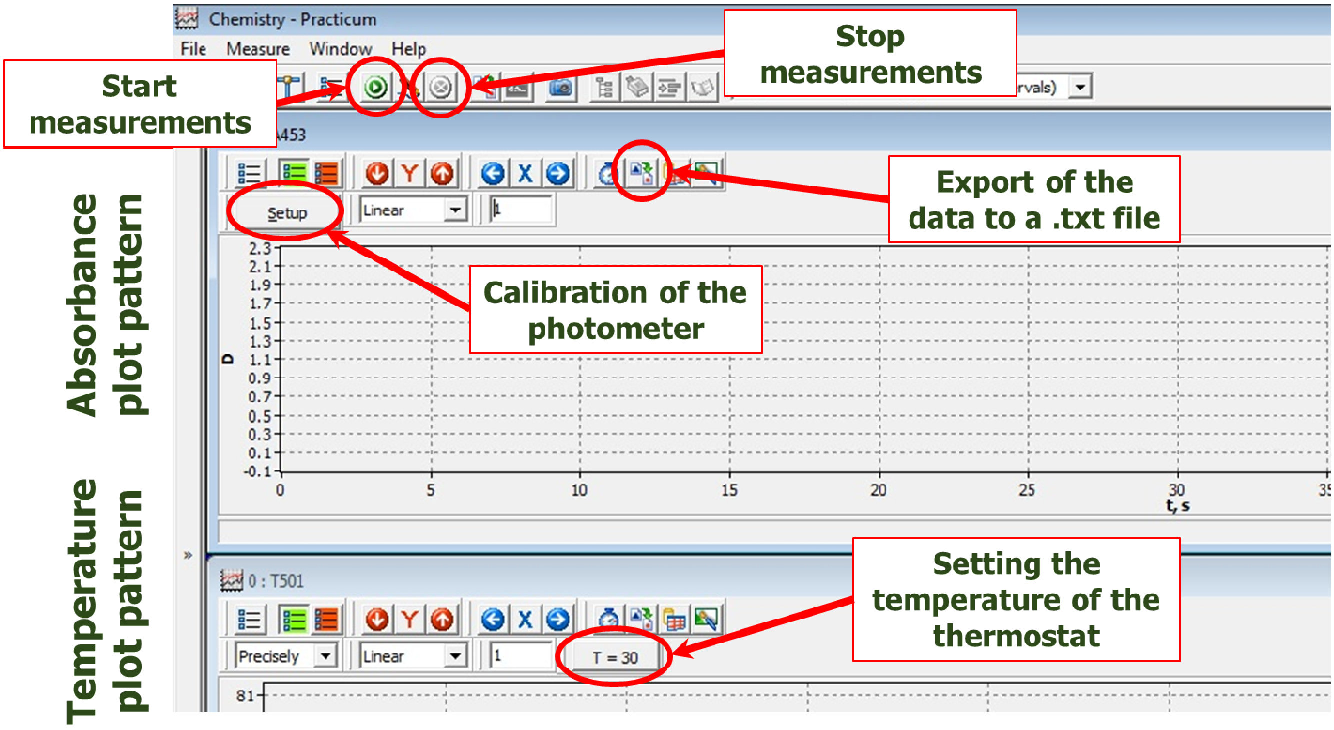


Fig. 6. “Chemistry-Practicum” software interface

Note! ***Setting the parameters (step 4) is needed only prior to the first measurement.***

5) Click the ▶ button («Start measure for chosen sensors») to switch on the thermostat and observe the lamp heating up the solution in the cuvette. Follow the current temperature reported in the line above the plot. Wait until the thermostat lamp switches off, reflecting the set up temperature is attained. Stop the measurements by clicking ⊗ button (is activated and turns to red-orange when the measurement is on).
6) Click any part of the absorbance plot pattern to activate it. Take 2 mL of the $KMnO_4$ solution using the 2 mL pipette. Click the ▶ button («Start measure for chosen sensors») in the Menu bar of the Measurements window and quickly blow out (press the pipette piston) the permanganate solution from the pipette into the cuvette.

Note! ***Make sure the temperature in the cuvette equals 30 ℃ before adding the $KMnO_4$ solution!***

7) Observe the progress of the kinetic curve on the screen. Continue measurement for 50 s after adding the $KMnO_4$ solution, then terminate the measurement by clicking the «Stop measurements» ⊗ button.

8) Save the data by clicking the button («Export all the data collected in an external file») in the Menu bar of the absorbance plot pattern, choose the **Desktop** and type the file name “DCF2” (change the name to “DCF4”, or “DCF6”, or “DCF8” in the subsequent experiments).

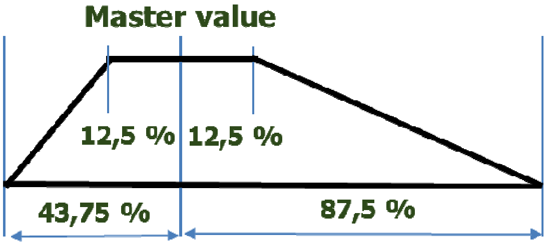
Note!

- ***Use only the names of the given format!***
- ***Always save the data on your Desktop before starting the next experiment, otherwise the current data set will be lost after the next click on the button.***
- ***Make sure absorbance plot pattern is active when exporting the data. Otherwise, you will export invalid results. In case no pattern is chosen, you will get a warning.***

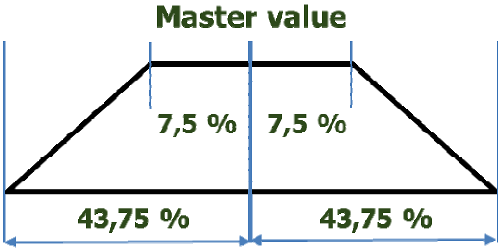
9) Empty the cuvette into the Waste bottle, wash thoroughly the cuvette with distilled water. Use black magnet from the outer side of the cuvette to avoid your stir-bar being dropped into the Waste bottle while washing. Wipe carefully the external surfaces of the cuvette with the napkin. Also, use the napkin to dab the thermostat lamp.

10) Repeat the steps 1), 2) 5)-9) with the other volumes of the DCF stock solution.

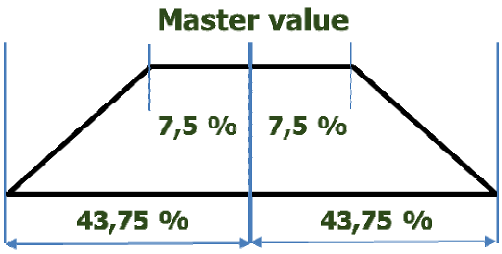
0.2 mL



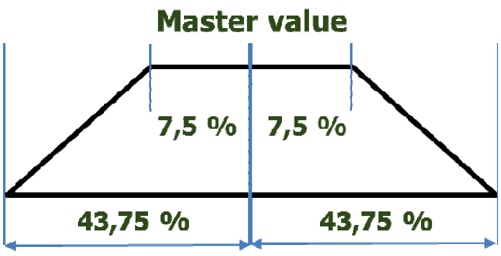
0.4 mL



0.6 mL



0.8 mL



10 marks maximum for each of 4 measurements. Students data will be recalculated by Science Committee. 40 marks in total.

Part C.

1. **Studying of the DCF containing medicine ("Control")**

1) Wash the volumetric flask and prepare the mixture as described above using a 0.4 mL aliquot of the medicine ("Control") instead of the DCF stock solution.
2) Repeat the steps 1), 2), 5)-9) described in Part B. When saving the data, name the file "DCFmed".
3) Repeat the measurement of the "Control" as necessary.

2. **Experimental data analysis**

1) Open the Excel file on your memory stick in Excel. One by one open your saved data files in Notepad by double clicking on them on Desktop. Choose Edit/Select All in the Menu bar, then right click and copy the selected data into the Excel sheet with the corresponding name (the volume of DCF added or "DCFmed") and choose Edit/Paste in the Menu bar. You will see the experimental data on the Excel sheet (time, s, in column A, and absorbance in column B).

2) Ignore the values before the maximum. Select columns A and B, and plot the data. Use the "Insert Scatter" icon shown on Fig. 7.

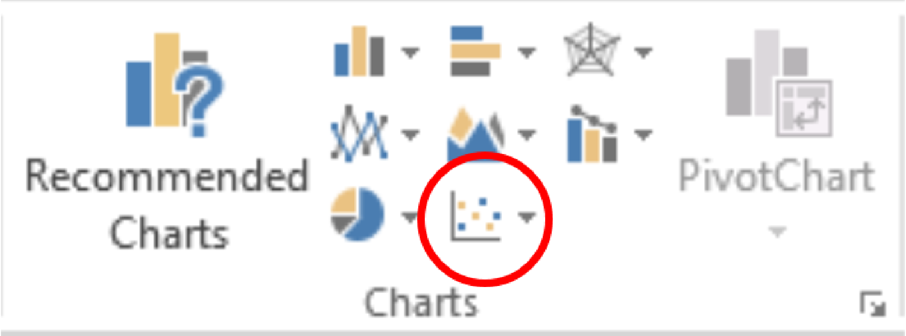
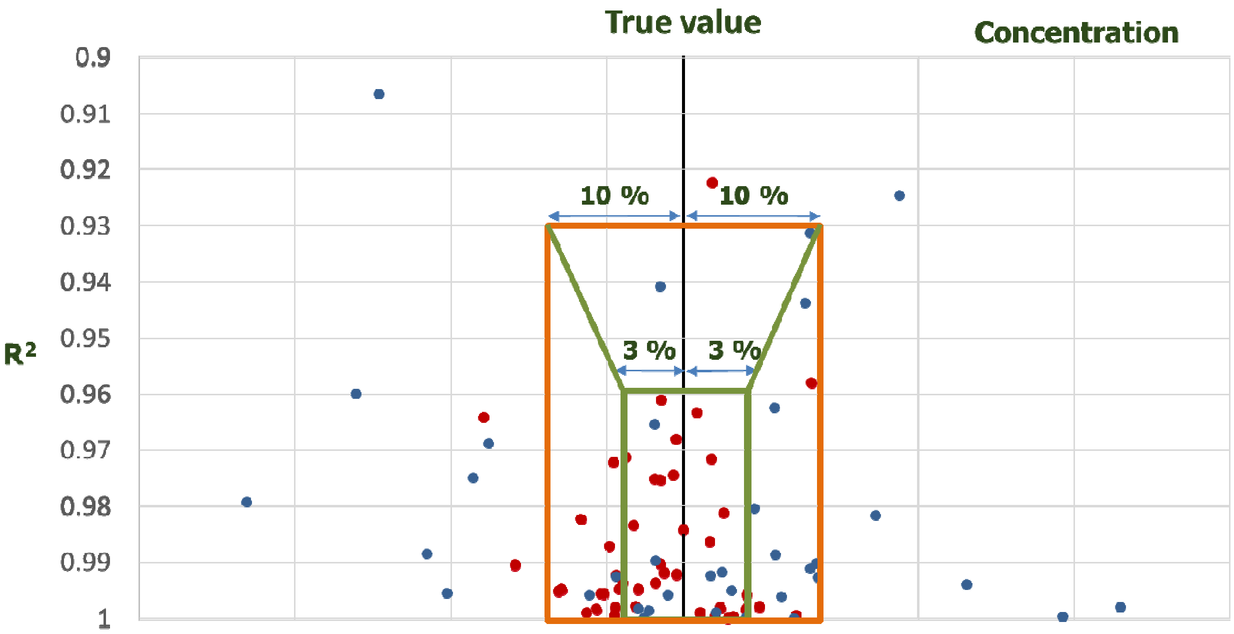


Figure 7. Position of the "Insert Scatter" icon

3) Choose the initial linear section of the remaining curve (15 to 20 data points), apply linear approximation by adding the linear trend line and bring the parameters to the chart area. Make sure that the R^2 value exceeds 0.98. If needed, decrease the number of the experimental data points plotted removing later data points. Still always search for the most wide range of the experimental data providing for the target R^2 value. Determine the value of the initial rate of absorbance change, v_0.

Note! ***You will get zero point for this part of the task if less than 12 values are included in the plotted data range.***

4) Analyze similarly the experimental data obtained with the other DCF concentrations and with the medicine solution "Control" ("DCFmed" file).
5) Calculate the DCF concentrations in the reaction mixtures (in mg/L). Write down the DCF concentrations and initial rates in appropriate cells of the "Results" Excel sheet.
6) Plot the calibration graph on the "Results" sheet and use it to determine the DCF concentration in the analyzed mixture prepared from the medicine ("Control"). Fill in the appropriate cells of the "Results" Excel sheet with the coefficients of linear approximation of the calibration graph. Calculate the DCF concentration in the medicine.



20 marks maximum (including 8 marks for data obtained and calculations). <u>To be graded similarly to the procedure in Task 1</u>.

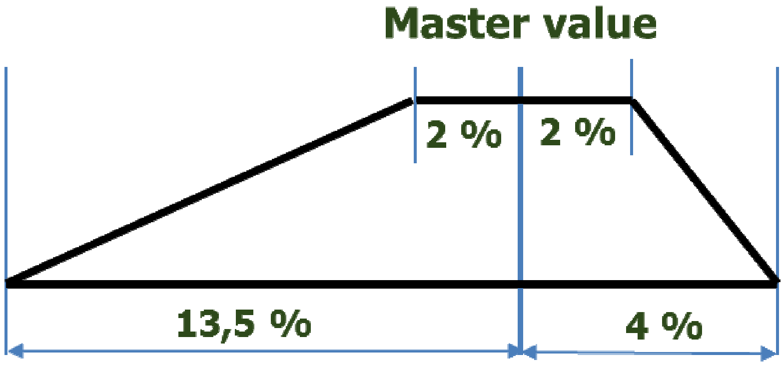
The grading scheme takes into account two values re-measured by the Science Committee: R-squared value (R^2) and obtained concentration of the control solution (Conc).

- If the value obtained is within region A, 100% of 12 marks
- If the value obtained is within region B, 0.1926*Conc-154.2857 (%) of 12 marks
- If the value obtained is within region C, 400*R^2-372 (%) of 12 marks
- If the value obtained is within region D, -0.1926*Conc+188.5714 (%) of 12 marks

Master value – 890.1 mg/L

7) Write down the accepted value in the cell F10 of the "Results" sheet.

8) On the "Results" Excel sheet, graphically determine the reaction order with respect to DCF and write down the exact obtained value in the cell I3.



10 marks for the determination of the reaction order

9) Once finished, save your file and invite your Lab assistant to demonstrate that you have got experimental data in the Excel file. Sign and get the Lab assistant's signature.

Note! ***Only the data saved on the memory stick will be considered as the result of the Task.***

Data present in Excel on the memory stick (to be ticked by the Lab assistant)

☐ Yes ☐ No

Student _______________

Lab assistant _______________

REPLACEMENTS WITH PENALTY

Item	Quantity	Student's signature	Lab assistant's signature

Sintesi organica

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Nitration of phenacetine (4-ethoxyacetanilide) with nitric acid in acetic acid as solvent

Caution:

Both acetic acid and 65 % nitric acid attack the skin. If it happens, the skin must be rinsed with water immediately and washed with a saturated aqueous solution of sodium carbonate. Vapours of nitric acid damage the respiratory tract; moreover, nitric gases evolved in the reaction flask are very toxic.

The glass joints of the various apparatus must be only slightly greased.

Apparatus:

250 ml four-necked flask with laboratory stirrer, thermometer, reflux condenser with gas vent, water bath, Bunsen burner.

Preparation:

40 ml of acetic acid are placed with a glass syringe pipette in the four-necked round bottom flask. 2.0 g of phenacetine are then dissolved in the acetic acid. Also, 2.5 ml 65 % nitric acid are added by using a glass syringe pipette under an effective hood. This mixture is heated for five minutes in a water bath at 90 ^{o}C.

Isolation and purification:

The hot water bath is replaced by ice water. After ca. 10 minutes the gas vent is removed and ca. 120 ml of distilled water are added through the reflux condenser into the flask in order to dilute the original solution. Stirring is continued until a temperature of ca. 5 ^{o}C is reached.

The precipitated solid is filtered off and then washed with a total of 100 ml of cold water and finally dried at 60^{o} C for 2.5 hours in a drying oven.

Evaluation of the experiment:

a) Melting points:

The melting point of phenacetine and its reaction product are to be determined and recorded in the note book. The melting point of phenacetine is higher than 120° C and that of the product is higher than 80° C.

b) Thin-layer chromatogram:

The relative position of the spots of the starting compound and its reaction product must be recorded. In order to reach it, little portions of the both samples must be dissolved in 1-2 ml of acetone. The solutions must be placed on the plate by using a capillary tube. To develop the chromatogram, a mixture of 90 ml toluene, 25 ml acetone, and 5 ml acetic acid is used.

After drying the spots are circled with a pen. The R_f -values must be recorded.

c) Developing reagent:

The developed TLC-plate must be sprayed under a hood with the available reagent solution consisting of iron(III) chloride and potassium hexacyanoferrate(III).

Interpretation of the results:

1.1 Which nitration product(s) has (have) been formed? The discussion should focused on the relative position of the spots in your chromatogram; describe your arguments in the note book.

1.2 Explain why such "mild conditions" have been used here for the nitration reaction. Explain why the nitration reaction has proceeded in spite of these "mild conditions".

1.3 Explain the observed colour reaction of phenacetine with the developing reagent.

1.4 Make a brief proposal, how the filtrate should be prepared to avoid environmental damage.

Chemicals:

Acetic acid (analysis grade)
Nitric acid (analysis grade); w = 65 % by mass
Phenacetine (analysis grade)
Toluene (analysis grade)

Acetone (analysis grade)
Developing reagent: 100 ml solution
200 ml solution
700 ml distilled water.

SOLUTION

a) Melting points:
4-ethoxy-N-acetylphenylamin (phenacetine) : 135 °C
4-ethoxy-2-nitroacetanilide : 103 °C (theoretic al value)

b), c) Documentation, Thin-layer chromatogram

Interpretation of the results:

1.1 The R_f -value of the nitration product is almost twice as great as that of the starting compound phenacetine. Although nitration has occurred, the molecules exhibit less dipolar character that indicates intramolecular hydrogen bridges. This is only possible if the acetylamino and nitro groups are located in 1.2-positions.

In accordance with the +M-effect of the acetyl amino group one should expect that the nitro group would be favoured in a (free) ortho-position because of the lowered activation energy. On the other hand, one would not expect multiple nitration because of the "mild reaction conditions" (see below) and also because of the electron withdrawing mesomeric effect (-M-effect) and the inductive electron withdrawal (-I-effect) of the nitro group that has entered the molecule.

Nitration product: 4-Ethoxy-2-nitroacetanilide
The melting point confirms this observation.

1.2 The nitration reaction is carried out relatively rapidly, at relatively low temperature in dilute solution and without using fuming nitric acid or "nitration acid".

Instead of sulphuric acid concentrated acetic acid is used. The molecules of the latter compound neither protonate the HNO_3 sufficiently nor do they do solvate the

NO_2^+ ions. As a result, the equilibrium reactions

$$HONO_2 + HONO_2 \rightleftharpoons H_2O^+\text{-}NO_2 + {}^-O\text{-}NO_2$$

and

$$H_2O^+\text{-}NO_2 \rightleftharpoons {}^+NO_2 + H_2O$$

are shifted far to the left. This effect is counterbalanced by the high reactivity (+M-effect) of phenacetine.

1.3 Phenacetine is oxidized by iron(III) ions and a molecule of p-quinone type and iron(II) ions are formed. The iron(II) ions react immediately with the hexacyanoferrate(III) ions to give Turnbull's Blue.

1.4 Neutralization with sodium or potassium hydroxide solution, use of calcium hydroxide solution and argumentation:

NO_3^--ions, CH_3COO^- ions and 4-ethoxy-2-nitroacetanilide are removed by biological metabolism.

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Synthesis of a derivative (NaHX) of the sodium salt of an organic acid

Apparatus:

1 beaker (250 cm^3), 2 beakers (50 cm^3), 1 pipette (10 cm^3; graduated at intervals of 0.1 cm^3), 1 measuring cylinder (50 cm^3), 1 capillary pipette (Pasteur pipette), 1 thermometer, 1 filter crucible (G4), apparatus for suction filtering, 1 glass rod.

Reagents:

Sodium salt of 1-naphtol-4-sulfonic acid (S), (sodium 1-naphtol-4-sulfonate), (M = 246.22 g mol^{-1}), sodium nitrite (M = 69.00 g mol^{-1}), aqueous solution of HCl (2 mol dm^{-3}), deionised water, absolute ethanol.

Procedure:

Mix the given lot of technical grade starting material, labelled I, (contains 1.50 g of sodium 1-naphtol-4-sulfonate, S) and 0.6 g of $NaNO_2$ with about 10 cm^3 of water in 50 cm^3 beaker. Cool in ice bath (a 250 cm^3 beaker) to the temperature 0 – 5 °C. Keeping the temperature in the 0 – 5 °C range, add dropwise 5 cm^3 of 2 M HCl (aq) to the reaction mixture. Stir for ten more minutes in an ice bath to effect the complete precipitation of the yellow-orange salt NaHX . n H_2O. Weigh the filter crucible accurately (± 0.5 mg). Filter the product with suction in the crucible and wash with a small amount (ca. 5 cm^3) of cold water and then twice (about 10 cm^3) with ethanol. Dry the product in the filter crucible at 110 °C for 30 minutes. Weigh the air-cooled anhydrous material together with the crucible and present it to the supervisor.

Calculate the percentage yield of NaHX (M = 275.20 g mol^{-1}).

The purity of the product NaHX influences your results in Problem 2!

Question:

Write the reaction equation using structural formulae.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis

Preparation of 2-Ethanoyloxybenzoic Acid (Acetylsalicylic Acid, also known as Aspirin) by Ethanoylation (Acetylation) of 2-Hydroxybenzoic Acid (Salycilic Acid) with Ethanoic Anhydride (acetic anhydride).

Relative atomic masses: C: 12.011; O: 15.999; H : 1.008

Reagents

2-hydroxybenzoic acid (melting point 158 °C)
Ethanoic anhydride (boiling point 140 °C)
Phosphoric acid (85 % H_3PO_4)
Ethanol
Deionised/distilled water

Procedure

In a 100 cm^3 Erlenmeyer flask mix 2.760 g of 2-hydroxybenzoic acid (from weighing bottle A) with 5.100 g of ethanoic anhydride (from flask B), and with cautious swirling add 5 – 7 drops of 85 % phosphoric acid. Heat the flask to 70 – 80 °C in a beaker of near boiling water and maintain the mixture at this temperature for 15 minutes. Remove the flask from the water bath and, with gentle swirling, add dropwise 1 cm^3 of deionised water to the still hot flask; then immediately add 20 cm^3 of the cold deionised water all at once to the reaction flask. Place the flask in an ice bath. If no crystals are deposited, or if oil appears, gently scratch the inner surface of the flask with a glass rod while the flask remains in the ice bath.

Using a Büchner funnel, filter the product under suction. Rinse the flask twice with a small amount of cold deionised water. Recrystallize the crude product in the 100 cm^3 Erlenmeyer flask using suitable amounts of water and ethanol. If no crystals form or if oil appears, scratch gently the inner surface of the flask with a glass rod. Filter the crystals under suction and wash with a small amount of cold deionised water. Place the crystals on the porous plate to draw water from them. When the crystals have been air dried, transfer the product to the small glass dish labeled C. This dish has previously been weighed. The dish containing the product should be given to a technician who will dry it in an oven for 30 minutes at 80 °C.

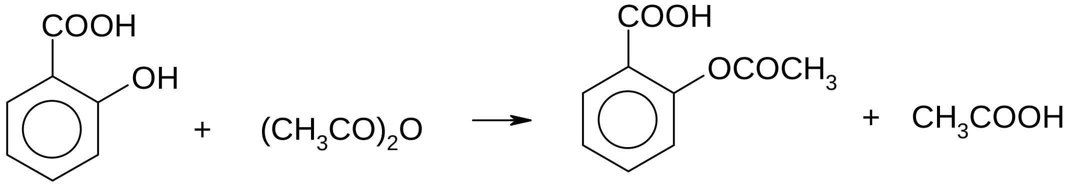
A technician should then weigh the cooled dish containing your product in your presence. Record the mass. The melting point will subsequently be taken by a technician to check the purity of your product.

Questions:

1. Write the balanced chemical equation for the reaction using structural formulae.
2. What is the percentage yield?

SOLUTION

1.

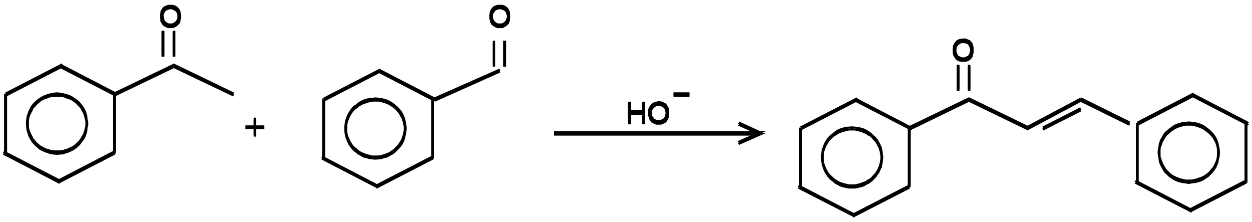


PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis involving Carbanions Chalcone

The aim of this experiment is to condense acetophenone and benzaldehyde in a mixed aldol condensation. After spontaneous dehydratation, an α,β - unsaturated ketone is obtained: the chalcone, 1,3-diphenylprop-2-en-1-on.



a) *Starting the condensation reaction*

In a 250 cm^3 ground neck Erlenmeyer (conical) flask, dissolve about 5 g of potassium hydroxide, KOH, (50 pellets) in 30 cm^3 of water, then add slowly under stirring 20 cm^3 of ethanol. From the automatic dispensers, add 9.6 g (0.08 mol = 9.5 cm^3) of acetophenone and 8.5 g (0.08 mol = 8.5 cm^3) of benzaldehyde. Set up a condenser in the vertical reflux position and reflux vigorously while stirring the mixture with the magnetic stirrer for an hour.

b) *Isolation of the crude chalcone*

After refluxing, cool the contents of the Erlenmeyer flask in an ice bath. The chalcone should crystallize. If crystals do not appear, scratch the inside wall of the flask with a glass rod. Collect the crystals in a Büchner funnel, wash them with a little ice cold ethanol, then air dry and weigh the crystals.

c) *Recrystallization of the chalcone*

Recrystallize this crude chalcone from ethanol, using a 100 cm^3 beaker. Use the heating plate located in the hood (fume chamber). When the crystallization is over (wait long enough and scratch if necessary), collect the crystals in a Büchner funnel, and air dry them.

Give your entire product to the supervisor who will measure its mass and melting-point.

Do not breathe the vapour while recrystallizing and measuring the melting point. It contains irrigating chalcone!!!

Questions:

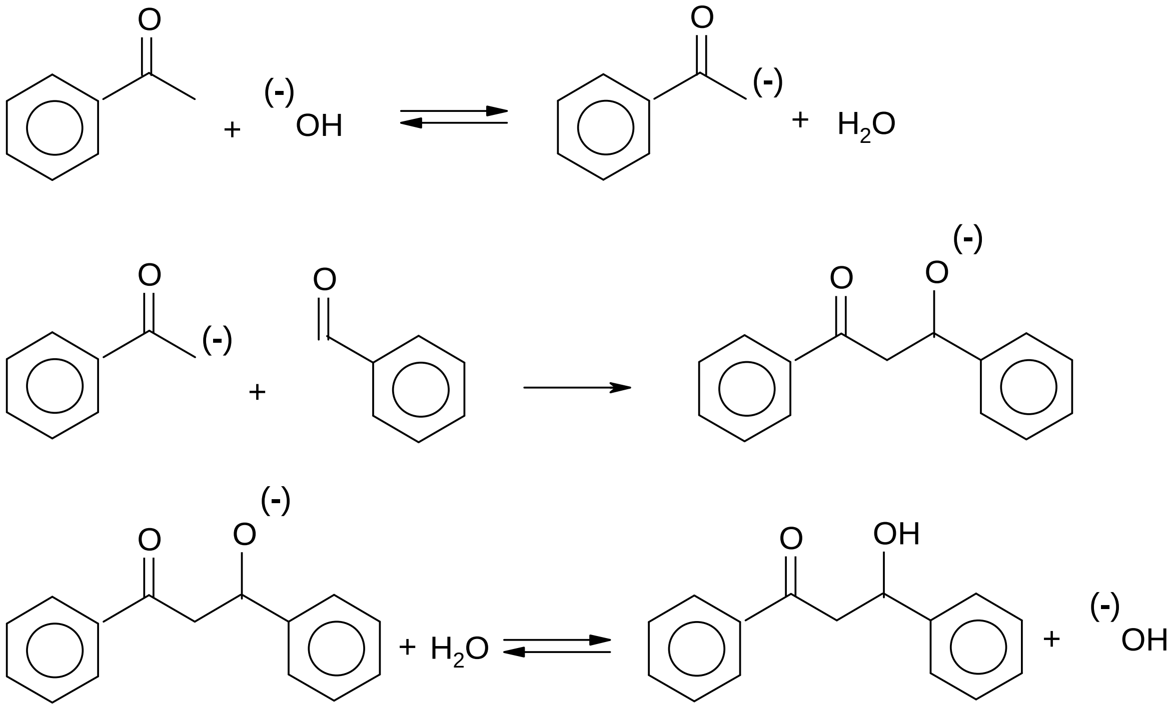
1.1 Write the mechanism for this reaction.

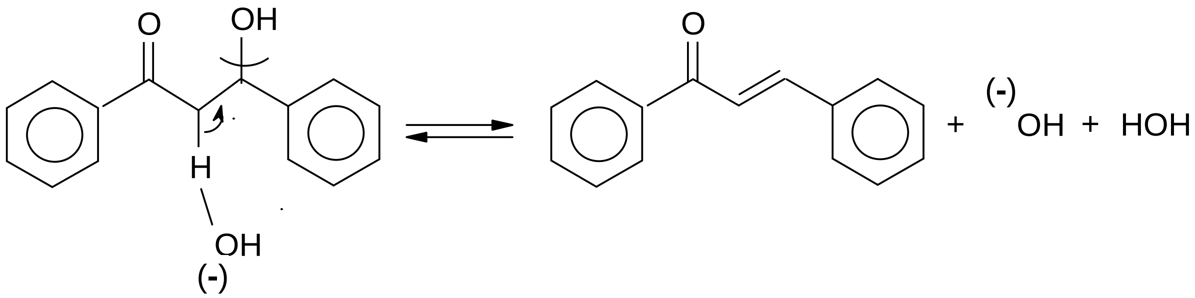
1.2 Give the mass of the crystals of the crude chalcon obtained and calculate the yield of crude product.

1.3 Calculate the yield of recrystallized product based on starting material and calculate the efficiency of the recrystallization process.

SOLUTION

1.1




O
OH
H
OH
(-)
O
+
(-)
OH
+
HOH

PRACTICAL PROBLEMS

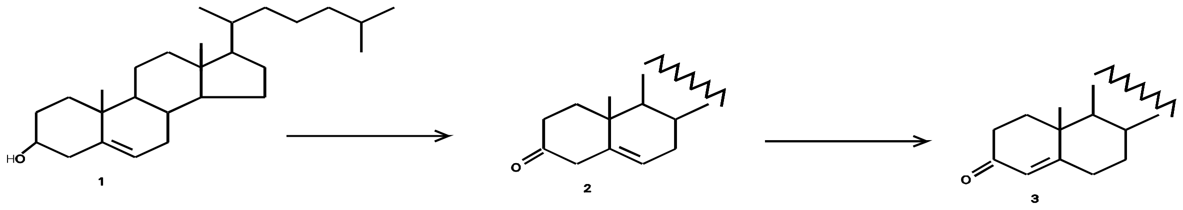
PROBLEM 1 (Practical)

Synthesis

Cholesterol (1) is a natural sterol metabolite present in animal and vegetal organisms. This compound can be oxidized by Jones' reagent into its corresponding 3-ketoderivative (2). The latter, when treated with bases, undergoes isomerization of the carbon-carbon double bond leading to α,β-unsaturated ketone (3).

The conversion of Δ^5-3β-hydroxy steroids into their corresponding Δ^4-3-ketones is an important reaction in steroid chemistry and represents the last step of the synthesis of a variety of commercial hormones.

You will be marked for the purity of the product (3).



Procedure:

a) Dissolve your pre-weighed sample of cholesterol (386 mg, 1 mmol) contained in a 50 cm^3 flask A with acetone (20 cm^3) warming gently the flask in a bath tub of hot water. When the sample is completely dissolved, cool the flask containing the solution to the temperature by cold water.

b) Add dropwise 0.40 cm^3 of Jones' reagent to the solution, gently swirling the flask in a bath of cold water. The formation of a green precipitate [$Cr_2(SO_4)_3$] is observed during the addition of Jones' reagent.

c) Remove the green precipitate by filtration with paper filter.

d) Add slowly water (10 cm^3) to the clean filtrate. The ketone (2) begins to precipitate.

e) Filter the precipitate over the Büchner funnel under reduced pressure, washing the crystals with small portions of a 2 : 1 acetone/water mixture.

f) Dissolve the ketone (2) in methanol (15 cm^3). Add to the solution just one drop of 5 % methanolic NaOH solution and warm the mixture in a bath of hot water for 10 min.

g) The Δ^4-3-ketosteroid (3) precipitates spontaneously, upon addition of water (ca. 2 cm^3) to the cooled reaction mixture. Filter the crystals over the Büchner funnel under reduced pressure and recrystallize the product by methanol. If you do not get the crystals, add a few drops of water. *Remember! You are getting a mark for the purity, not the yield*.

h) Dry carefully the crystals on a porous plate. Determine the melting point of the ketone (3) and write its value on your student's report. Taking into account the correction reported on the top of the thermometer (see example at the end).

i) Put the crystals in the plastic vial B, write on it your personal identification number (see the left corner of your badge), and deliver it to one of the supervisors.

The melting point of the ketone (3) will be checked by the lab supervisors.

SOLUTION

Points were given accordingly to the amount of product.

Some additional points were given for melting point measurements.

PROBLEM 2 (Practical)

Qualitative Determination of Paracetamol in a Sample of Unknown Drug

Introduction

Three organic compounds are most widely used as pain relieving drugs: acetylsalicylic acid (ortho-acetoxybenzoic acid), phenacetine (*para*-ethoxyacetanilide), and paracetamol (*para*-hydroxyacetanilide). Paracetamol is now the most popular, being the base of a large number of well known patented pharmaceuticals (panadol, solpadeine, coldrex, calpol, efferalgan etc.), as it is now considered as the safest and highly efficient drug.

You were given a sample of unknown drug which claims to contain paracetamol. Your task is to prove or disprove this claim experimentally. To do this you shall have to prepare an authentic sample of *para*-hydroxyacetanilide, and run a thin layer chromatography test.

Reagents

- *Para*-aminophenol, 3.10 *g* in a weighing beaker
- Acetic anhydride, 4.00 cm^3 in an Erlenmeyer flask
- Ethanol
- Eluent (heptane : ethyl acetate : ethanol = 41 : 47 : 12 by volume)
- Sample of unknown drug in a test tube, 1 % solution in ethanol
- Water (use tap water for all purposes)

Procedure

Preparation of para-hydroxyacetanilide

A 50 cm^3 round bottom flask is equipped with reflux condensor and installed on a laboratory stand over a hot plate. Note that the space between the top of hot plate and the bottom of flask be about 1-1.5 cm. Use two clamps to properly support the flask and condenser. Remove the hot plate. Do not switch on the hot plate until you finish with adding reagents and reassembling the apparatus. With reflux condensor temporarily removed, 3.10 g of *para*-aminophenol is placed to the flask using a funnel (use a glass rod to push it through the funnel, if necessary). Water (10 cm^3) is then added through the same funnel. The condenser is mounted back, and acetic anhydride (4.00 cm^3) is carefully poured to the reaction mixture through the condenser (*attention*! acetic anhydride has a strong irritating smell. In case of spill immediately wash hands with water and ask the supervisor to help with the disposal of spilled compound). Carefully stir the contents by slightly relieving clamps and waving the flask 2 - 3 times. Be careful as the mixture and the flask gets very hot due to the reaction heat. Place back the hot plate and switch it on. The reaction mixture is heated for 15 minutes beginning from the time when you switch on the hot plate. Then, the heater is switched off and removed from the apparatus. The mixture is allowed to cool first by immersing the flask into a bath with cold tap water. You may do this immediately after you remove the plate as the flask is made of highly durable glass. After approximately five minutes unattach the condenser and pour the contents into an empty 100 cm^3 pyrex glass beaker. Put the beaker into a metal dish filled with ice and water. Accurately rub the walls of beaker with spatula and observe the crystallization of crude product as small white crystals.

Assemble a suction filtration device: put the frit filter onto a rubber ring and a heavy-wall flask. Connect the flask to a suction vacuum pump and turn on water in the pump by turning tap. (*Attention*! Never turn off the water tap if your device is under vacuum. First always disconnect the flask from vacuum pump by carefully pulling off the rubber tubing from the inlet.)

The crystalline precipitate is quantitatively moved onto a filter by spatula. Remaining solid can be washed with small portions of ice cold water (as small as possible, as the compound possesses an essential solubility in water, and the losses of dissolved compound must not outweigh the losses due to incomplete transfer of product to the filter). The product in the filter is carefully washed with 2 - 3 portions of 2 - 3 cm^3 of cold water by a) connecting the vacuum suction flask to the atmosphere; b) addition of water and careful mixing it with the precipitate using a spatula; c) reapplying vacuum; d) pressing the precipitate with flat tip of a glass rod to squeeze out as much water as possible.

Several crystals of material are used for chromatography test (see below). All other precipitate is moved to a sheet of filtering paper in a Petri dish, and spread out over the filter in a thin layer, and allowed to dry on a shelf to exclude accidental spill. For rapid drying it is critical to spread it as thin as possible, to break all large pieces, and to stir it and spread again every 3-5 minutes to expose all wet crystals to air. It is established after a numerous repetition of this procedure, that after 30 min the product contains no more than 5 % of water. Such wetness is considered as insignificant for evaluating the results of the preparation.

Chromatography test

(If for some reason you have failed to obtain *para*-hydroxyacetanilide, you can obtain a sample for chromatography from your supervisor.)

While still wet several crystals of the material obtained by you are dissolved in a tube in 1 - 2 cm^3 of ethanol. The unknown drug is already dissolved in ethanol and given to you as 1 % solution. These solutions are used for thin layer chromatography, as follows:

Prepare a sheet of chromatography plate covered with silica. Using a sharp pencil draw a start line and marks for sample spots. A small spot of each solution is placed on a chromatography plate using a capillary. The spots are allowed to dry for 1-2 minutes.

The plate is immersed into a beaker containing the eluent and allowed to be eluted. Use forceps to move the plate in and out of the beaker. After the elution, remove the plate from the flask, mark the front of eluent, and allow it to dry under the hood for 5 minutes. Examine the chromatogram under UV light in a special cabinet. Outline the dark spots (if there are any) with a sharp pencil.

Weighting of sample

After you complete the chromatography, your product usually is almost dry and is ready for weighting. Ask you supervisor to weight an empty weighing beaker. Put the dry product into a weighted beaker and give it to the supervisor for weighting. Weights are written in your answer sheet by the supervisor. Calculate the weight of the product.

Do the following and fill in the answer sheet form

2.1 Draw the structures of three main pain relieving drugs mentioned above.

2.2 Draw the reaction equation involved in the preparation of *para*-hydroxyacetanilide. Calculate the stoichiometric amounts of reagents needed for the reaction. How much acetic anhydride is taken in excess over the stoichiometry? The density of acetic anhydride is 1.08 g cm^{-3}.

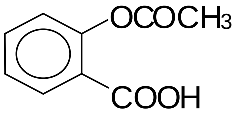
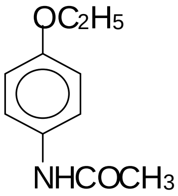
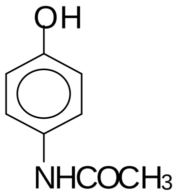
2.3 Calculate the yield of product obtained by you.

2.4 Calculate and compare the values of R_f of unknown drug and your product.

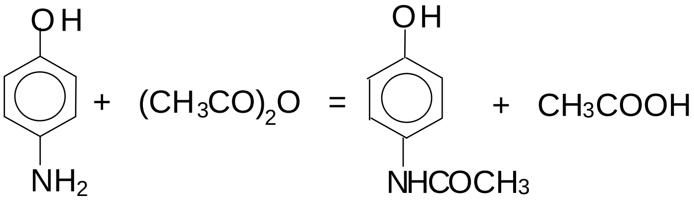
2.5 Is it likely that paracetamol is contained in the sample of drug?

SOLUTION

2.1

Acetylsalicylic acid	Phenacetine	Paracetamol
		

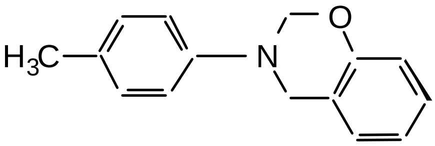
2.2



2.5 Yes, the sample is likely to contain paracetamol.

PROBLEM 3 (Practical)

Synthesis of the Substituted Dihydro-1,3-benzoxazine (C)



C

Benzoxazines have long been recognized as useful biologically-active compounds. One such compound (**C**) will be prepared using the three-step synthesis described below. All of the product obtained in Step I should be used in Step II and similarly all of the product from Step II should be used in Step III. You will be evaluated on both the yield and purity of the final product.

<u>Chemicals available</u>

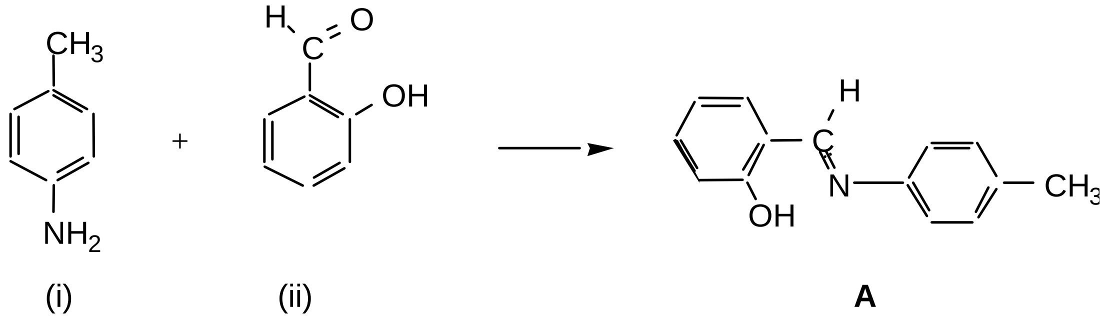
5 cm^3 reaction vial containing 2.5 cm^3 of ethanolic 1-amino-4-methylbenzene (0.22 g),
vial containing 0.25 g of 2-hydroxybenzaldehyde,
vial containing 0.1 g of sodium borohydride,
vial containing 0.042 g of paraformaldehyde,
test tube containing dilute ethanolic KOH,
(50 mg of KOH dissolved in 10 cm^3 of ethanol),
wash bottle containing dry ethanol,
Ice is available in each laboratory room.

Molar masses:

M(H) = 1.008 g mol^{-1}	M(C) = 12.011 g mol^{-1}	M(N) = 14.007 g mol^{-1}
M(O) = 15.999 g mol^{-1}	M(Na) = 22.990 g mol^{-1}	M(B) = 10.811 g mol^{-1}

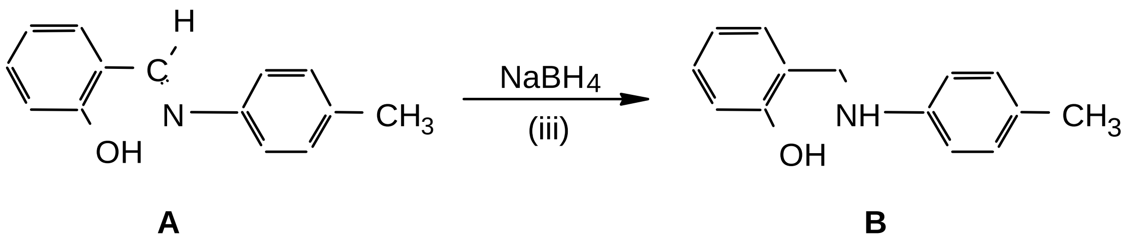
Procedure

STEP I



1. Place the small magnetic stirbar in the 5 cm^3 reaction vial containing solution (i) and stir.
2. Add the 2-hydroxybenzaldehyde from vial (ii) dropwise to the stirred solution in vial (i). After a short period of time a yellow solid will crystallize out. This is intermediate product **A**.
3. Isolate the yellow solid (**A**) by vacuum (suction) filtration and wash it with ice-cold ethanol.

STEP II

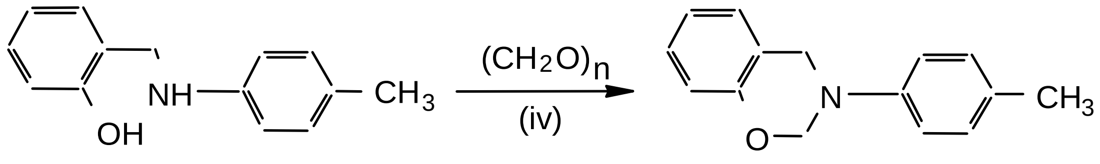


1. Add the impure Product A from Step I to a 5 cm^3 reaction vial containing approximately 1.5 cm^3 of ethanol.
2. Surround the vial with ice/water, and stir the reaction vigorously with the spatula while carefully adding small amounts of sodium borohydride (iii) over a period of about

   5 minutes until the bright yellow colour disappears. The reaction will bubble.

   Note that you have been given more sodium borohydride than is required for this reaction.
3. Isolate the intermediate Product B by vacuum (suction) filtration, wash it with ice-cold ethanol, and air dry the solid for approximately 5 minutes.

STEP III



B **C**

1. Dissolve all of the paraformaldehyde (iv) in approximately 2.5 cm^3 of ethanolic potassium hydroxide (v) in a 5 cm^3 vial. Stir to dissolve all of the solid.
2. Add all of product **B** from Step II to the vial. Stir and gently reflux the mixture for 15 minutes. A clear solution should be obtained.
3. Concentrate the solution by carefully boiling off some of the ethanol leaving approximately 1 cm^3 in the vial and allow the vial to cool. The crystals which form are the required product **C**.
4. Isolate the crude product **C** by vacuum (suction) filtration and air dry the crystals.
5. Recrystallize the crude product from ethanol. Air dry the crystals for 15 minutes.
6. Determine the melting point* and then mass of the final product.
7. Place all of your remaining product in the numbered vial labelled “PRODUCT C” and hand it in for evaluation.

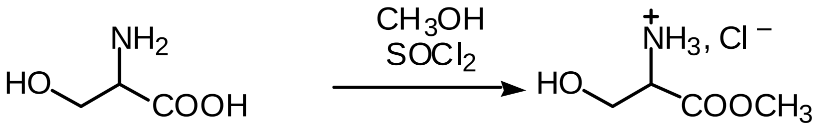
* Note: A melting point is always recorded as a range -- from when the crystals first begin to melt until the last crystal has melted. The melting point apparatus should be allowed to cool to approximately 50 degrees before you use it. The supervisors will be rechecking both your reported melting point and mass for product C.

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 °C 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.

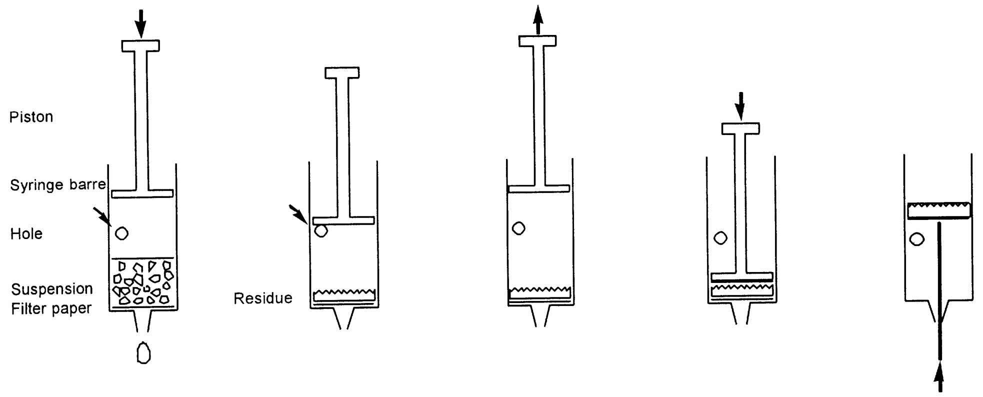
The solid is then collected on a piece of filter paper in order to absorb residual solvent. When dry, the residue is placed in a tarred plastic sample tube with lid (Eppendorf tube) found in the box. The sample tube is then closed and weighed.

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.

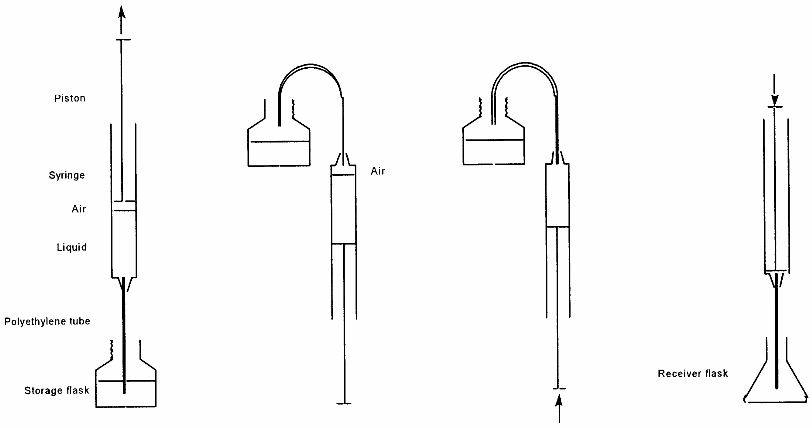
Filtration procedure for practical problem 2

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.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Preparation of 2-Iodobenzoic Acid

This laboratory task involves preparation of 2-iodobenzoic acid from 2-aminobenzoic acid. The procedure consists of diazotization of 2-aminobenzoic acid followed by reaction with KI (in H_2SO_4).

Procedure

1) Quantitatively transfer the given sample of solid 2-aminobenzoic acid into a 100 cm^3 beaker placed in the ice-bath. Add 7.2 cm^3 of H_2SO_4 (2.6 M) (labelled H_2SO_4) and mix the contents thoroughly for 1 minute with the help of a glass rod. Cool the solution for 5 minutes.
2) Using a measuring cylinder, measure out 4.4 cm^3 of supplied cooled $NaNO_2$ solution from the vial placed in the ice-bath.
3) With the help of a dropper, slowly add the cooled $NaNO_2$ solution to the acid solution with constant gentle stirring using a glass rod to obtain an almost clear solution (3 – 5 minutes).
4) Remove the beaker from the ice bath and then slowly add 9.4 cm^3 of KI solution from the stoppered tube, with stirring.
5) Get hot water from the laboratory expert. Keep the beaker in hot water for 5 minutes.
6) Filter the crude product and wash it thoroughly with distilled water (10 cm^3). Collect the washings along with the main filtrate.
7) Neutralize the combined filtrate by gradually adding the given solid Na_2CO_3 until effervescence ceases. Dispose of the filtrate in the appropriate plastic bucket.

Purification of the crude product

Place the funnel containing the precipitate on a 100 cm^3 conical flask. Pour about 15 to 20 cm^3 of the supplied $NaHCO_3$ solution (using test tube) over the filter paper so as to dissolve the precipitate completely.

8) Add the supplied charcoal powder to the filtrate and mix it thoroughly. Filter the solution to remove charcoal.

9) Add dilute H_2SO_4 gradually to the filtrate till effervescence ceases. Filter the purified product. Use 10 -15 cm^3 distilled water to wash the precipitate. Keep the filter paper with the product on a watch glass.
10) Cover the product with the same funnel and hand over the product to the laboratory expert for drying (for a minimum of one hour).

Towards the end of the practical session have the product weighed by the laboratory expert and record the same.

SOLUTION

The following values were required to be written on the Answer Sheet :

- Mass of the product.
- The calculated theoretical yield (based on 2 aminobenzoic acid) in g.
- The yield obtained as a percentage of the theoretical yield.
- Colour of the product obtained.

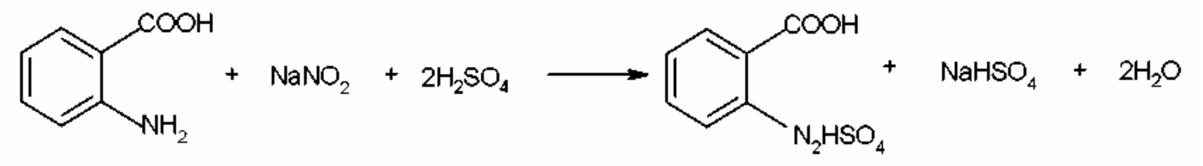
Tasks:

Write down the balanced chemical equations for:

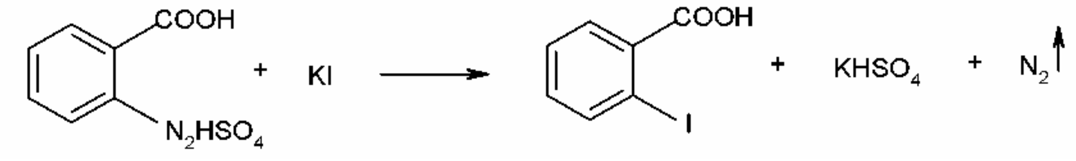
(a) diazotization of 2-aminobenzoic acid using $NaNO_2$ and H_2SO_4.
(b) the reaction of KI with the diazotized product.

Solutions of the tasks:

a)



b)

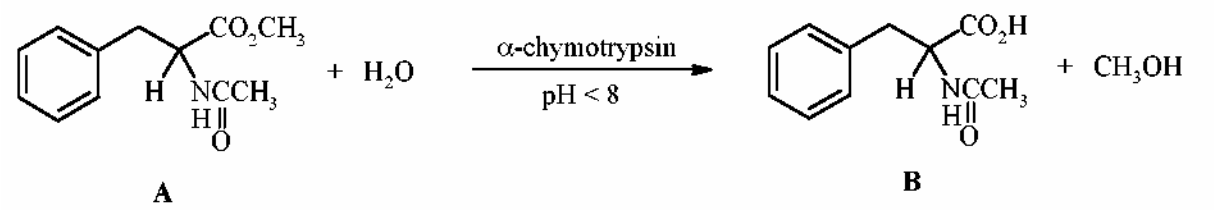


PRACTICAL PROBLEMS

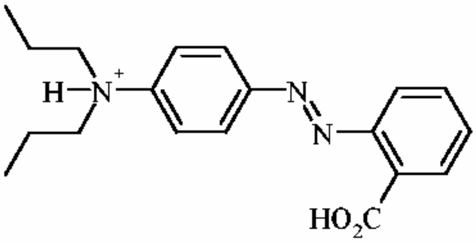
PROBLEM 1 (Practical)

Enzymatic Hydrolysis of Methyl *N*-Acetyl-phenylalaninate

α-Chymotrypsin, a protease enzyme recognizing derivatives of natural α-amino acids, catalyses the hydrolysis of esters. In this experiment the enzymatic hydrolysis of racemic methyl N-acetyl-phenylalaninate **A** is investigated (Scheme).



The rate of formation of *N*-acetyl-phenylalanine **B** can be monitored by titration with 0.100 M NaOH in the presence of propyl red as a pH indicator.



Propyl red (protonated form)
At pH < 5: pink; at pH > 6: yellow

Procedure

Note: the required amount of α-chymotrypsin will be supplied in a sample vial by the laboratory assistant on request.

Racemic methyl *N*-acetyl-phenylalaninate **A** [500 mg, the exact mass (± 1 mg) is indicated on the label of the vial marked as NacPheOMe] is transferred quantitatively into a 50 cm^3 Erlenmeyer flask and dissolved in methanol (~ 2.5 cm^3). Subsequently, propyl red (0.02 % solution in ethanol; 4 drops) is added. The kinetic experiment is started by adding α-chymotrypsin (10.0 cm^3 of a 0.05 % solution in distilled water) in one portion (*start the stopwatch*).

When the reaction mixture turns pink, it is immediately titrated with 0.100 M NaOH until the colour changes to yellow. When the pink colour reappears, add just enough titrant to restore the pale yellow colour, swirling the flask continually during the addition. You only need to record the reading on the burette every 5 minutes. (*Note: at the beginning colour changes occur very frequently.*)

Monitor the reaction for 75 minutes. A graph showing the amounts of NaOH consumed in cm^3 versus time is constructed, in order to visualize the kinetic course of this enzymatic reaction.

SOLUTION

The competitors were expected to show on the answer sheet the following data, tables, graphs or calculations:

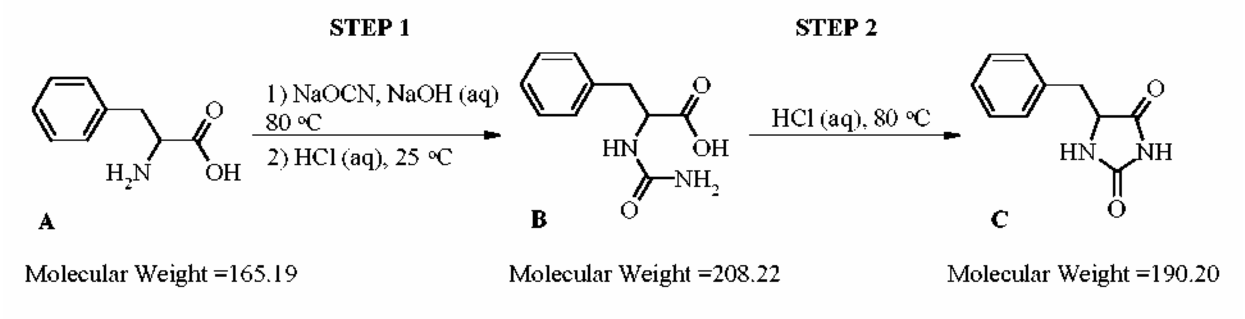
1. Amount of the starting racemic methyl *N*-acetyl-phenylalaninate **A** (in mg and mmol).
2. Table with time measured and the total consumption of NaOH in cm^3.
3. A graph of the total consumption of NaOH vs time.
4. Calculation of the amount of 0.100 M NaOH consumed in this experiment in mmol.
5. Calculation of the degree of hydrolysis of
   methyl *N*-acetyl-(*R,S*)-phenylalaninate **A** in mol %.

PROBLEM 2 (Practical)

Synthesis of Benzylhydantoin

Introduction

α-Amino acids are the building blocks for peptides and proteins. They are also frequently used as starting material for the synthesis of pharmaceuticals. In this experiment natural *S*-phenylalanine **A** is converted in two steps into benzylhydantoin **C**, which is a useful intermediate for the preparation of various physiologically active derivatives.



Procedure

STEP 1

*Retain a tiny amount of starting material **A** for the TLC analysis (see below).* A long-necked round-bottomed flask is charged with (*S*)-phenylalanine **A** (500 mg, 3 mmol, the exact amount is indicated on the label of the vial), sodium cyanate (300 mg, 4.6 mmol), water (3 cm^3) and a stirring bar. Two drops of aqueous sodium hydroxide (1 M) are added to the stirred suspension. The flask is equipped with a condenser (distillation column) and the reaction mixture is heated to 80 °C on a sand bath while stirring magnetically.

Important

In order to reach the appropriate temperature in time and not lose too much time, start the electric heating of the sand bath immediately at the beginning of this experiment. Check the temperature of the sand bath regularly and carefully with a thermometer.

After heating the reaction mixture at 80 °C for at least 30 minutes, the resulting clear solution is cooled to room temperature and poured into a small Erlenmeyer flask. Rinse the round-bottomed flask with a little water. The solution is acidified by dropwise addition of hydrochloric acid (4 M) to pH < 3 with magnetic stirring. Some water is added to the resulting white suspension in order to facilitate stirring.

The white precipitate is then filtered off by suction, washed with ample water (on the filter) and then washed twice with a small amount of di-isopropyl ether to remove most of the adhering water. The urea derivative **B** is left on the filter under suction for at least 3 minutes to remove as much solvent as possible.

A small amount of the obtained urea derivative **B** is retained for TLC-analysis later.

STEP 2

The urea derivative **B** is now transferred into a long-necked round-bottomed flask and hydrochloric acid (4 M, 3 cm^3) is added. A stirring bar is introduced and the suspension is stirred thoroughly whilst heating at 80 ^{o}C on a sand bath. A clear solution is obtained. After a reaction time of 30 minutes, the reaction mixture, which may already contain some precipitate, is cooled to room temperature. The obtained suspension is filtered by suction, washed thoroughly with water and finally washed twice with a small amount of di-isopropyl ether. The product is left on the filter under suction for at least 3 minutes. It is then collected on a filter paper and dried in the air for at least 30 minutes.

The final product **C**, its precursor **B** and starting material **A** (see above) are subjected to TLC-analysis. For this purpose small amounts of either compound are dissolved in a tiny amount of pure acetone. Small samples of these solutions are applied to a TLC plate, using the supplied capillary tubes. The analysis is carried out with two TLC plates in one run. The TLC-plates are developed with a solution of 2% formic acid in ethyl acetate as the eluent. After the elution the TLC-plates are analysed using a UV-lamp. The starting line, solvent front and the UV-active spots are clearly marked with a pencil. Copy the diagram in the box on the answer sheet. The R_f values are determined. Finally, the TLC-plate with the best analysis is wrapped in parafilm and placed in a plastic bag with a sealing strip.

The final product **C** is transferred into a sample vial of which the empty weight has been pre-determined (weight is indicated on the label). Weigh the vial with product and calculate the yield of the product **C**.

The examination committee will check the quality of the benzylhydantoin that you have prepared by determining its melting point using an automatic melting point apparatus.

SOLUTION

The competitors were expected to show the following data, tables, graphs or calculations on the answer sheet:

1. Mass of your starting material **A** (see label on the vial) in mg.
2. Amount of benzylhydantoin **C** obtained.
3. Calculation of the yield of benzylhydantoin **C** in %.
4. R_f value of urea derivative **B.**
5. R_f value of benzylhydantoin **C.**
6. A copy of the TLC diagram with indication of the front base line of the solvent.
7. Conclusions from the TLC analysis:
   Compound **B**: is pure; contains some **A**; contains several contaminants.
   Compound **C**: is pure; contains some **B**; contains some **A** and **B**;
   contains several contaminants.
8. Appearance of benzylhydantoin **C**: white colour, yellowish colour, sticky, crystalline, powder.
9. Melting point of benzylhydantoin **C** was determined by the examination committee.
10. The TLC plate was necessary to pack in an envelope and leave it to a laboratory superviser.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis of the Dipeptide *N*-acetyl-*L*-prolinyl-*L*-phenylalanine Methyl Ester (Ac-*L*-Pro-*L*-Phe-OCH_3)

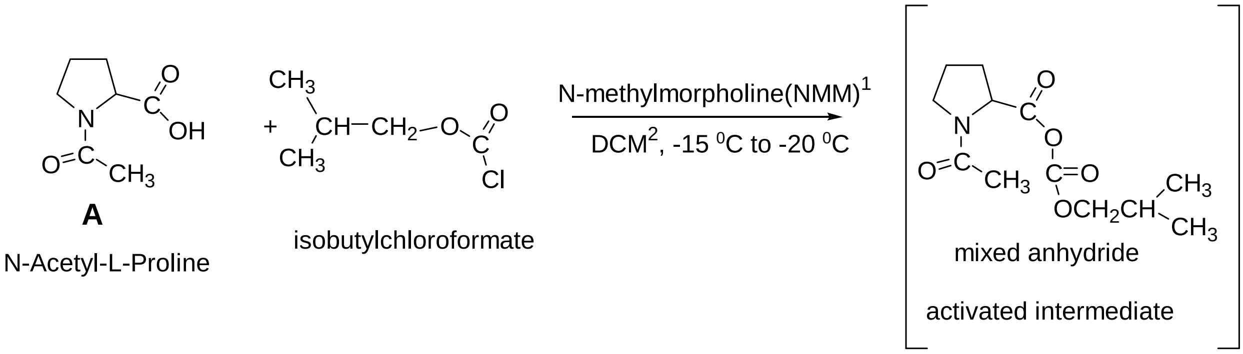
Introduction

Peptide synthesis is now a well-refined art and many of their synthetic procedures can be readily adapted to the elementary laboratory. Interest in peptides, always high, has heightened even more with the recent discovery of the importance of the so-called “opiate” peptides as well as of other biological active peptides.

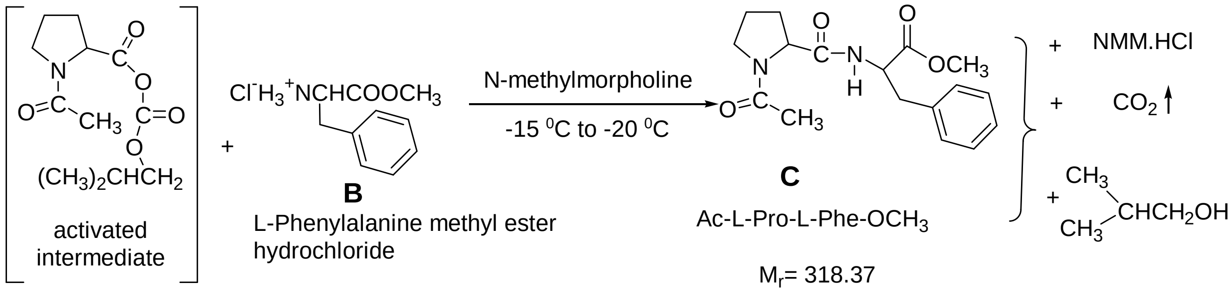
In this experiment the one-pot procedure for synthesizing the title dipeptide from its components, suitably protected amino acids, is described.

Reactions

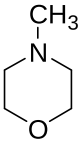
STEP 1



STEP 2



[1] *N*-methylmorpholine (NMM) =



[2] DCM = Dichloromethane

Procedure

STEP 1

Place the 1.50 g (0.0095 mol) sample of *N*-acetyl-*L*-proline (labelled AcPro), which you have been given, into a 50-cm^3 round-bottom flask. Add 20 cm^3 dichloromethane (labelled DCM) in the graduated cylinder. Use some of the 20 cm^3 DCM to wash out the AcPro vial and add the remaining DCM also into the round-bottomed flask. Plug the flask with a septum, clamp it loosely to a support stand and cool it to –15 °C to –20 °C in the ice/sodium chloride cold bath provided by the supervisor. Allow approximately 5 minutes for cooling. Add 1.2 cm^3 (0.0109 mol) of *N*-methylmorpholine (labelled NMM) to the flask, by means of a syringe. Then, slowly add 1.5 cm^3 (0.0116 mol) isobutyl-chloroformate (labelled IBCF) to the flask by means of a second syringe. During the addition, swirl the reaction mixture gently by hand, and continue swirling for another 10 min. The temperature should remain in the range –20 ^{o} to –15 ^{o}C.

STEP 2

Remove the septum and quickly add all the *L*-phenylalanine methyl ester hydrochloride (2.15 g, 0.0100 mol), (labelled $HCl \cdot H_2NPheOCH_3$) using the polypropylene powder funnel. Plug the flask again with the septum. Immediately add 1.2 cm^3 (0.0109 mol) of *N*-methylmorpholine (labelled NMM) using a third syringe, while the reaction mixture is swirled by hand. *ATTENTION: Leave the needle part of the syringe in the septum for the remainder of the reaction*. Allow the reaction to proceed for 60 min at –15 °C to –20 °C, swirling periodically by hand.

During this waiting period you are highly advised to start working on the Analytical Chemistry experiment.

After 60 min at –20 ^{o}C to –15 ^{o}C, remove the 50 cm^3 round-bottomed flask from the ice/sodium chloride bath and place the flask in the 250 cm^3 beaker and let it warm up to room temperature. Transfer the contents of the flask into the 50 cm^3 separating funnel by means of the glass funnel. Rinse the flask with a small amount of dichloromethane (3 – 5 cm^3), which is in a vial (labelled DCM). Wash the organic layer successively with two 20 cm^3 portions of 0.2 M aqueous HCl solution, two 20 cm^3 portions of 1 % aqueous

$NaHCO_3$ solution (read caution comment in next paragraph) and finally one 10 cm^3 portion of saturated solution of sodium chloride (labelled brine).

Important

After each washing allow the separating funnel to stand for enough time, so that the two phases separate completely. Also, take into consideration that the organic phase (DCM) is always the lower layer and contains the product. All the aqueous washings are collected in the same Erlenmeyer flask (empty if necessary).

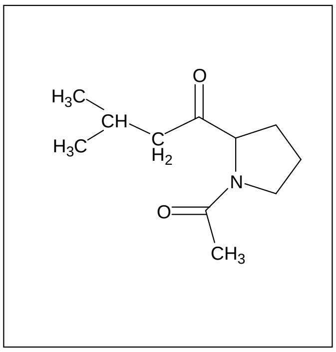
CAUTION: Keep in mind, also, that during washing with 1 % $NaHCO_3$, the CO_2 liberated is exerting pressure on the separating funnel stopper, so be sure to let the gas out through the stopcock before and after each shaking, while holding the funnel upside down.

Before continuing, wash the glass funnel, the 50 cm^3 cylinder and the 50 cm^3 round-bottom flask with water and then dry them with acetone. Your supervisor will show you where to dispose of the water and the acetone.

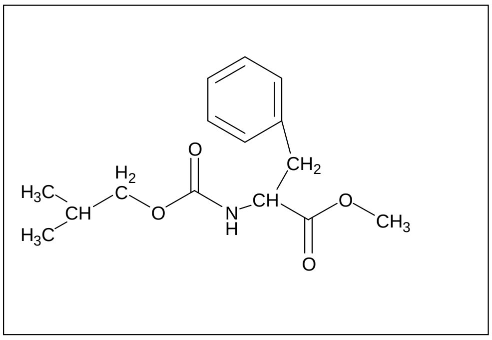
Pour the organic layer into a clean 50 cm^3 Erlenmeyer flask. Add the anhydrous sodium sulphate, which is in a vial labelled Na_2SO_4, to the Erlenmeyer flask containing the organic layer. The organic phase should become clear. Filter it through the cleaned and dried funnel, whose stem you have previously stuffed with a small piece of cotton to trap any solids, into the cleaned and dried 50 cm^3 round-bottom flask. Rinse the Erlenmeyer flask with a small amount of dichloromethane (3 – 5 cm^3). Removal of the organic solvent is done under reduced pressure, using a rotary evaporator apparatus. This will be done for you by a laboratory supervisor, who will add 20 cm^3 of diethylether to the residue in your flask, which will cause precipitation of your product. After cooling for 5 minutes in the ice bath, scrape the walls of the flask with a spatula, filter by suction the crystallized dipeptide through a fritted glass funnel. Wash twice with diethylether (5 cm^3 each time).

Leave the product on the filter under suction for at least 3 minutes. Then collect it on weighing paper, weigh it in the presence of a supervisor and then transfer it into a sample vial and label it with your student code. Write the mass of your product (**C**) on the label and on your answer sheet (on the next page).

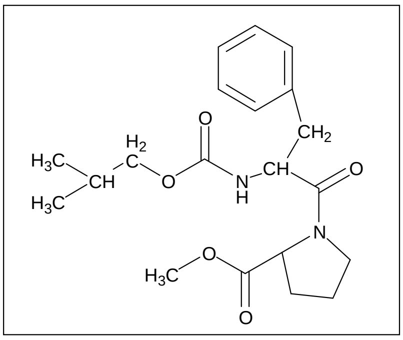
During the reaction between the phenylalanine methylester **B** and the activated mixed anhydride intermediate (step 2) the formation of the desired dipeptide product **C** is usually accompanied by a by-product the correct structure of which is one of the three structures **I**, **II**, **III** given below. Circle the Roman numeral corresponding to the correct structure.



I



II



III

TLC- Analysis

You have two Eppendorfs, one empty and one with a tiny amount of substance **B**. Put a small amount of **C** into the empty Eppendorf, and dissolve both **B** and **C** in a few drops of methanol. Use the supplied capillary tubes to apply small samples of these solutions to the TLC plate. Develop the TLC plate with a solution of chloroform-methanol-acetic acid (7 : 0.2 : 0.2) as eluant. The appropriate amount of eluant has been placed in the proper vial by the supervisor.

After the elution, analyze the TLC-plate using a UV-lamp. Clearly mark the starting line, solvent front and the UV-active spots.

Draw the diagram in the box on the answer sheet. Determine the R_f values.

Finally place the TLC-plate in a small plastic bag with a sealing strip and put it in an envelope provided by the supervisor. Write your student code on the envelope.

The examination committee will check the quality of the *N*-acetyl-*L*-prolinyl-*L*-phenylalanine methyl ester that you have prepared by determining its angle of optical rotation and consequently its specific rotation, $[a]^{t}_{D,}$ using an accurate polarimeter apparatus.

SOLUTION

The following values were required to be written in the Answer Sheet

- Mass of Ac-*L*-Pro-*L*-Phe-OCH_3 obtained (product **C**).
- The yield of Ac-*L*-Pro-*L*-Phe-OCH_3 **C.**
- The TLC diagram with indication of the base line and the front of the solvent.
- R_f value of *L*-phenylalanine methyl ester hydrochloride (material B) and that of R_f value of Ac-*L*-Pro-*L*-Phe-OCH_3 (product C).

- Conclusions from the TLC analysis:

  Compound **C:**
  - Is pure,
  - Contains some **B**,
  - Contains several contaminants,
  - No conclusion.

- Specific rotation of the dipeptide Ac-*L*-Pro-*L*-Phe-OCH_3 C (to be measured later by the examination committee)

  $[a]_D^T$ = 45 °

- The correct structure of the by-product: **II.**

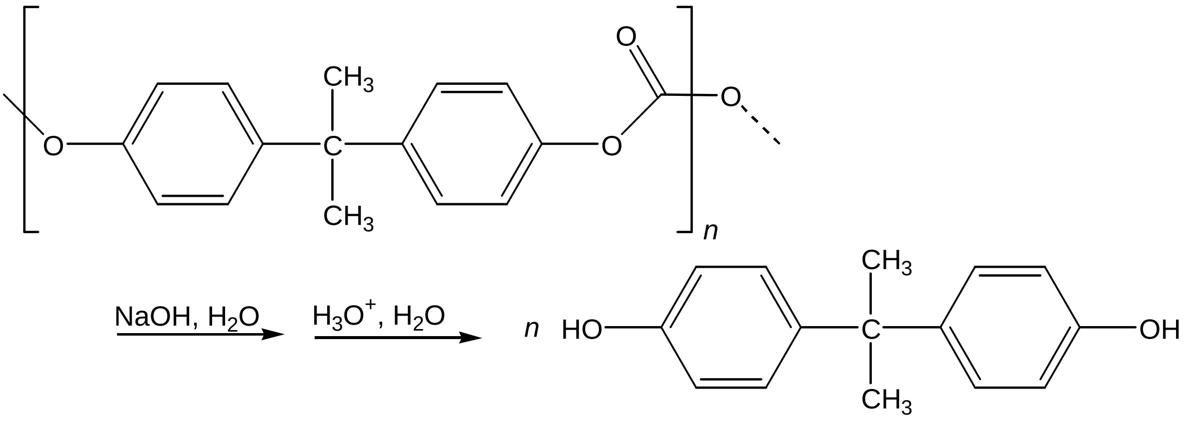
PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

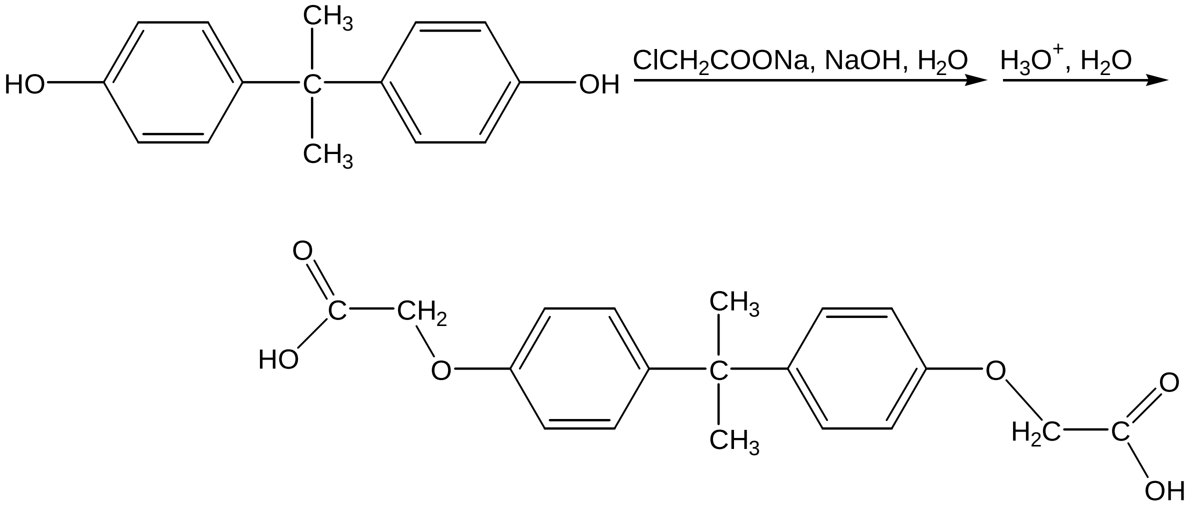
Two-Step Organic Synthesis of 2,2-Bis(*p*-phenyleneoxyaceticacid)propane (Bisphenol A bis(carboxymethyl)ether)

Introduction

In the first step the sodium salt of bisphenol A results as an intermediate from the alkaline hydrolysis of a polycarbonate. By adding an acid this salt is converted into the free 2,2-bis(4-hydroxyphenyl)propane (bisphenol A).



In the second step bisphenol A reacts with sodium chloroacetate to form the phenolic ether, bisphenol A bis(carboxymethyl)ether.



- In each step the product has to be isolated.
  (Drying and weighing will be done by the organizer.)
- For the product of step 2 three melting point tubes have to be filled.
  (Filling of the melting point tubes in step 1 will be done by the organizer.)
  (The melting points will be determined by the organizer.)
- When the organizer receives your labelled beaker A of step 1 you will get 2.00 g of bisphenol A as starting material for the second step.
- Answer the additional questions on the answer sheet **P1**.
- Do not remove the Ceran plate from the magnetic stirrer.

Procedures

Step 1: Preparation of bisphenol A by alkaline hydrolysis of a polycarbonate

Preparation:

- Put the pre-weighed 2.54 g of polycarbonate (No. **1**), 4.0 g of sodium hydroxide (No. **5**) and 3 cm^3 of demineralized water into a 100 cm^3 Erlenmeyer flask with ground-glass joint.
- Close the flask with a plastic plug and swirl it gently so that the solution does not contact the ground-glass joint. For aeration open the plastic plug occasionally. Strong heating can be observed, as the sodium hydroxide partially dissolves.
- Remove the plastic plug after swirling for about 4 minutes, add a magnetic stirring bar and put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Finally, add 20 cm^3 of ethanol (No. **2**) through the condenser while stirring the reaction mixture.
- Heat the reaction mixture under reflux for 60 minutes. In the beginning adjust the thermostat of the heating plate to maximum. When the mixture starts boiling reduce the heat carefully, so that the mixture is kept under gentle reflux.
- A white precipitate is formed on heating.

During this waiting period you are highly advised to start working on the analytical chemistry experiment.

Isolation:

- Stop heating after one hour, allow the reaction mixture to cool down to ambient temperature, remove the condenser, add 25 cm^3 of demineralized water and transfer the reaction mixture into a 400 cm^3 beaker. Rinse the Erlenmeyer flask with 25 cm^3 of demineralized water and add this to the contents of the beaker.
- Finally, fill up to 150 cm^3 with demineralized water.
- If the reaction mixture is not clear, the mixture has to be filtered over fibre glass into an Erlenmeyer flask.
- Add slowly 15 cm^3 of hydrochloric acid (No. **3**) stirring the mixture simultaneously with a glass rod. A rather oily or sometimes crystalline precipitate is formed.
- Ask your instructor for some seed crystals of bisphenol A (No. **27**) in order to accelerate the crystallization.
- Stir the reaction mixture thoroughly with the glass rod. For a quantitative crystallisation continue stirring from time to time till the supernatant aqueous solution is nearly clear.
- Collect the crude product by vacuum filtration, wash it twice with 10 cm^3 portions of demineralized water and transfer it quantitatively into the tared and labelled beaker A.
- For drying and weighing deliver your labelled beaker A into the instructor room.
- Afterwards you will get a small jar filled with 2.00 g of bisphenol A (No. 28), your starting material of the second step.
- On delivery of your product and on receipt of the starting material you have to sign. Even if you do not have any bisphenol A, please bring the empty beaker A to the instructors' room in order to get the starting material for step 2.

Step 2: Reaction of Bisphenol A with Chloroacetic Acid forming 2,2-Bis(p-phenyleneoxyacetic acid)propane
(Bisphenol A bis(carboxymethyl)ether)

Preparation:

- Pour all the bisphenol A (No. **28**) you have received from the organizer when you had finished step 1 into a 100 cm^3 Erlenmeyer flask with ground-glass joint.
- Add 10 cm^3 of an aqueous sodium-hydroxide solution (No. **6**), 1 cm^3 of demineralized water and a magnetic stirring bar.

- Put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Heat the reaction mixture with gentle stirring until a clear solution is formed.
- Remove the heating plate and the condenser and add 5.0 g of the sodium salt of chloroacetic acid (No. **4**) to the reaction mixture.
- After reconnecting the flask with the reflux condenser, heat the mixture to reflux with vigorous stirring for 30 min.
- Initially a clear solution is formed on heating. In some cases a colorless solid precipitates. If the complete mixture becomes solid in the course of the reaction, heating must be stopped.
- After that, 50 cm^3 of ethanol (No. **2**) are added carefully through the condenser (beware of sudden boiling!). The mixture is stirred and heated under reflux for 5 minutes. A colourless solid precipitates, or the crystallisation which has already started is completed.

Isolation:

- After leaving it to cool down for 5 minutes, transfer the reaction mixture with another 50 cm^3 of ethanol (No. **2**) quantitatively to a beaker. The reaction mixture should be stirred vigorously.
- The magnetic stirring bar is removed and the reaction mixture is filtered through a suction filter. Solids which separate in the filtrate are rejected. Rinse the beaker with 10 cm^3 of ethanol (No. **2**). The precipitate is washed twice with 10 cm^3 portions of ethanol (No. **2**). (The filtrate must be disposed of in the organic solvent waste!)
- Transfer the precipitate quantitatively into a beaker, add a stirring bar and dissolve it in 150 cm^3 of demineralized water. The mixture must be stirred vigorously. Larger lumps of the solid must be crushed with the spatula.
- If the solution is not clear, it has to be filtered over a folded filter paper into an Erlenmeyer flask.
- The slow addition of 5 cm^3 of hydrochloric acid (No. **3**) to the stirred reaction mixture results in the formation of a white precipitate.
- Collect the crude product by vacuum filtration, wash it twice with 10 cm^3 portions of demineralized water and transfer it quantitatively into the tared and labelled beaker B.

- Take a small sample of the product with a micro spatula, crush it and dry it on a shard. Fill three melting point tubes with the homogenized, dried sample. For a close-packed and 5 mm high filling use the 75 cm glass tube and the measure.
- Put all three melting point tubes into the test tube B, which is labelled with your student code, and give it together with your labelled beaker B with the product to the instructor. On delivery you have to sign.

SOLUTION

1.1 You started with 2.54 g of polycarbonate. Determine the theoretical yield of bisphenol A in g.

M_1(polycarbonate) = $M_1(C_{16}H_{14}O_3)_nH_2 \approx M_1(C_{16}H_{14}O_3)$ = 254.30 g mol^{-1}

m_1 = 2.54 g

M_2 ($C_{15}H_{16}O_2$) = 228.31 g/mol

$m_2 = m_1 \times M_1^{-1} \times M_2$

Theoretical yield of bisphenol A: 2.28 g

1.2 Determine your theoretical yield of bisphenol A bis(carboxymethyl)ether in g based on 2.00 g bisphenol A.

M_2 ($C_{15}H_{16}O_2$) = 228.31 g/mol

m_2 = 2.00 g

M_3 ($C_{19}H_{20}O_6$) = 344.39 g/mol

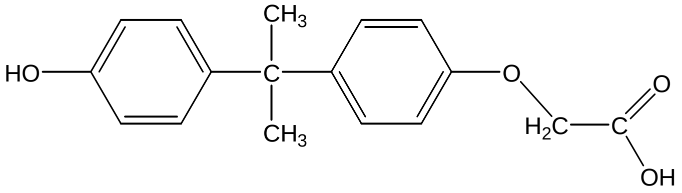
$m_3 = m_2 \times M_2^{-1} \times M_3$

Theoretical yield of bisphenol A bis(carboxymethyl)ether: 3.02 g

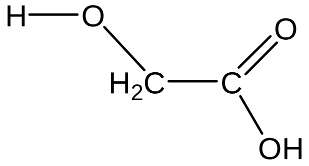
1.3

Unwanted by-products are possible in the second step. Write down the structural formulas of two most probable unwanted by-products.

1. Bisphenol A reacts only once with sodium chloroacetate (monosubstitution):



2. Alkaline hydrolysis of sodium chloroacetate:

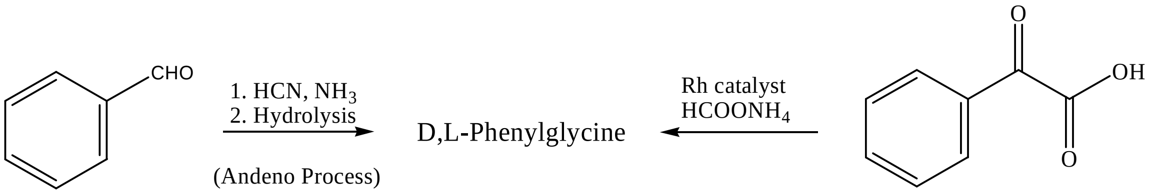


PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

The Synthesis of D,L-Phenylglycine and Its Enantiomeric Resolution

One of the enantiomeric forms of phenylglycine is an important raw material for the preparation of β-lactam antibiotics. Industrial production of optically active phenylglycine is prepared by the Andeno process. The starting benzaldehyde was treated with HCN/NH_3 following hydrolysis to give the racemic D,L-phenylglycine. The desired enantiomeric phenylglycine was then resolved by (+)-camphorsulfonic acid [(+)-CSA].



Benzaldehyde D,L-phenylglycine Benzoylformic acid

In this experiment, you are going to synthesize racemic D,L-phenylglycine (also referred to as *R*- and *S*-isomers, respectively) from an alternative method called reductive amination. Treatment of benzoylformic acid under Rh metal catalyzed conditions gives D,L-phenylglycine. The racemic D,L-phenylglycine is resolved by the treatment of (+)-CSA in water. The solubility of D-phenylglycine•(+)-CSA salt is 5.75 g/100g H_2O, while that of L-phenylglycine•(+)-CSA salt is >150 g/100g H_2O at 25 ℃. The chemical yield and the optical purity of the diastereomeric salt will be measured.

EXPERIMENTAL PROCEDURE

Step 1. Preparation of D,L-phenylglycine

The following pre-weighted chemicals can be used directly without further weighing: Benzoylformic Acid; Ammonium Formate; Rh Catalyst; (+)-camphorsulfonic acid [(+)-CSA].

1. To a 50 mL round-bottomed flask is added a magnetic stirring bar, pre-weighed (approximate 1.80 g, exact mass will be on your sample bottle, write down the mass

on your answer sheet and get the lab assistant to confirm the weight.) of benzoylformic acid (NOTE: irritant, do not contact with skin), 7.57 g of ammonium formate (HCO_2NH_4), 37.2 mg of Rh catalyst (NOTE: the catalyst is wrapped in a weighing paper in a plastic bag. Handle with care!) and 22 cm^3 of the pre-mixed solvents at ambient temperature.

2. Put a reflux condenser (use the Teflon sleeve; you can trim off 1 cm from the smaller end for a better fit) into the neck of the flask and plug the condenser with a septum. For pressure equilibration, put a needle in the septum before starting the heating. Clamp the apparatus tightly to the stand in your hot plate/stirrer. Put the flask onto a hot water bath [hot water provided by the organizer] and stir the reaction mixture gently. (NOTE: the solvent is air cooled, so there is no tap water running through the condenser.) The temperature of the water bath needs to be maintained in the range of 68 to 72 ℃ by adjusting the thermostat of the hot plate/stirrer.
3. The mixture will become cloudy and the color of the solution will change from clear yellowish to dark-greenish when the product starts to precipitate (generally requiring 25 ~ 35 minutes). The hot water bath should then be removed and the solution allowed to stir in the water bath (ambient temperature) for an additional 10 minutes.
4. Add 15 cm^3 of deionized water to the resulting mixture and stir for 10 minutes.
5. Pre-weigh the bigger fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Use the stir bar retriever to remove the stir bar. Collect the product by filter suction through a fritted glass funnel under a reduced pressure (rotary aspirator apparatus). Wash the solid four times thoroughly with ethanol (10 cm^3 each). For each washing, **break the aspirator pressure**, use a glass rod to perturb the solid when adding ethanol, and reapply the rotary aspirator.
6. For rapid drying, you have to spread the product over the fritted glass funnel. For drying, give the fritted glass funnel to the lab assistant. The product is dried in the oven at 100 ℃ for 1.5 hour.

During the drying period you can start working on Experiment 2 (analytical experiment) and you will be notified when your product is ready. Step 2 of experiment 1 will need at least 1 hour.

7. Weigh the dried product [(D,L)-phenylglycine], record the data and calculate the chemical yield (based on the starting benzoylformic acid). Get the lab assistant to confirm the weight. The purity of the product will be determined by ^1H NMR spectrum

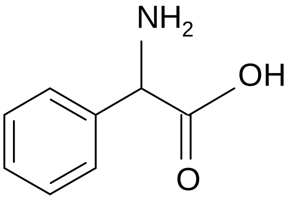
analysis. Turn in the product in a vial (**blue label** with ^{1}H NMR and your student code) to the lab assistant, and receive a new batch of D,L-phenylglycine for step 2.

Step 2. Enantiomeric Resolution of D,L-phenylglycine by (+)-Camphorsulfonic Acid [(+)-CSA]

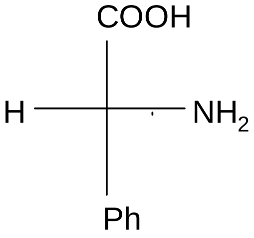
1. To a 25 cm^3 round-bottomed flask add the pre-weighed sample of D,L-phenylglycine provided (The exact mass will be on your sample bottle, write down the mass on your answer sheet and get the lab assistant to confirm the weight). To this, add the pre-weighed (+)-camphorsulfonic acid [(+)-CSA] (1.80 g). Clamp the apparatus tightly to a stand in a magnetic stirrer. Add deionized water (4 cm^3) and place the flask in a hot water bath and heat it to a temperature in the range of 90 ~ 100 °C. Keep the mixture at this temperature for 10 minutes until it turns clear.
2. Remove the hot water bath and allow the mixture to cool down to ambient temperature for 10~15 minutes. With the flask plugged with a septum, cool the flask in ice bath (Styroform) for 15 minutes. Crystals should appear in about 20 minutes, if not, you may ask for seed crystals to induce the crystallization.
3. Pre-weigh the smaller fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Collect the product by filtering the solution through a fritted glass funnel under a reduced pressure. Wash the solid thoroughly two times with ice cooled distilled water (5 cm^3 each).
4. For drying, give the fritted glass funnel to the lab assistant. The product will be dried over in oven at 100 °C for 20 min. You will be notified when your product is ready. Weigh the product, and get the lab assistant to confirm the weight. Record the data and calculate the chemical yield (based on starting D,L-phenylglycine).
5. The optical purity of the diastereomeric salt will be measured using an accurate polarimeter apparatus by the examination committee. Transfer the dried product to a sample vial (pink label labelled with $[\alpha]_D$ and your student code) and give the sample vial to the lab assistant**.** The organization committee will weigh an appropriate amount of the product (0.055 ~ 0.065g) for measurement of optical purity.

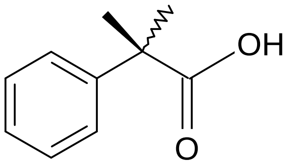
SOLUTION

1.4 Structural formula (A) and stereochemical formula (B) of the isolated phenylglycine: (Task appeared in the answer sheet only.)



A



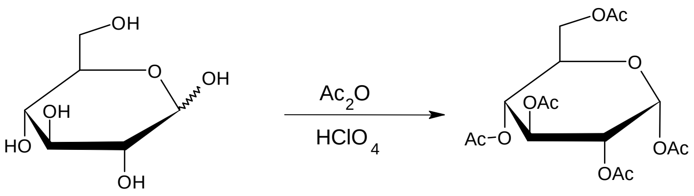


B

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis of α-D-glucopyranose pentaacetate

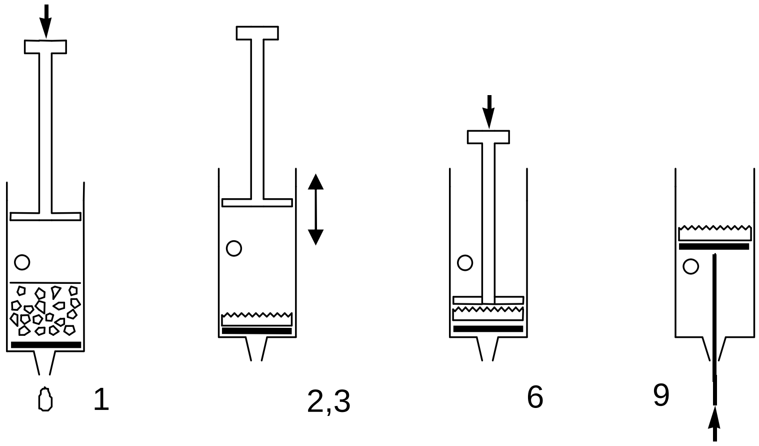


Caution: Use gloves while manipulating acetic acid and acetic anhydride. Let the lab supervisors know if any is spilled.

Add and mix 12 cm^3 of pure acetic acid to 12 cm^3 of acetic anhydride (provided in an Erlenmeyer flask) and add 3.00 g glucose (acetic anhydride is in excess). Add with a Pasteur-pipette 5 drops of 30% $HClO_4$ dissolved in acetic acid. After the addition of the catalyst the solution might warm up considerably.

Let the mixture rest covered for 10 minutes and swirl it from time to time. Pour the reaction mixture into 100 cm^3 of water in a beaker. Scratch the wall of the beaker with a glass rod to initiate crystallization, and let it crystallize for 10 minutes. Filter and wash the product two times with 10 cm^3 of water using the syringe and the porous polypropylene filter disc.

Filtration using a plastic syringe



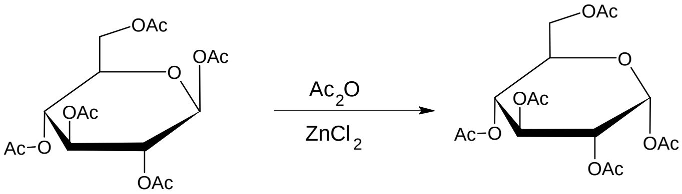
1. Pull out the piston. Fill the syringe from above with the suspension to be filtered. The syringe can be filled to the level of the hole. Replace piston.
2. Cover the hole with your finger and press in the piston as far as the hole.
3. Open the hole and draw the piston back. Do not draw in air through the filter.
4. Repeat steps 2-3 a few times to expel the liquid.
5. Repeat steps 1-4 until all solids are on the filter.
6. Press the piston against the filter cake and squeeze out the liquid.
7. Wash the product twice with 10 cm^3 of water repeating steps 1-4.
8. Press the piston against the filter cake and squeeze out the water.
9. Pull the piston out with the hole closed to lift out the filter cake. (Pushing with the end of the spatula can help.)

1.1 Place your product in the open Petri dish marked with your code. Leave it on your table. The organizers will dry it, weigh it and check it for purity.

1.2 Calculate the theoretical yield (mass) of your product in g. (M(C) = 12 g mol^{-1}, M(O) = 16 g mol^{-1}, M(H) = 1.0 g mol^{-1}

Synthesis of α-D-glucopyranose pentaacetate from β-D-glucopyranose pentaacetate

An alternative synthesis of α-D-glucopyranose pentaacetate starts from readily available β-D-glucopyranose pentaacetate. In this experiment we will study the kinetics of this reaction with thin layer chromatography.



Add 1.5 cm^3 acetic anhydride to 50 mg of anhydrous $ZnCl_2$ (preweighed in a test tube). Add 100 mg of pure β-D-glucopyranose pentaacetate (BPAG) and swirl until dissolved. Take three drops from this mixture into an Eppendorf tube, add 0.5 cm^3 methanol and save it.

Place the test tube in the heating apparatus under the hood closest to your desk. Place the test tube in the heating block preadjusted to 70ºC. Mix the contents of the test tube from time to time. During the reaction take three drops of sample from the mixture with a Pasteur pipet after 2, 5, 10, and 30 minutes. Mix immediately each sample with 0.5 cm^3 of methanol to stop the reaction in an Eppendorf tube.

Prepare a silica TLC plate with the collected samples to study the reaction kinetics. Apply the necessary reference compounds as well to help identification of the spots on the plate. Mark the spots with a pencil, and develop the plate in isobutyl acetate/ isoamyl acetate (1:1) eluent. Heat the plates with a heat-gun (under the hood!) to visualise the spots (the colour is stable). You can ask for a second plate without penalty points if needed for proper evaluation.

1.3 Copy your plate on the answer sheet and place your plate in the labelled zip lock bag.

1.4 Interpret your experiment and choose the correct answer.

The acetylation reaction of glucose is exothermic.

☐ a) Yes
☐ b) No
☐ c) Cannot be decided based on these experiments

The isomerisation reaction of β-D-glucopyranose pentaacetate can be used for the preparation of pure α-D-glucopyranose pentaacetate.

☐ a) Yes
☐ b) No
☐ c) Cannot be decided based on these experiments

SOLUTION

1.1 Yield of the product in g, measured by the organizer.

The samples are dried by the organisers. The typical yield is 70 %.

Purity is checked by solubility (acetone) and TLC. If there is no insoluble material and no impurity is detectable by TLC, the full points for the yield are received.

1.1 Calculation of the theoretical yield of the product in g:

$C_6H_{12}O_6 \rightarrow C_{16}H_{22}O_{11}$

$$m = \frac{3.00\ \text{g} \times 390\ \text{g mol}^{-1}}{180\ \text{g mol}^{-1}} = 6.50\ \text{g}$$

1.3 The developed TLC plate was expected to be sketched on the answer sheet.

Full points were given if both standards and all samples are present.

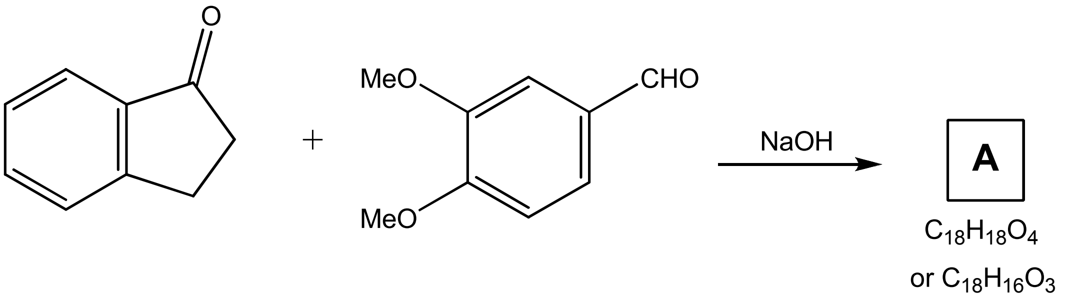
1.4 Solutions: a), a).

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

An Environmentally Friendly Aldol Condensation

In attempts to become more environmentally friendly, increasing attention is being paid to minimising the large amounts of solvents used in chemical reactions. In the following experiment, an aldol condensation reaction is carried out in the absence of solvent.



Chemicals

- 3,4-dimethoxybenzaldehyde, 0.50 g pre-weighed in vial,
- 1-indanone, 0.40 g pre-weighed in vial,
- NaOH, 0.10 g pre-weighed in vial,
- HCl, aqueous solution, c = 3.0 mol dm^{-3}, 10 cm^3 in a bottle,
- Diethyl ether : Heptane (1:1), 25 cm^3 in a bottle,
- Ethyl ethanoate, 1 cm^3 in a small vial,
- Sample of 1-indanone dissolved in ethyl ethanoate, 1.0 cm^3 in small vial,
- Sample of 3,4-dimethoxybenzaldehyde dissolved in ethyl ethanoate, 1.0 cm^3 in small vial,
- Ethyl alcohol (9:1 mixture with H_2O): 100 cm^3 in a bottle.

Procedure

(a) Add 3,4-dimethoxybenzaldehyde (DMBA 0.50 g, 3.0 mmol) and 1-indanone (0.40 g, 3.0 mmol) to a 25 cm^3 beaker. Use a metal spatula to scrape and crush the two solids together until they become a clear oil.

(b) Add NaOH (0.1 g, 2.5 mmol) to the reaction mixture, crush any lumps formed and continue scraping and crushing until the mixture becomes solid.

(c) Allow the mixture to stand for 20 minutes. Then add 4 cm^3 of aqueous HCl solution (c = 3 mol dm^{-3}) and scrape around the beaker so as to dislodge all product from the walls. Use a flat-ended glass rod to crush any lumps present.

1.1 Measure and record the pH of the solution.

(d) Isolate the crude product using vacuum filtration through a Hirsch funnel. Rinse out the beaker with 2 cm^3 of aqueous HCl solution (c = 3 mol dm^{-3}) and pour over the crude product in Hirsch funnel to wash, continuing to pull air through the solid for 10 minutes to facilitate drying.

1.2 Report the mass of the crude product (which may still be a little wet), using the vial labelled ‘CPA’ as a container.

(e) Take a TLC to assess whether the reaction is complete, using Et_2O : heptane (1 : 1) as the eluant. Solutions of both starting materials in ethyl ethanoate are provided. The crude product is soluble in ethyl ethanoate.

[Note: Three TLC plates are provided. You may use them all, but you must only submit *one* in your labelled Ziploc bag. This should be the plate that you draw in your answer booklet.]

1.3 Using UV light to visualize, draw around the spots on the plate in pencil to show where they are, copy your plate onto the answer sheet, and place your plate in the Ziploc bag labelled with your student code.

Determine and record the relevant R_F values.

(f) Using a 100 cm^3 conical flask with a stir bar in the bottom, recrystallize the product from a mixture of EtOH : H_2O (9 : 1). (N.B. A hot filtration, using the glass funnel provided, is required as part of this process to remove small amounts of insoluble impurities.) Any lumps may be crushed using the flat-ended glass rod. Allow the conical flask containing the filtered solution to cool to room temperature and then cool in an ice bath (use the polystyrene tray to make the ice bath in) for one hour before filtration through a Büchner funnel to collect your product. Suck air through for 10 minutes to dry the product. Place your product in the vial marked with your code and labelled 'RPA'.

1.4 Report the mass of the purified product.

Product **A** could have one of the two formulae: $C_{18}H_{18}O_4$ or $C_{18}H_{16}O_3$.

1.5 Draw the structure of every geometrical and/or stereoisomer with formula:

i) $C_{18}H_{18}O_4$,

ii) $C_{18}H_{16}O_3$

that could be formed in this reaction. Indicate how many peaks you would expect in total in the ^{13}C NMR spectrum of each.

1.6 The ^{13}C NMR spectrum for **A** is shown in the practical instructions. Peaks due to the solvent, $CDCl_3$, are marked with an asterisk. With the aid of the spectrum, decide which is the correct formula for **A**. Mark on the answer sheet one of the two boxes below to indicate which you have chosen:

$C_{18}H_{18}O_4$: ☐ $C_{18}H_{16}O_3$: ☐

1.7 Report the mass and calculate the percentage yield of the purified product, based on the formula you gave for its structure.

SOLUTION

1.1 Values of pH = 1 – 2 are accepted.

1.2 Because the sample is not completely dry, often this mass is above 100 % of that expected. Usual range is 800 – 1000 mg (94 – 117 %). Zero points for any less than 400 mg (product has been lost).

1.3 Evaluation:

Maximum points if both standards plus crude product are present and no starting materials remain and student has co-spotted crude product with one or both starting materials and solvent front is marked and plate is not over- or under-loaded.

Minus points if:

- plate has no co-spots,
- substantial amount of either or both starting materials remain,
- over- or under-loading occurs which does not interfere with evaluation,
- over- or under-loading occurs and does interfere with evaluation,
- over- or under-loading occurs and prevents evaluation,
- any sample is missing.

The relevant R_F values:

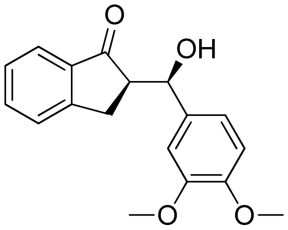
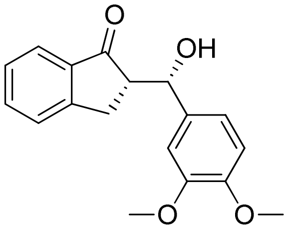
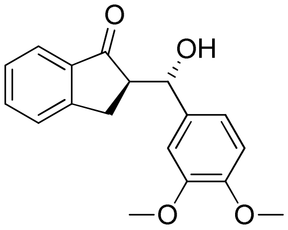
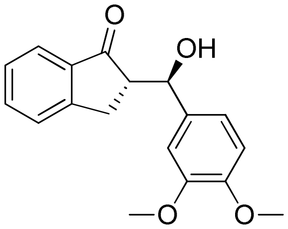
Chemical	R_F
3,4-DMBA	0.16 – 0.25
1-Indanone	0.34 – 0.43
CPA	0.11 – 0.20

Maximum points if both starting materials and reaction product are present with R_f values which fall within those given.

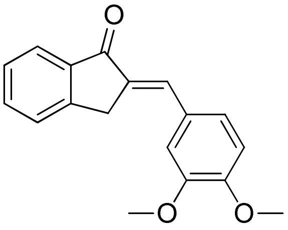
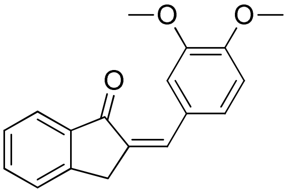
Minus points if:

- R_F values are missing for one or more chemicals,
- both starting materials and reaction product are present with R_F values which fall outside those given due to the plate running too long or the student having marked the solvent front incorrectly,
- both starting materials and reaction product are present with R_F values which fall outside those given, due to an inability to calculate R_F values.

1.4 For $C_{18}H_{18}O_4$:

Structure	Number of ^{13}C NMR signals expected:
	18
	18
	18
	18

For $C_{18}H_{16}O_3$:

Structure	Number of ^{13}C NMR signals expected:
	18
	18

1.5 $C_{18}H_{16}O_3$: ☑

1.6 Mass: 0.5 g (example mass of product)

Calculation:

For formula $\mathbf{C_{18}H_{18}O_4}$: Molar mass = 298.324 g mol^{-1}

Expect: 0.3 mmol maximum = 0.895 g

$$\frac{0.5\ \text{g}}{0.895\ \text{g}} \times 100 = 56\ \%$$

For formula $\mathbf{C_{18}H_{16}O_3}$: Molar mass = 280.308 g mol^{-1}

Expect: 0.3 mmol maximum = 0.841 g

$$\frac{0.5\ \text{g}}{0.841\,\text{g}} \times 100 = 59.5\ \%$$

YIELD:

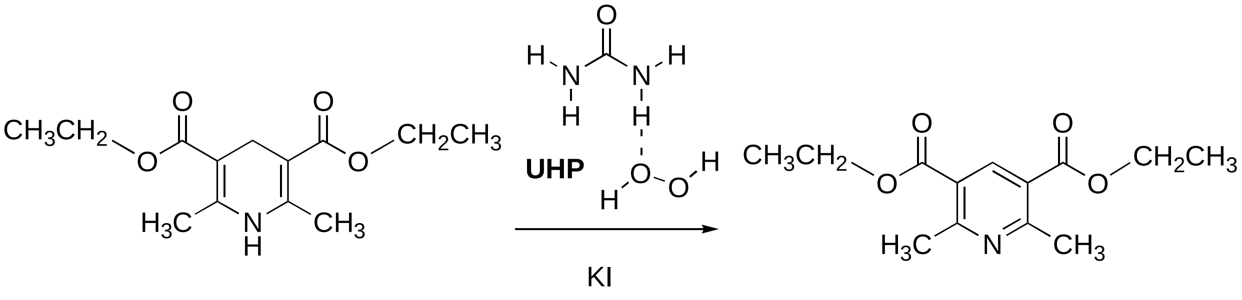
The samples were also weighed by the organizer, before and after drying for one hour in a vacuum desiccator. Sample purity was then checked by ^{1}H and ^{13}C NMR. The evaluations of the results were adapted to the results obtained by the above measurements.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Reaction of Hantzsch Ester with Urea Hydrogen Peroxide

In this experiment, you are required to synthesize a pyridinedicarboxylate derivative from 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylic acid diethyl ester (1,4-DHP or Hantzsch ester) by oxidation with urea hydrogen peroxide (UHP), an environmentally-friendly oxidant.



1,4-DHP

Chemicals

- Hydrochloric acid, c = 0.5 mol dm^{-3}, 50 cm^3
- 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylic acid diethyl ester, $C_{13}H_{19}NO_4$; (1,4-DHP), powder, 1 g
- 1,4-DHP for TLC, 3 mg
- Ethanol, C_2H_5OH, 10 cm^3
- Ethyl acetate, $CH_3COOC_2H_5$, 25 cm^3
- Heptane, C_7H_{16}, 20 cm^3
- Potassium iodide, KI, 150 mg
- Sodium metabisulfite, $Na_2S_2O_5$, 1 g
- Sodium hydrogen carbonate, saturated aqueous solution, 25 cm^3
- Urea hydrogen peroxide, $CH_4N_2O\bullet H_2O_2$, (UHP), 1 g

Procedures

(1) Place a 22 mm magnetic stirring bar in a 100 cm^3 test tube. Fix the test tube on a magnetic stirrer using a clamp. Add 1,4-DHP (1 g) (labelled as 1,4-DHP powder), and

potassium iodide (150 mg) to the test tube, followed by ethanol (5 cm^3), with a 5 cm^3 graduated pipette.

(2) Add 1 g UHP (wear gloves) and stir the mixture. (Caution: this reaction is exothermic.)

(3) For thin layer chromatography (TLC) analysis, prepare a mixture of ethyl acetate and heptane (1 : 2 in volume) using a measuring glass and place an appropriate amount of the mixture in a TLC developing chamber. Add 1 cm^3 of ethyl acetate to the vial (labelled as 1,4-DHP TLC) to dissolve 1,4-DHP (3 mg).

(4) Check your TLC plates before using. If they are damaged, they can be replaced without penalty. Draw a start line on the lower portion of a TLC plate with a pencil (see Fig. 1.1).

(5) During the reaction, the reaction mixture becomes clear (usually within 20 min). When the reaction mixture becomes clear (the precipitates may form when it cools, but precipitates will not affect the TLC analysis), take a small portion of the mixture using a glass capillary and load it to make two spots in the centre and right positions on the TLC plate. Load an appropriate amount of the 1,4-DHP solution prepared in procedure (3) in the centre and left positions, so that there are three spots on the plate, with the centre spot containing both the reaction mixture and 1,4-DHP (see Fig. 1.1). Develop the TLC plate in the TLC chamber (see Figs. 1.1 and 1.2). Mark the solvent front with the pencil. Visualize the spots using a UV lamp (254 nm) and draw a line around the UV-active spots on the TLC clearly with the pencil. Assess the completion of the reaction based on the TLC results. Repeat the TLC analysis after ten minutes, if you find significant amounts of 1,4-DHP in the reaction mixture. [Note that you will perform TLC analysis again in procedure (8).] Place the last TLC plate in a zipper storage bag marked “A.”

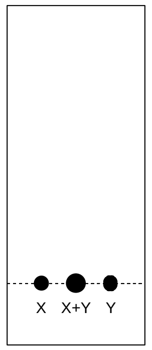


Fig. 1.1 Spots on the TLC plate before development;
X: 1,4-DHP, Y: Reaction mixture.

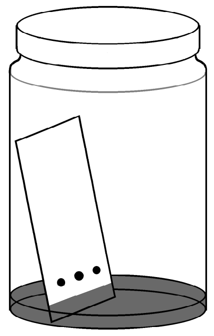


Fig. 1.2 TLC plate placed in the TLC developing chamber.

(6) Set up the suction filtration equipment (see Fig. 1.3). Connect the suction flask to the diaphragm vacuum pump. Place a Büchner funnel fitted with a rubber adapter onto the suction flask. Place a glass microfiber filter sheet on the funnel.

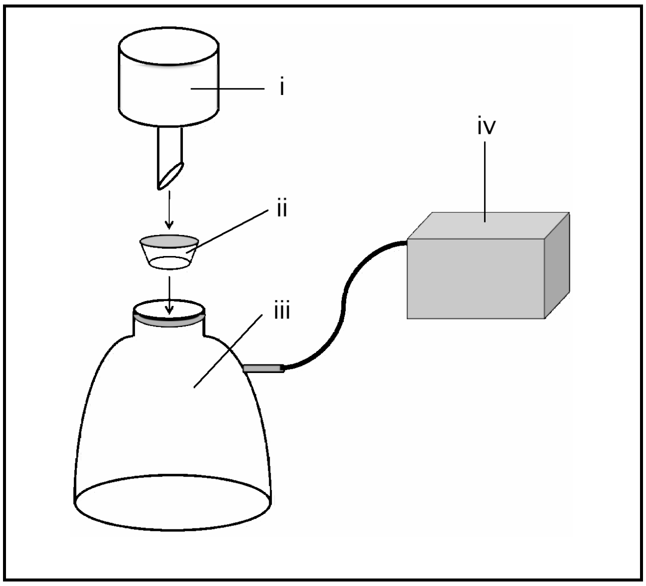


Fig. 1.3 Suction filtration equipment:
i - Büchner funnel; ii - rubber adopter;
iii - suction flask; iv - diaphragm vacuum pump.

(7) Add water (5 cm^3) to the reaction mixture using a 10 cm^3 plastic graduated cylinder. Add sodium metabisulfite (1 g), transfer the contents of the tube (including the stirring bar) into a 200 cm^3 conical beaker and wash the test tube with water (30 cm^3). Place the 200 cm^3 conical beaker on the magnetic stirrer and stir the solution. Add saturated sodium hydrogen carbonate solution in small portions using a 2 cm^3 graduated pipette until the pH of the aqueous phase becomes just over 7 (check the pH with pH test paper). Filter the precipitate formed through the Büchner funnel with suction using the diaphragm vacuum pump, and wash the precipitate with a small portion of water. Suck air through the precipitates for a minute to dry the product.

(8) Transfer the filtrate from the suction flask to a 300 cm^3 conical beaker. Transfer the filtrate (2 cm^3) to a 10 cm^3 test tube using a 2 cm^3 graduated pipette. Place a 10 mm magnetic stirring bar in the test tube and fix it securely with the clamp. Add 1 cm^3 of ethyl acetate to the test tube using a 2 cm^3 graduated pipette and stir the solution vigorously for 30 seconds on the magnetic stirrer. Stop stirring and wait for the solution to separate into two layers. Analyze the upper layer by TLC to see if there is any product remaining in the filtrates. Spot the filtrates on the plate in the same way as procedure (5). Mark the solvent front and the spot(s), if any. Place the TLC plate in a zipper storage bag marked “B.” If you detect the product on the TLC plate, add more saturated sodium hydrogen carbonate solution.

(9) At this stage, if you find a precipitate formed, filter and wash it. If you find no precipitate, skip this filtration process.

(10) Suck air through the precipitate for 10 minutes to dry the product. Place your product and the glass microfiber filter sheet in the crystallization dish. Cover the dish with the lid marked with your code. Avoid placing the stirring bar in the dish. Place the crystallization dish with the lid in a zipper storage bag marked "C."

1.1 Copy (sketch) the TLC plate in bag "A" on your answer sheet.

1.2 Determine and record the R_f values (to the 2nd decimal place) of the spots on the TLC plate in bag "A."

1.3 Draw the structural formula of the organic cation before adding sodium hydrogen carbonate.

1.4 What is (are) the final product(s) derived from UHP? Give the chemical formula(e) of the product(s).

1.5 Submit the following:

i) TLC plate in bag "A".

ii) TLC plate in bag "B".

iii) Your product and filter paper in the crystallization dish placed in bag "C".

SOLUTION

1.1 Indication of the solvent front line and the base line is expected.

Some points will be subtracted if:

i) there are less than three spots loaded on the base line,

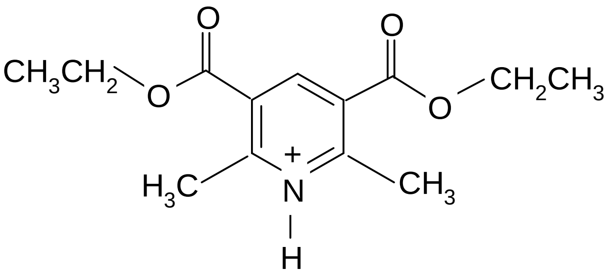
ii) the spots are not separated on the TLC after development,

iii) the solvent front line and/or the base line is missing.

1.2

Spot	R_f value
1,4-DHP	0.32 – 0.42
Product	0.61 – 0.71

1.3



1.4 H_2O and CH_4N_2O

1.5 The following rules for evaluation of the practical results in this problem were suggested by the organizer and approved by the International Jury:

Evaluation of the TLC plates.

Points will be subtracted:

- if the outline to be drawn with a pencil around the UV-active spots, is unclear or missing,
- if the solvent front line and/or base line is missing.

Evaluation of the product and filter paper in the crystallization dish (in bag "C").

i) A technician should weigh the product and calculate the percent yield after drying at 60 °C.

ii) In most cases the sample is pure and dissolved in $CDCl_3$ completely. The special calculation based on the percent yields and an approved graph is applied only if no 1,4-DHP or by-products are observed in the ^{1}H NMR spectrum and the product is completely soluble in $CDCl_3$.

iii) If there are peaks of 1,4-DHP (ca δ 2.19 ppm) and the corresponding pyridine product (ca δ 2.85 ppm) in the ^{1}H NMR spectrum and the percent yield is 100 % or less, the actual percent yield is calculated by an equation proposed by the organizer and approved by the International Jury.

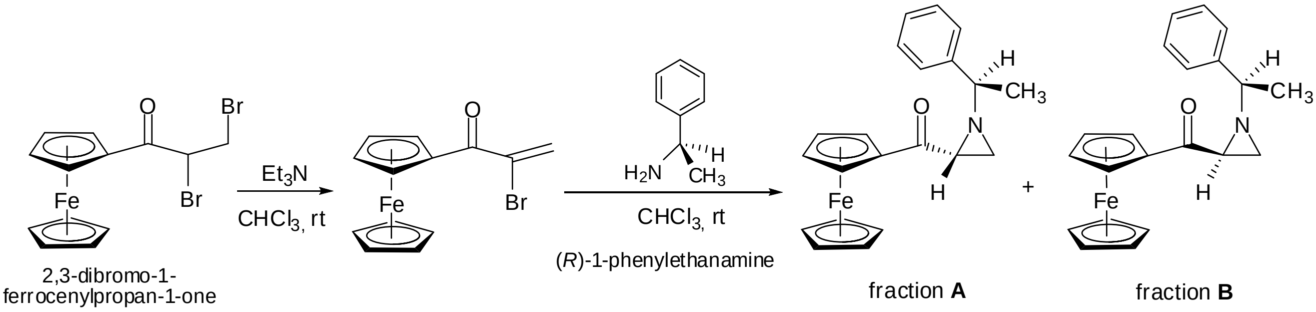
iv) Some points subtraction is suggested:

- if insoluble material remains after the addition of $CHCl_3$ for ^{1}H NMR measurements,
- if by-products are detected evidently in the ^{1}H NMR spectrum.

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.



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.

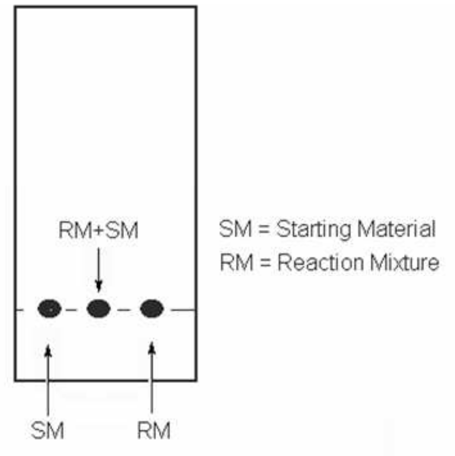


Figure 3.1. TLC plate

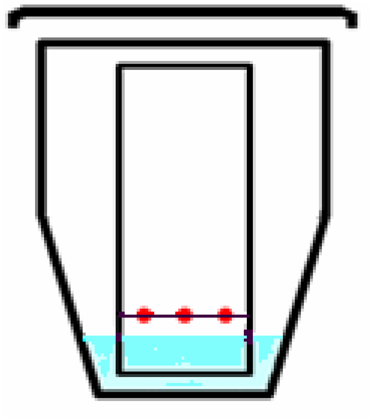


Fig. 3.2 TLC plate placed in the TLC developing chamber.

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.

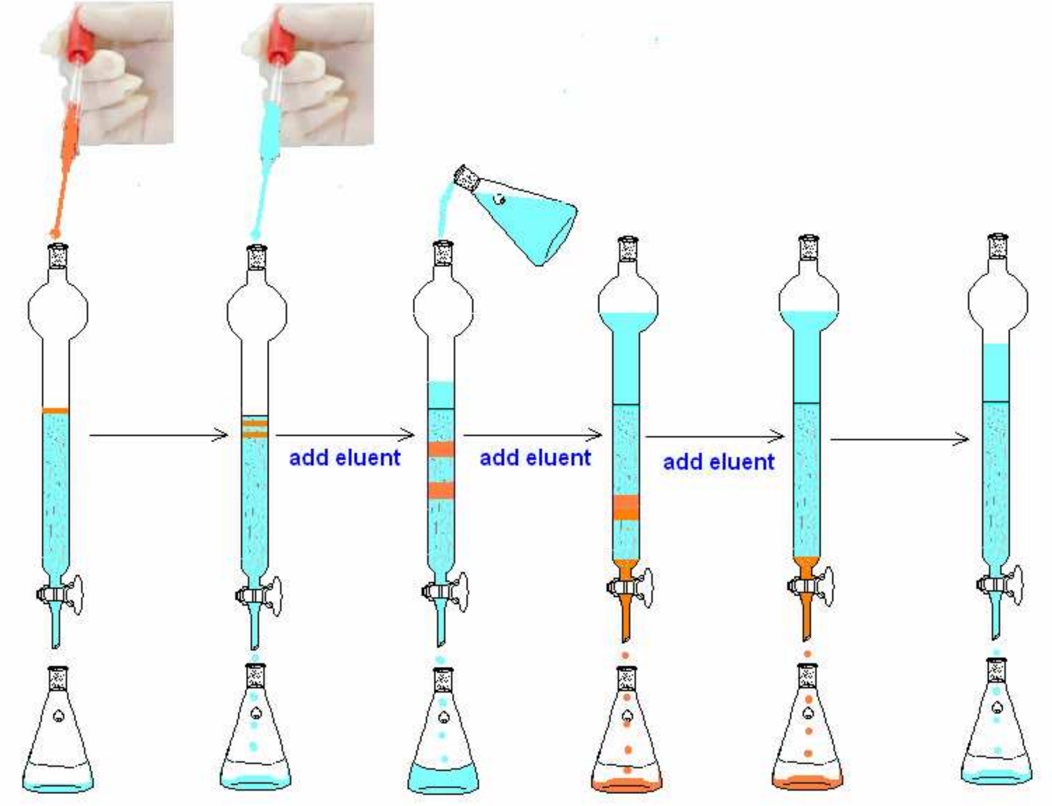


Figure 3.3. Flash Column Chromatography

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.

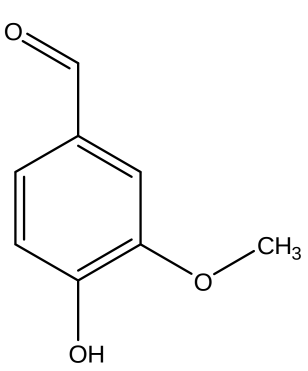
PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis of 2,4-dinitrophenylhydrazones

Hydrazones belong to the class of *imines*, which contain a nitrogen-nitrogen single bond adjacent to a carbon-nitrogen double bond. Hydrazones are formed when NH_2-containing hydrazine reacts with aldehydes or ketones under appropriate conditions. Because the hydrazone derivatives of the carbonyl compounds are often stable, crystalline, highly coloured solids, they are used to confirm the identity of aldehydes and ketones.

In this task you will have to identify two substituted benzaldehydes (shown below) by studying the products of their reactions with 2,4-dinitrophenylhydrazine.



Reagents

- 2,4-Dinitrophenylhydrazine
- Sulfuric acid, concentrated
- Aldehyde solution, 1 mmol in ethanol
- Ethanol
- NaOH solution
- Acetone

Procedure

Equip one 50 cm^3 beaker with a magnetic bar. Fix the beaker on the stirrer using the metal ring attached to the stand. Place the content of vial (200 mg of 2,4-dinitrophenylhydrazine) into the beaker and start stirring carefully. Only in the presence of your lab assistant, carefully pour one sample of concentrated sulfuric acid (1 cm^3) onto the solid. Using pipettes add 1.6 cm^3 of water and 4 cm^3 of ethanol to the reaction mixture. Then using a pipette add dropwise the content of the aldehyde solution bottle (either "aldehyde 1" or "aldehyde 2", each contains 1.00 mmol of the aldehyde). Bright precipitate starts forming at once. Continue stirring for 10 min, then add 10 cm^3 of water and stir for another 3 min.

Separation and purification of the product

Using scissors carefully cut out a filter paper circle, *ca.* 1 cm bigger in diameter than that of the glass filter. Wet the filter circle with water, and carefully put it on the filtering surface. The paper filter should fit evenly and tightly. If you fail to cut out an even circle, take a new filter from the table of common use and repeat cutting out. Assemble apparatus. Remove the stirring bar from the beaker using the spatula and transfer the reaction product onto the filter. Turn on the water-jet pump and filter out the precipitate. Put a little amount of water in the beaker and transfer the leftover product onto the filter. Wash the solid on the filter with water until the pH of the drops coming out the funnel are neutral. Then wash the solid twice with ethanol using no more than 3 cm^3 each time. (Note: Hydrazone is slightly soluble in ethanol.)

Dry out the solid on the filter with working water-jet pump, loosening and squeezing the product with a glass rod from time to time. After ca*.* 20 - 30 min transfer carefully the dried powder into the self-made filter paper box for the final drying in the air. Put the box with the product in a safe place (e.g. on the shelf). Turn off the water-jet pump when you do not use it!

As soon as your products seem dry, we advise you weigh them to avoid queuing at the balances. To collect the products, use the plastic tubes with your student code. Fill in the answer box below.

Note: The products you synthesized will be further re-examined by lab staff.

Repeat the above procedures with the other aldehyde.

Plastic tube **1**	Plastic tube **2**
Mass of empty tube __________ mg Mass of tube with product______ mg Mass of product __________ mg	Mass of empty tube _________ mg Mass of tube with product ______ mg Mass of product _________ mg

Tasks:

1.1 Write down the structures of 2,4-dinitrophenylhydrazine and both products.

1.2 What kind of stereoisomerism (if any) is possible for these hydrazones? Tick the appropriate box.

☐ R/S ☐ E/Z ☐ threo/erythro ☐ manno/gluco ☐ D/L

1.3 What is the role of sulfuric acid in 2,4-dinitrophenylhydrazone formation? Tick the appropriate box.

☐ stoichiometric reagent ☐ catalyst ☐ reducing agent ☐ oxidizing agent

1.4 How would the rate of the reaction change, if the synthesis is carried out in neutral medium? Tick the appropriate box.

☐ highly increase ☐ slightly increase
☐ no change ☐ the reaction would proceed very slow

1.5 How would the rate of the reaction change, if it is carried out in alkaline medium? Tick the appropriate box.

☐ highly increase ☐ slightly increase
☐ no change ☐ the reaction would not proceed

Characterization

Place small amount ("on the tip of a spatula") of each product in an individual 25 cm^3 beaker. Add 10 cm^3 of acetone to each beaker. The best results will be obtained if the colours and their intensities in each beaker are similarly yellow. Pour 5 cm^3 of $NaHCO_3$ solution into each beaker. Stir the resulting mixtures with the glass rod using different ends.

1.6 Record your observations of the solutions colour change. Tick the appropriate box.

☐ The colour does not change in either beaker.

☐ The colour changes significantly in both beakers.

☐ The colour changes significantly only in one beaker.

Add 2 cm^3 of NaOH solution to each of the resultant mixtures from the question **1.6**. Stir the reaction mixtures with the glass rod.

1.7 Record your observations of the solutions colour change in the box.

☐ The colour does not change in either beaker.

☐ The colour changes significantly in both beakers.

☐ The colour changes significantly only in one beaker.

1.8 What structural features of your products explain the colour change in the reaction with $NaHCO_3$? Tick the appropriate box.

☐ the presence of MeO group at position 4 in the benzene ring;

☐ the presence of MeO group at position 3 in the benzene ring;

☐ the presence of the OH group at position 4 in the benzene ring;

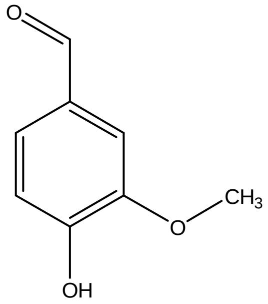
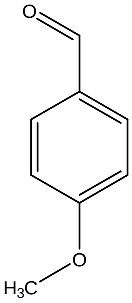
☐ the presence of both MeO and OH groups.

1.9 Which of the listed processes is responsible for the colour change observed in the reaction of 2,4-dinitrophenylhydrazones with aqueous NaOH? Tick the appropriate box.

☐ alkaline hydrolysis ☐ dehydration ☐ hydration

☐ deprotonation ☐ dehydrogenation

1.10 Draw the structures of the main organic species present in each test reaction medium in the answer boxes below.

Initial aldehyde:	Initial aldehyde:
	

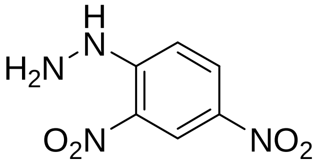
$NaHCO_3$	$NaHCO_3$
NaOH	NaOH

1.11 Put the numbers **1** or **2** under each structure. Calculate the percent yields of both hydrazones

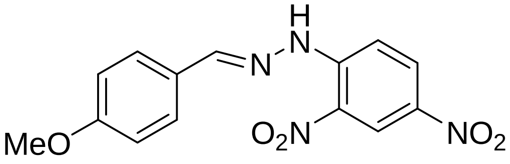
---

SOLUTION

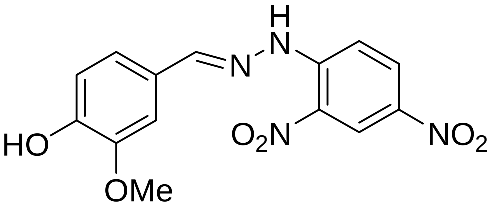
1.1 2,4-dinitrophenylhydrazine



Product 1:



Product 2:



1.2 ☑ E/Z

1.3 ☑ catalyst

1.4 ☑ the reaction would proceed very slow

1.5 ☑ the reaction would not proceed

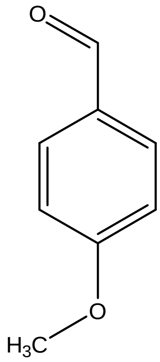
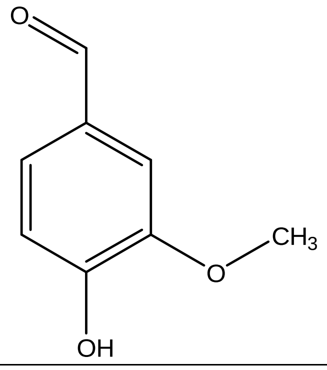
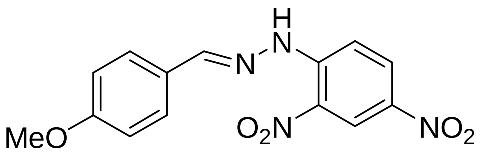
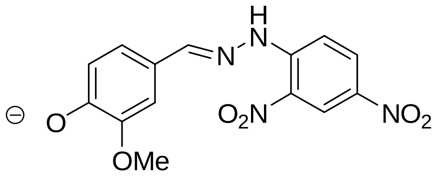
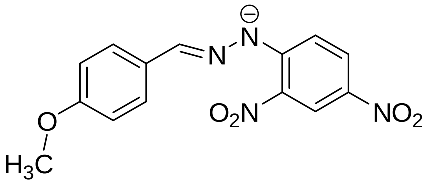
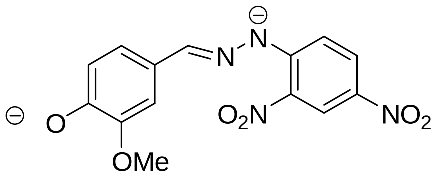
1.6 ☑ The colour changes significantly only in one beaker.

1.7 ☑ The colour changes significantly in both beakers.

1.8 ☑ the presence of the OH group at position 4 in the benzene ring;

1.9 ☑ deprotonation

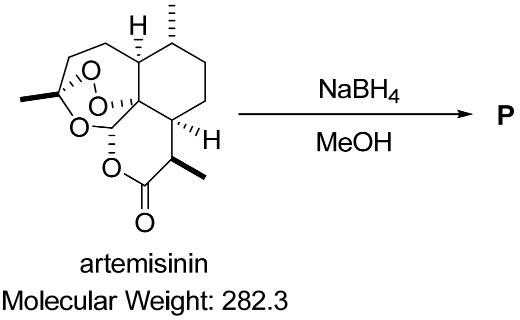
1.10

Initial aldehyde: 	Initial aldehyde: 
Product 1 in $NaHCO_3$ 	Product 2 in $NaHCO_3$ 
Product 1 in NaOH 	Product 2 in NaOH 

Practical Problem 2 13 % of the total	Code:		Task	1	2	3	4	5	Total
	Examiner		Mark	35	15	20	4	2	**76**
			Grade						

Practical Problem 2. Synthesis of a derivative of Artemisinin

Artemisinin (also known as Quinghaosu) is an antimalarial drug isolated from the yellow flower herb *Artemisia annua* L., in Vietnam. This drug is highly efficacious against the chloroquine-resistant *Plasmodium falciparum*. However, artemisinin has a poor solubility in both oil and water so that one needs to prepare its new derivatives to improve the applicability of this drug. The reduction of artemisinin is an attractive method to synthesize new derivatives of artemisinin as shown in Scheme 1.



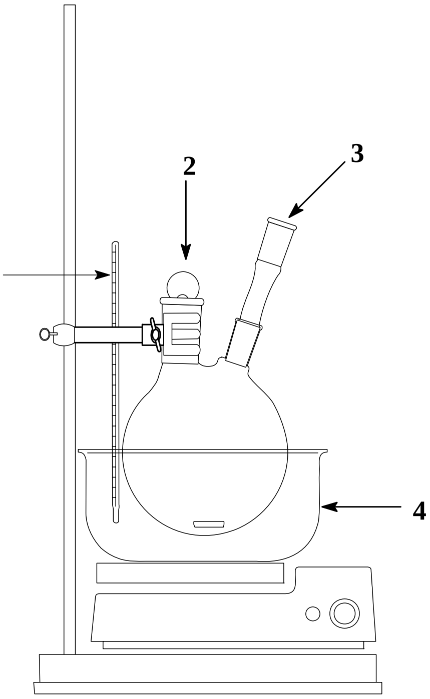
Scheme 1

In this practical exam you are going to reduce artemisinin to product **P** and check its purity using Thin-Layer Chromatography (TLC).

Experimental Set-up

- The experimental set-up is shown in Figure 2.1.

- By moving the finger clamp, you can adjust the position of the two-neck round-bottom flask.



1: Digital thermometer; 2: Plastic Stopper; 3: $CaCl_2$ drying tube; 4: Ice Bath

Figure 2.1. Reaction system for Problem 2

Procedure

Step 1. Synthesis of a Derivative of Artemisinin

1. Prepare an ice bath with a temperature between –20 and –15 °C by mixing ice and sodium chloride in the plastic pot (approximate ratio of NaCl : crushed ice = 1 scoop : 3 scoops). Use the digital thermometer to monitor the temperature. Place the bath on the magnetic stirrer. Put a layer of three tissues between the bath and the stirrer.
2. Connect the $CaCl_2$ drying tube to the small neck of the round-bottom flask and close the other neck with the plastic stopper.
3. Place a magnetic stirring bar into the dry round-bottom flask and set up the reaction system onto the clamp-stand so that the system is immersed in the ice bath. Monitor the temperature using the digital thermometer.
4. *Setting aside a tiny amount (ca. 2 mg) of artemisinin for TLC analysis*, open the stopper and add the 1 gram of artemisinin through the bigger neck.
5. Use the glass funnel to add 15 mL of methanol (measured using the 50-mL graduated cylinder). Close the stopper and turn on the magnetic stirrer. (*Set the magnetic stirrer to* <u>*level 4*</u>). Start the stopwatch to keep track of the time.
6. After *ca.* 5 min stirring, open the stopper and add carefully 0.53 g of $NaBH_4$ in small portions over 15 min using a spatula. Close the stopper in between addition. *(Caution: Adding $NaBH_4$ rapidly causes side-reactions and overflowing).* Keep stirring for 50 min. Maintain the temperature of the ice bath below –5 °C; remove

some of the liquid and add more NaCl-crushed ice mixture if necessary. Cool the vial containing the 1 mL of acetic acid in the ice bath.

During this waiting time, you are advised to finish calculations from Problem 1, answer the questions below, and prepare further experimental steps.

7. Prepare 50 mL of ice-cold distilled water *(cooled in the ice bath)* in the 100 mL-conical flask. Measure *ca.* 20-22 mL *n*-hexane in the 50 mL measuring cylinder and cool it in the ice bath. After the reaction is complete, keep the reaction flask in the ice bath below 0 °C. Remove the $CaCl_2$ tube, open the stopper, and add gradually *ca.* 0.5 mL of the cold acetic acid from the vial into the reaction flask until the pH is between 6 and 7. (Use the glass rod to spot the reaction mixture on to the pH paper.) With stirring, slowly add the 50 mL of ice cold water over 2 min. A white solid precipitates in the reaction flask.
8. Assemble the vacuum filtration apparatus. Put a filter paper onto the Büchner funnel, wet the filter paper with distilled water and open the vacuum valve. Transfer the reaction mixture on to the filter, and remove the stirring bar from the reaction flask using the spatula. Wash the product three times with portions of 10 mL ice-cold water *(cooled in the ice bath).* Wash the product two times with portions of 10 mL ice-cold *n*-hexane *(cooled in the ice bath).* Continue to use the pump to dry the solid on the filter. After *ca.* 5 min, carefully transfer the dried powder on to the watch glass labeled with your code and put into the labeled Petri dish. **Turn off the vacuum valve when you do not use it!** *Note: Your sample will be collected, dried and weighed later by the lab assistant.*

Task 2.1 – the recording of your yield –will be performed after the exam by the lab assistants.

Step 2. TLC Analysis of the product

1. Check your TLC plate before use. Unused damaged plates will be replaced upon request without penalty. Use the pencil to draw the start front line, and the line where the solvent front will be run to **exactly as shown in Figure 2.2**. Write your student code on the top of the TLC plate in pencil.

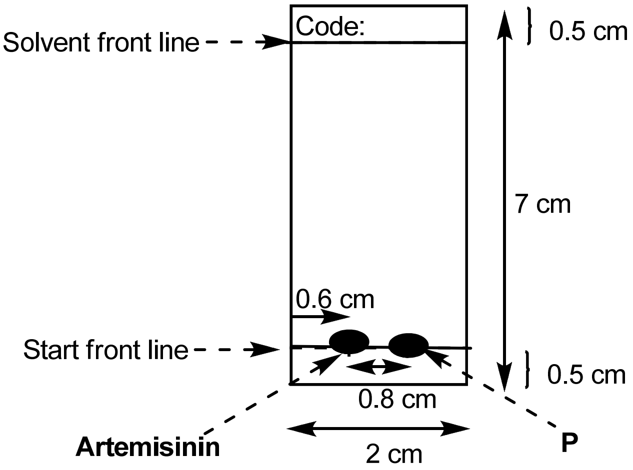


Figure 2.2. Instruction of TLC plate preparation

2. Dissolve *ca.* 1 mg of artemisinin *(a spatula tip)* in *ca.* 0.5 mL of methanol in the labeled very small test tube (use the labeled 5 mL graduated pipette). Dissolve *ca.* 1 mg of the product in *ca.* 1 mL of methanol in the labeled test tube.
3. Spot the artemisinin solution and the product solution on the TLC plate using two different glass capillary spotters so the finished plate is as shown in Figure 2.2.
4. Prepare the TLC developing chamber. Use the 5 mL graduated cylinder to make 5 mL of a mixture of *n*-hexane/ethyl acetate (7/3, v/v) as the solvent system. Pour the mixture of *n*-hexane/ethyl acetate into the chamber *(Note: The solvent level should not reach the spots on the plate if prepared as shown).* Cover and swirl the chamber and allow it to stand for 2 min.

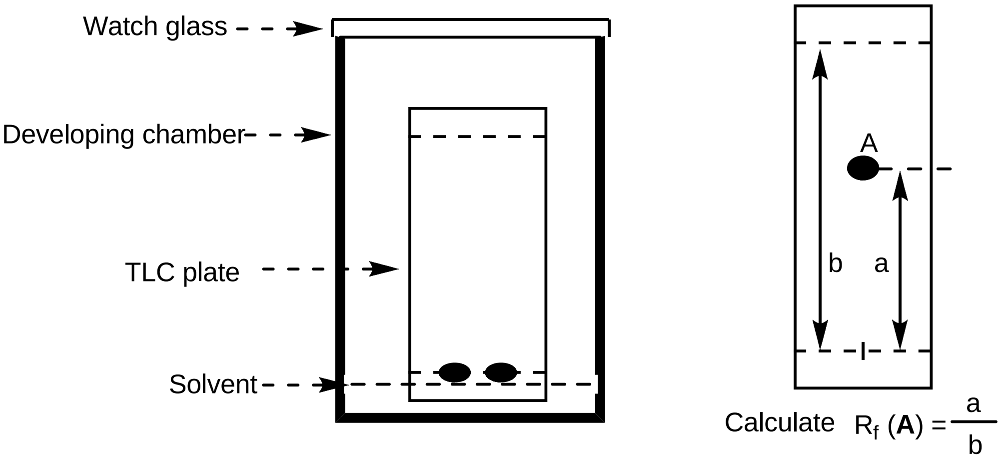


Figure 2.3. A TLC plate placed in the TLC developing chamber and instruction for R_f calculation of compound **A**

5. Insert the TLC plate upright into the TLC developing chamber. Wait until the solvent system reaches the pre-drawn solvent front line. (*Note: You are advised to work on some question below while you wait for the TLC to run.*)
6. When the solvent front reaches the line, remove the TLC plate using the tweezers and then dry the solvent using the hair dryer set at level 1.
7. Dip the piece of cotton wool into the cerium staining reagent, *taking care not to let the tweezers come into contact with the solution since the metal stains the plate*. Carefully apply the stain to the whole TLC plate.
8. Heat the TLC plate using the hair dryer set at level 2 (***Attention: Do NOT set the hair dryer to COLD***) until the blue spots of artemisinin and the product appear on the TLC plate.
9. Ask the lab assistant to take a photo of your final TLC plate together with your student code.
10. Circle all the visualized spots and calculate the R_f values of both artemisinin and the product (*See instruction in Fig. 2.3*). Store your TLC plate in the Petri dish.

***Task 2.2*: Fill the values of R_f in Table below.**

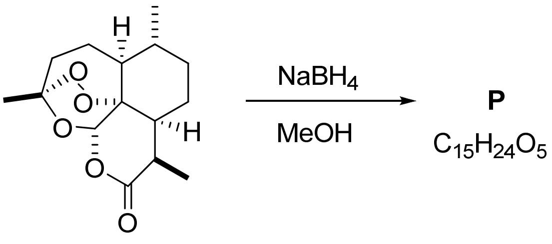
$R_{f,\ \mathrm{Artemisinin}}$	$R_{f,\ \mathrm{Product}}$	$R_{f\ Artemisinin}/R_{f\ Product}$
---------------------	-------------------------	-------------------------

***Task 2.3*: Check the *total number* of developed spots on the TLC plate:**

1 ☐ 2 ☐ 3 ☐ 4 ☐ 5 ☐

Step 3. Identifying the reaction product P

The reduction of artemisinin leads to the formation of two stereoisomers (**P**). Comparing the ^{1}H-NMR spectrum (in $CDCl_3$) of one of these isomers with the spectrum of artemisinin shows an extra signal at $\delta_H = 5.29$ ppm as a doublet, and also an extra signal as a broad singlet at $\delta_H = 2.82$ ppm.



artemisinin
$C_{15}H_{22}O_5$

***Task 2.4*: Suggest structure for P.** (*You do not need to draw the stereochemistry of the compounds*).

P

***Task 2.5*: P is mixture of two stereoisomers. What is their stereochemical relationship? Check the appropriate box below.**

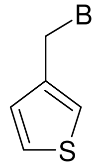
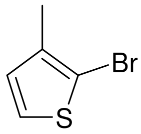
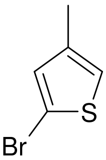
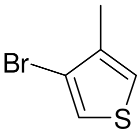
Z/E Isomers	Enantiomers	Diastereomers	Constitutional Isomers
☐	☐	☐	☐

TASK 1. Tuning bromination selectivity by catalysis (15 points).

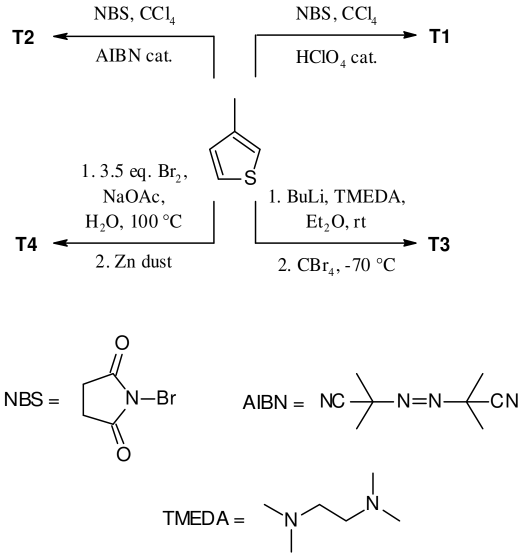
Quest. #	**Q1**	**Q2**	**Q3**	**Q4**	**Q5**	**Q6**	Total
Marks	2	39	4	2	1	2	50

Selectivity of chemical reactions is one of the most challenging problems of contemporary research. In many cases, reaction conditions and the catalysts applied are keys to achieving high selectivity of organic reactions. In this task, you will study one of such cases. 3-Methylthiophene can theoretically be transformed into four monobrominated derivatives **T1-T4**, which have been actually synthesized and characterized in detail. Structures of **T1-T4** and the values of refractive indexes are given in Table 1.

Table 1. Structures and refractive indexes of monobrominated thiophenes.

Designation	**A**	**B**	**T3**	**T4**
Structure				
n_D^{20}	1.5961	1.5706	1.5786	1.5795

The selective synthesis of each of **T1-T4** can be performed using 3-methylthiophene as the starting material. **T1** and **T2** can be obtained by direct bromination using different catalysts, whereas **T3** and **T4** are the products of "one pot" multistep synthesis (see Scheme 1).



Scheme 1. Selective synthesis of monobrominated thiophenes.

Q1. Assign the structures given in Scheme 1 with **T1, T2** to the structures given in the Table 1. Fill in the boxes below with one of A-B.

☐ T1 ☐ T2

In this task, you will:

- Synthesize a monobrominated thiophene derivative using one of the catalysts from the list below;
- Measure the product refractive index (n_D)
- Compare the results obtained with literature data and decide on the product structure and the catalysts given.

List of possible catalysts

- $HClO_4$ in CCl_4
- AIBN in CCl_4

PROCEDURE

Note!

- ***Apparatuses used in this task are shown in Fig. 1 and 2.***
- ***Always equip every joint with the Teflon sleeve. Immediately place every piece of the used glassware in the corresponding container. Always keep the container tightly closed.***
- ***You can use cotton gloves when handling hot things!***

Step 1. Clamp the three-necked flask on the laboratory stand on top of the hot-plate magnetic stirrer. (Fig.1). Apply the dropping funnel and the reflux condenser to the corresponding necks and put the big magnetic stir-bar into the flask through the open neck. Ask your lab assistant to switch on water supply in the reflux condenser (**Do not do it yourself!**). Transfer NBS quantitatively into the flask using spatula and big plastic funnel. Transfer ~15 mL of CCl_4 into the 25 mL glass beaker. Pour ~2/3 of the solvent volume from the beaker into the flask. Shake the Catalyst and quantitatively add it through the same plastic funnel into the flask. Add the rest of the solvent from the beaker to the flask. Close the open neck with the stopper. Put the flask into the ice bath filled with water and ice to ~ 2/3 of its volume. Start stirring the mixture.

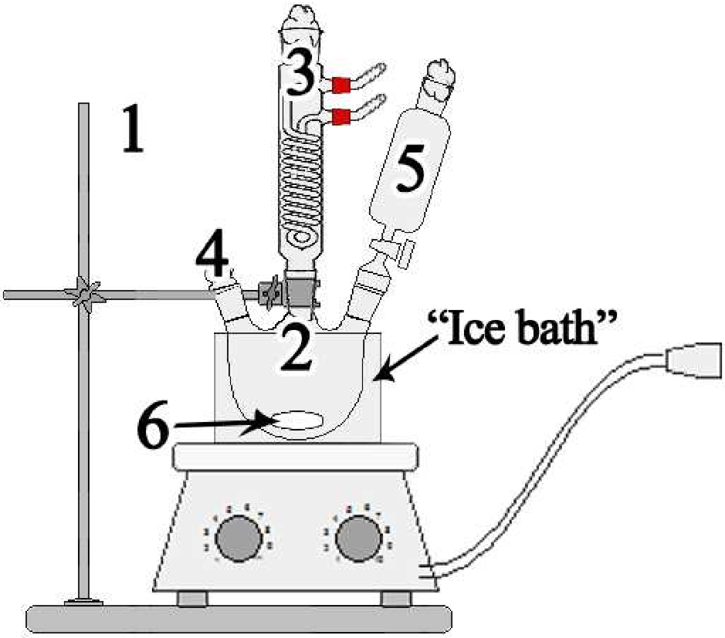


Fig. 1. Set up needed to implement Steps 1-4 of the synthesis. Refer to page 4-5 for the numbers

Step 2. Using the big plastic funnel quantitatively transfer the solution of 3-methylthiophene to the dropping funnel with **tap closed**. Apply a piece of the cotton wool to the open end of the dropping funnel and reflux condenser. Under vigorous stirring, add the solution of 3-methylthiophene dropwise during ~ 3 min. Replace the dropping funnel by a glass stopper. Use the Teflon sleeve. Remove the ice bath. Dry the plate and bottom of the flask with napkin.

Step 3. Wrap up the flask with aluminum foil. Switch on the heater (position 3). Bring up the mixture to boiling and boil it for 10 min. Prepare the ice bath (~2/3 of the volume) while the mixture boils.

Step 4. Switch off the heater and carefully **(hot!)** remove the hot-plate magnetic stirrer aside. Dip the flask equipped with the condenser and stoppers into the ice bath for 3-5 min. Keep gently swirling the flask from time to time to provide the faster cooling. Then remove the reflux condenser and load 0.02 g of K_2CO_3 using the big funnel applied to the open neck. Close the neck with a glass stopper and shake the flask several times. Turn off the water supply and unscrew the adaptors of the tubings from the reflux condenser. Let the residual water leak out of the condenser and immediately place it into the container for the used glassware. Remove the clamp keeping the flask in the ice bath.

Step 5. Weigh the 10 mL receiver flask for product with the glass stopper, both marked with your student code. Write down the value in the answer sheet. Put the small magnetic stir-bar in the 50 mL pear-shaped distillation flask. Screw on the adaptors with tubings to the Liebig condenser and fix it on the stand with the red clamp. Turn on the water supply yourself and make sure there is no water leakage.

Step 6. Assemble the distillation apparatus as shown on Fig. 2 supplying all the joints with the teflon sleeves and clips. First, attach two 10 mL and one 50 mL receiver flasks to the distilling receiver cow. Then connect the vacuum hose to the cow and complete assembling. Fix the apparatus over the magnetic stirrer to adjust it on height. Use the adjustable lab jack lift support.

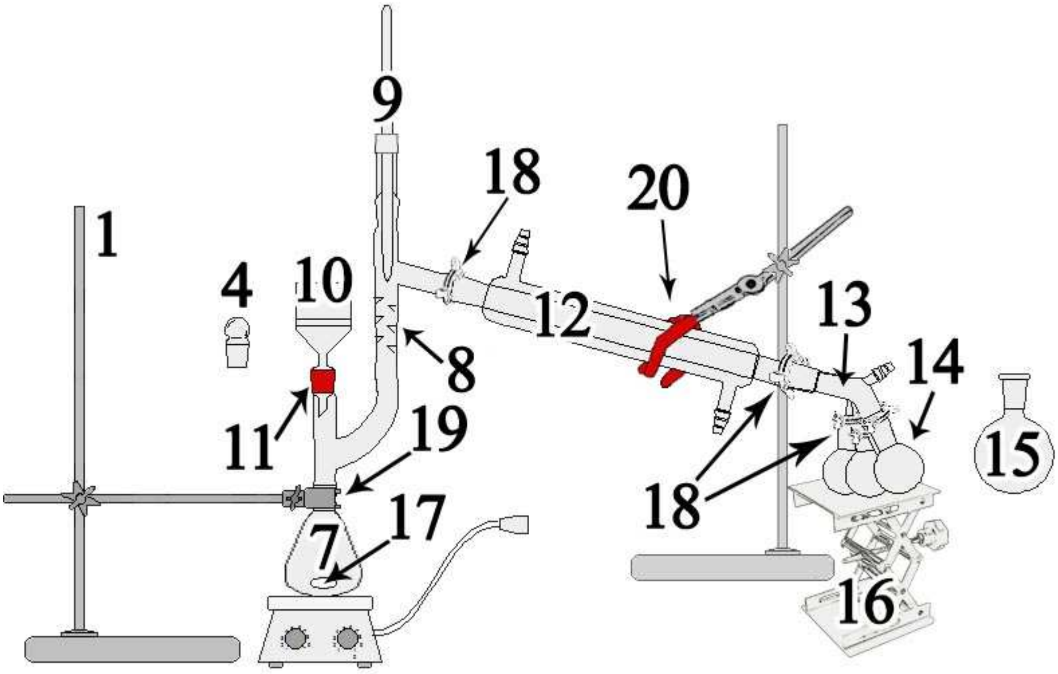


Fig. 2. Set up needed to implement Steps 5-10 of the synthesis. Refer to page 4-5 for the numbers

Step 7. Remove the hot-plate magnetic stirrer aside. Insert the fritted glass filter into the Claisen distillation adapter using the rubber spacer. Turn on the water-jet pump and switch on the digital manometer. Remove the three-necked flask from the ice bath and dry it with a napkin. Carefully transfer the reaction mixture from the three-necked flask to the filter (**Attention! If you do it too fast, the mixture can be partially sucked into the curved part of the adaptor**). When finished, turn off the pump and replace the filter with a glass stopper, use the teflon sleeve.

Step 8. Tightly wrap up the flask and distillation adaptor with aluminum foil up to the thermometer joint. Bring back the magnetic stirrer and turn on stirring and heating (position 6). **Do not turn on the water-jet pump!** Collect the distilled solvent into the 50 mL receiver. When the solvent distillation is over, turn off heating and stirring and carefully **(hot!)** remove the hot-plate magnetic stirrer aside. Replace the receiver flask containing the distilled solvent by a new 10 mL receiver. Close the 50 mL flask with a glass stopper and deliver it to your lab assistant.

Step 9. Remove the foil and put the pear-shaped bottom flask into the ice bath for 2-3 min to bring the temperature below ambient. Remove the ice bath; dry the flask with a napkin. Bring back the magnetic stirrer under the flask **(Attention! The hot-plate may be still hot!).** Turn on stirring. Wrap up the flask tightly with aluminum foil. Switch on the water-jet pump. When vacuum is stabilized (follow the reading of the digital manometer), turn on the heater (position 6). Observe the initial stage of the targeted product distillation and collect the first 3-5 drops into an attached receiver flask not labeled with your student code. Then rotate the cow and collect the targeted product into the receiver flask with your student code. Write down the product boiling point and pressure reading from the digital manometer into the answer sheet.

Step 10. When the targeted product is collected, turn off the heater, remove the foil and carefully **(hot!)** remove the hot-plate magnetic stirrer aside. Cool down the apparatus to ambient temperature using the ice bath. **Ask your lab assistant to disconnect the vacuum line.** Disconnect the receiver flask with the targeted product and **immediately** close it with the glass stopper labeled with your student code. Do not attempt to drag the teflon sleeve out if it remains in the receiver. Place the flask into the 50 mL plastic beaker labeled "For the receiver with the product". Immediately attach a new receiver instead of the removed one and apply the joint clip. **Leave the apparatus as it is.**

Step 11. Measure the refraction index **(before weighing)** following the instruction below. Record the temperature from the refractometer.

Weigh the receiver with the targeted product closed with the labeled stopper. Calculate the mass and yield of the product (take the mass of the teflon sleeve equal to 149 mg). The molar masses of 3-metylthiophene and the product equal 98 and 177 g mol^{-1}, respectively.

Q2. Write down all the result in the hereunder Table.

#	Parameter /Characteristics	Value	Units
1	Mass of the receiver flask with the glass stopper, both marked with student code		g
2	Mass of the product		g
3	Yield of the product		%
4	Refraction index for the product		-
5	Temperature recorded from the refractometer		°C
6	Boiling point of the product		°C
7	Pressure at the Boiling point		mmHg

Deliver the product to your lab assistant and get it signed.

The targeted product delivered: ____________________________

Student signature ___________________ Lab assistant signature ___________________________

REFRACTO 30GS – OPERATING INSTRUCTIONS

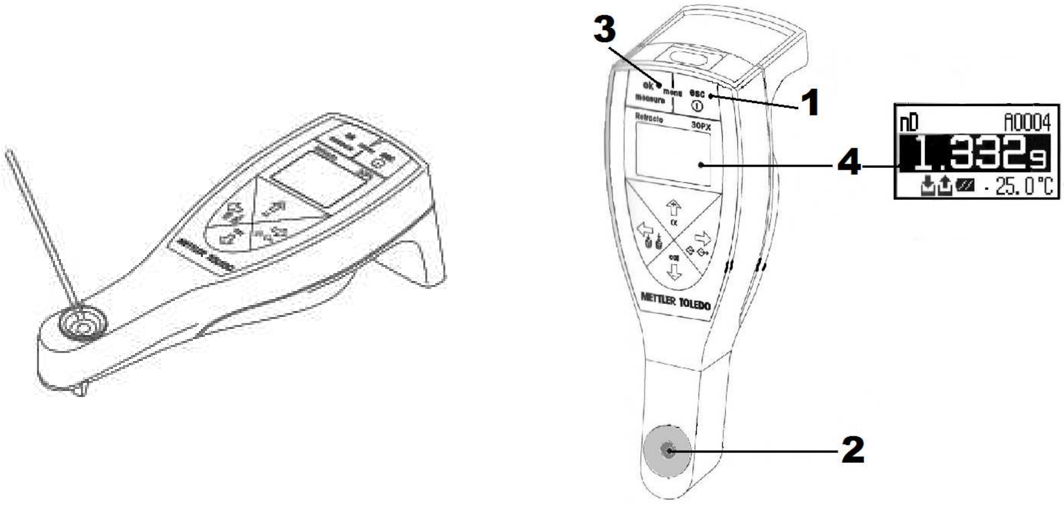


Fig. 3. Using the Refracto 30GS

1. To switch Refracto 30GS on, press and hold “ESC” button (1) until the display appears. The instrument is ready for operation. It switches off automatically if not operated for 10 min.
2. Clean the cell and glass rod with a napkin wetted with the solvent from the washing bottle labeled “cleaning solvent”. Dry both with another napkin.
3. Make sure the sample to be measured has reached ambient temperature and is homogeneous.
4. Apply 2-3 drops of the sample onto the measuring cell (2) using the glass rod.
5. To start the measurement press and hold the ok button (3) until the beep.
6. Take the value of the refraction index and the temperature from digital display (4) and write down the result in the answer sheet.
7. Clean up the cell and the glass rod.

Q3. By comparing the obtained and literature data, draw the structure of the product and catalyst given.

The Product obtained	**The Catalyst given**

Q4. Draw the structure of the 3-methylthiophene-based reactive intermediates behind the selectivity in the case of **T1** and **T2**.

T1	**T2**

Q5. Write down the product (**T1** or **T2**) formed as a result of direct bromination of 3-methylthiophene with NBS under the given conditions / catalyst used.

$ZnBr_2$	
Dibenzoyl peroxide	
LiBr in AcOH	
Visible light or UV light	

Q6. In the synthetic pathways to **T3** and **T4**, draw the structures of the compounds formed in the first steps of each pathways shown on Scheme 1.

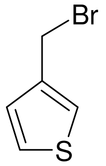
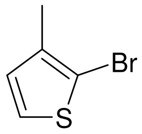
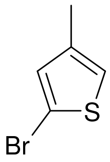
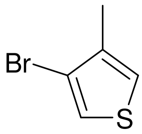
T3	**T4**

TASK 1. Tuning bromination selectivity by catalysis (15 points).

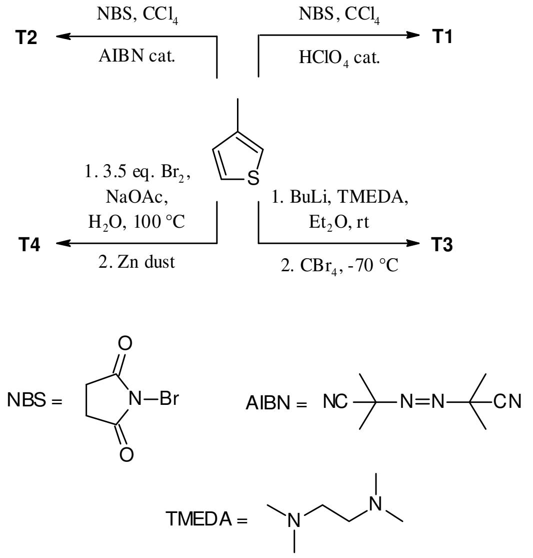
Quest. #	**Q1**	**Q2**	**Q3**	**Q4**	**Q5**	**Q6**	Total
Marks	2	39	4	2	1	2	50

Selectivity of chemical reactions is one of the most challenging problems of contemporary research. In many cases, reaction conditions and the catalysts applied are keys to achieving high selectivity of organic reactions. In this task, you will study one of such cases. 3-Methylthiophene can theoretically be transformed into four monobrominated derivatives **T1-T4**, which have been actually synthesized and characterized in detail. Structures of **T1-T4** and the values of refractive indexes are given in Table 1.

Table 1. Structures and refractive indexes of monobrominated thiophenes.

Designation	**A**	**B**	**T3**	**T4**
Structure				
n_D^{20}	1.5961	1.5706	1.5786	1.5795

The selective synthesis of each of **T1-T4** can be performed using 3-methylthiophene as the starting material. **T1** and **T2** can be obtained by direct bromination using different catalysts, whereas **T3** and **T4** are the products of "one pot" multistep synthesis (see Scheme 1).



Scheme 1. Selective synthesis of monobrominated thiophenes.

Q1. Assign the structures given in Scheme 1 with **T1, T2** to the structures given in the Table 1. Fill in the boxes below with one of A-B.

B	T1	A	T2

2 marks

In this task, you will:

- Synthesize a monobrominated thiophene derivative using one of the catalysts from the list below;
- Measure the product refractive index (n_D)
- Compare the results obtained with literature data and decide on the product structure and the catalysts given.

List of possible catalysts

- $HClO_4$ in CCl_4
- AIBN in CCl_4

PROCEDURE

Note!

- ***Apparatuses used in this task are shown in Fig. 1 and 2.***
- ***Always equip every joint with the Teflon sleeve. Immediately place every piece of the used glassware in the corresponding container. Always keep the container tightly closed.***
- ***You can use cotton gloves when handling hot things!***

Step 1. Clamp the three-necked flask on the laboratory stand on top of the hot-plate magnetic stirrer. (Fig.1). Apply the dropping funnel and the reflux condenser to the corresponding necks and put the big magnetic stir-bar into the flask through the open neck. Ask your lab assistant to switch on water supply in the reflux condenser (**Do not do it yourself!**). Transfer NBS quantitatively into the flask using spatula and big plastic funnel. Transfer ~15 mL of CCl_4 into the 25 mL glass beaker. Pour ~2/3 of the solvent volume from the beaker into the flask. Shake the Catalyst and quantitatively add it through the same plastic funnel into the flask. Add the rest of the solvent from the beaker to the flask. Close the open neck with the stopper. Put the flask into the ice bath filled with water and ice to ~ 2/3 of its volume. Start stirring the mixture.

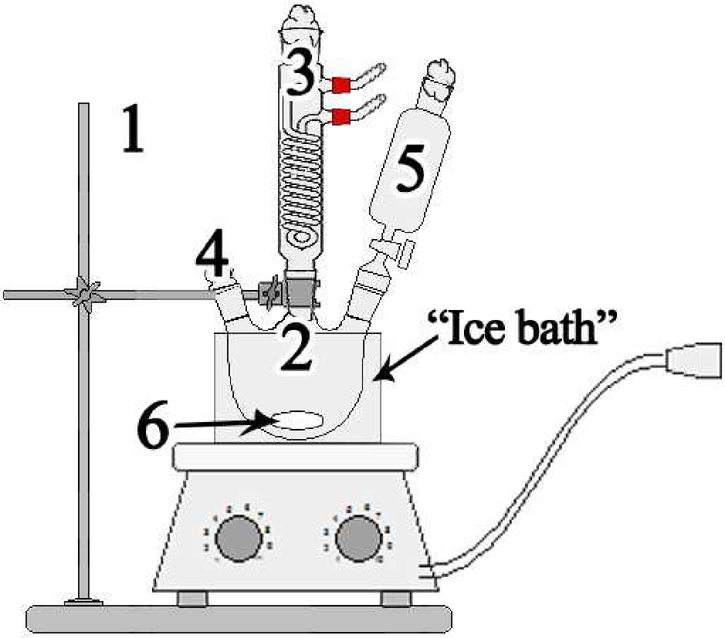


Fig. 1. Set up needed to implement Steps 1-4 of the synthesis. Refer to page 4-5 for the numbers

Step 2. Using the big plastic funnel quantitatively transfer the solution of 3-methylthiophene to the dropping funnel with **tap closed**. Apply a piece of the cotton wool to the open end of the dropping funnel and reflux condenser. Under vigorous stirring, add the solution of 3-methylthiophene dropwise during ~ 3 min. Replace the dropping funnel by a glass stopper. Use the Teflon sleeve. Remove the ice bath. Dry the plate and bottom of the flask with napkin.

Step 3. Wrap up the flask with aluminum foil. Switch on the heater (position 3). Bring up the mixture to boiling and boil it for 10 min. Prepare the ice bath (~2/3 of the volume) while the mixture boils.

Step 4. Switch off the heater and carefully **(hot!)** remove the hot-plate magnetic stirrer aside. Dip the flask equipped with the condenser and stoppers into the ice bath for 3-5 min. Keep gently swirling the flask from time to time to provide the faster cooling. Then remove the reflux condenser and load 0.02 g of K_2CO_3 using the big funnel applied to the open neck. Close the neck with a glass stopper and shake the flask several times. Turn off the water supply and unscrew the adaptors of the tubings from the reflux condenser. Let the residual water leak out of the condenser and immediately place it into the container for the used glassware. Remove the clamp keeping the flask in the ice bath.

Step 5. Weigh the 10 mL receiver flask for product with the glass stopper, both marked with your student code. Write down the value in the answer sheet. Put the small magnetic stir-bar in the 50 mL pear-shaped distillation flask. Screw on the adaptors with tubings to the Liebig condenser and fix it on the stand with the red clamp. Turn on the water supply yourself and make sure there is no water leakage.

Step 6. Assemble the distillation apparatus as shown on Fig. 2 supplying all the joints with the teflon sleeves and clips. First, attach two 10 mL and one 50 mL receiver flasks to the distilling receiver cow. Then connect the vacuum hose to the cow and complete assembling. Fix the apparatus over the magnetic stirrer to adjust it on height. Use the adjustable lab jack lift support.

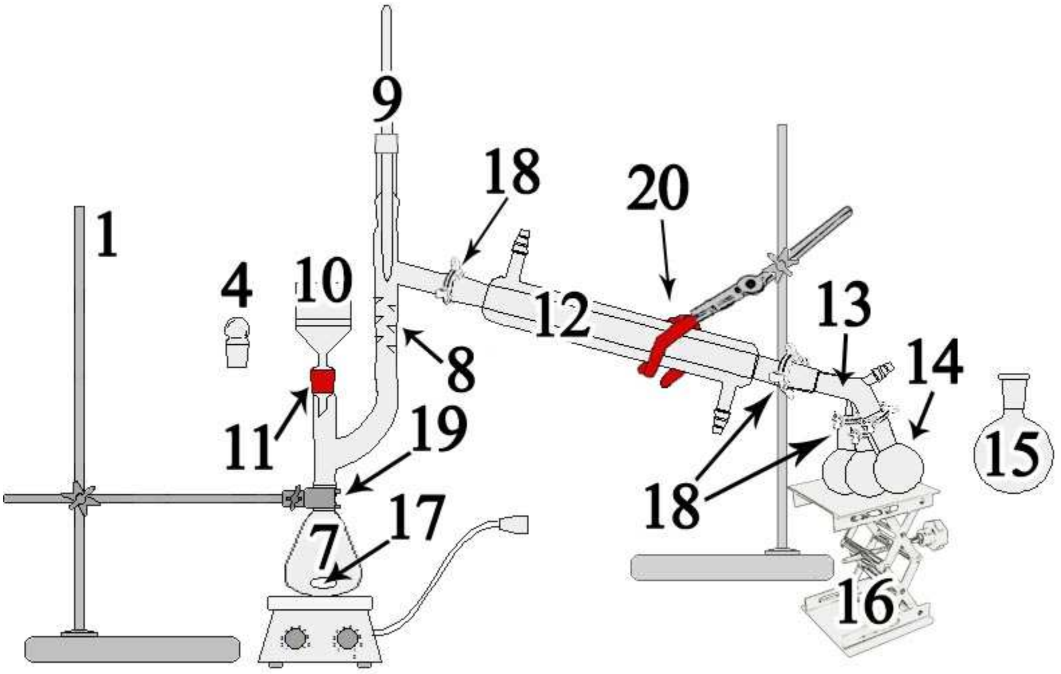


Fig. 2. Set up needed to implement Steps 5-10 of the synthesis. Refer to page 4-5 for the numbers

Step 7. Remove the hot-plate magnetic stirrer aside. Insert the fritted glass filter into the Claisen distillation adapter using the rubber spacer. Turn on the water-jet pump and switch on the digital manometer. Remove the three-necked flask from the ice bath and dry it with a napkin. Carefully transfer the reaction mixture from the three-necked flask to the filter (**Attention! If you do it too fast, the mixture can be partially sucked into the curved part of the adaptor**). When finished, turn off the pump and replace the filter with a glass stopper, use the teflon sleeve.

Step 8. Tightly wrap up the flask and distillation adaptor with aluminum foil up to the thermometer joint. Bring back the magnetic stirrer and turn on stirring and heating (position 6). **Do not turn on the water-jet pump!** Collect the distilled solvent into the 50 mL receiver. When the solvent distillation is over, turn off heating and stirring and carefully **(hot!)** remove the hot-plate magnetic stirrer aside. Replace the receiver flask containing the distilled solvent by a new 10 mL receiver. Close the 50 mL flask with a glass stopper and deliver it to your lab assistant.

Step 9. Remove the foil and put the pear-shaped bottom flask into the ice bath for 2-3 min to bring the temperature below ambient. Remove the ice bath; dry the flask with a napkin. Bring back the magnetic stirrer under the flask **(Attention! The hot-plate may be still hot!).** Turn on stirring. Wrap up the flask tightly with aluminum foil. Switch on the water-jet pump. When vacuum is stabilized (follow the reading of the digital manometer), turn on the heater (position 6). Observe the initial stage of the targeted product distillation and collect the first 3-5 drops into an attached receiver flask not labeled with your student code. Then rotate the cow and collect the targeted product into the receiver flask with your student code. Write down the product boiling point and pressure reading from the digital manometer into the answer sheet.

Step 10. When the targeted product is collected, turn off the heater, remove the foil and carefully **(hot!)** remove the hot-plate magnetic stirrer aside. Cool down the apparatus to ambient temperature using the ice bath. **Ask your lab assistant to disconnect the vacuum line.** Disconnect the receiver flask with the targeted product and **immediately** close it with the glass stopper labeled with your student code. Do not attempt to drag the teflon sleeve out if it remains in the receiver. Place the flask into the 50 mL plastic beaker labeled "For the receiver with the product". Immediately attach a new receiver instead of the removed one and apply the joint clip. **Leave the apparatus as it is.**

Step 11. Measure the refraction index **(before weighing)** following the instruction below. Record the temperature from the refractometer.

Weigh the receiver with the targeted product closed with the labeled stopper. Calculate the mass and yield of the product (take the mass of the teflon sleeve equal to 149 mg). The molar masses of 3-metylthiophene and the product equal 98 and 177 g mol^{-1}, respectively.

Q2. Write down all the result in the hereunder Table.

#	Parameter /Characteristics	Value	Units
1	Mass of the receiver flask with the glass stopper, both marked with student code		g
2	Mass of the product		g
3	Yield of the product		%
4	Refraction index for the product		-
5	Temperature recorded from the refractometer		°C
6	Boiling point of the product		°C
7	Pressure at the Boiling point		mmHg

Deliver the product to your lab assistant and get it signed.

The targeted product delivered: ______________________________

Student signature ____________________ Lab assistant signature ____________________________

The grading scheme takes into account two values re-measured by the Science Committee: mass of the Product (m, g) and its refraction index (n_D) (Fig. 1).

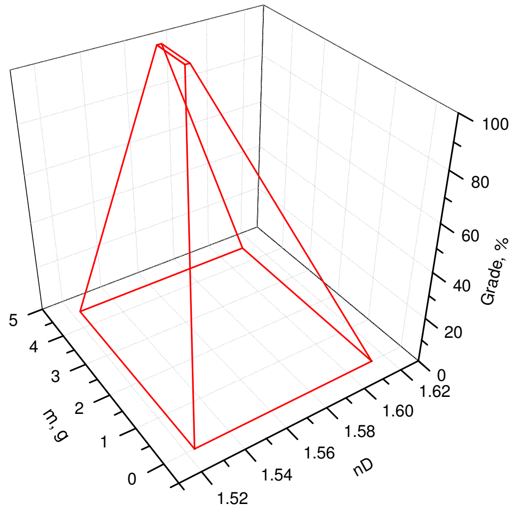


Fig. 1. The 3D diagram.

There are several regions (A-D) on the hereunder projection of the 3D diagram (Fig. 2).

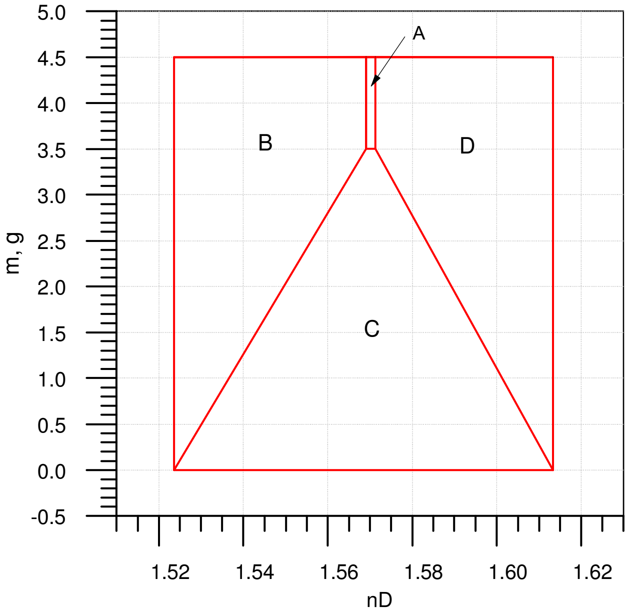


Figure 2. Mass-n_D plot.

- If the value obtained is within region A, 100% of 30 marks
- If the value obtained is within region B, 2202.643*n_D-3355.95 % of 30 marks
- If the value obtained is within region C, 28.57143*m % of 30 marks
- If the value obtained is within region D, -2380.95*n_D+3841.1905 % of 30 marks

Refraction index measurement skills: 4 marks if a student's result differs from the re-measured value not more than by 0.4 %.

Weighing skills: 2 marks if a student's result differs from the re-weighed value not more than by 0.02%.
Correct calculation of mass: 1 mark.
Correct calculation of yield: 1 mark.
Measurement of the Boiling point: 1 mark

REFRACTO 30GS – OPERATING INSTRUCTIONS

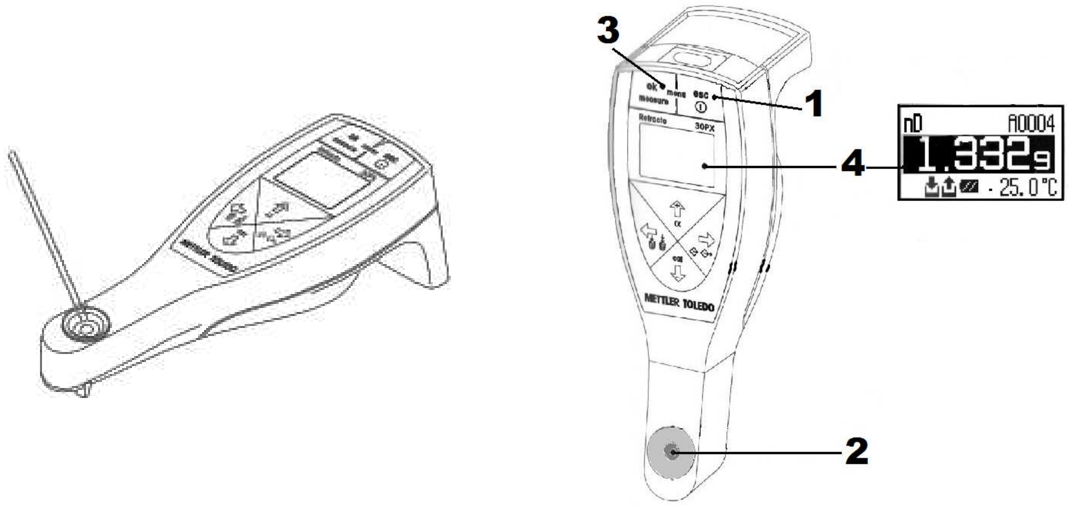
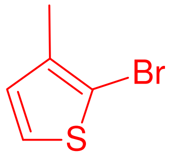


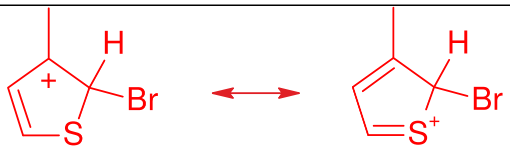
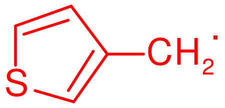
Fig. 3. Using the Refracto 30GS

1. To switch Refracto 30GS on, press and hold "ESC" button (1) until the display appears. The instrument is ready for operation. It switches off automatically if not operated for 10 min.
2. Clean the cell and glass rod with a napkin wetted with the solvent from the washing bottle labeled "cleaning solvent". Dry both with another napkin.
3. Make sure the sample to be measured has reached ambient temperature and is homogeneous.
4. Apply 2-3 drops of the sample onto the measuring cell (2) using the glass rod.
5. To start the measurement press and hold the ok button (3) until the beep.
6. Take the value of the refraction index and the temperature from digital display (4) and write down the result in the answer sheet.
7. Clean up the cell and the glass rod.

Q3. By comparing the obtained and literature data, draw the structure of the product and catalyst given.

The Product obtained	**The Catalyst given**
 3 marks	$HClO_4$ 1 mark 0 mark, if inconsistent with Q1

Q4. Draw the structure of the 3-methylthiophene-based reactive intermediates behind the selectivity in the case of **T1** and **T2**.

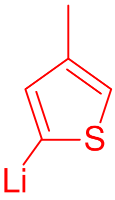
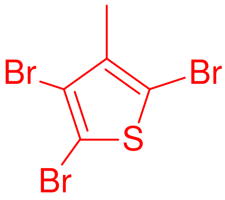
T1	**T2**
 1 mark for any of the structures	 1 mark

Q5. Write down the product (**T1** or **T2**) formed as a result of direct bromination of 3-methylthiophene with NBS under the given conditions / catalyst used.

$ZnBr_2$	T1
Dibenzoyl peroxide	T2
LiBr in AcOH	T1
Visible light or UV light	T2

0.25 marks each, 1 mark in total

Q6. In the synthetic pathways to **T3** and **T4**, draw the structures of the compounds formed in the first steps of each pathways shown on Scheme 1.

T3	**T4**
 1 mark	 1 mark

Chemicals and Equipment (Task 2).

I. Chemicals and materials

Chemicals	Labeled as	Health Statements [a]
3-Pentanone (MW 86.13), ~0.86 g[b] in a vial	**A**	H225-H319-H335-H336
***p*-chlorobenzaldehyde (MW140.57)**, ~3.5 g[c] in a vial	**B**	H302-H315-H319-H335
Ethanol, 200 cm^3 in a wash-bottle	**Ethanol**	H225-H319
2 mol dm^{-3} **NaOH** solution in water (**labelled as 2N NaOH**), 25 cm^3 in a bottle	**2N NaOH**	H290-H314

[a] See **page 34 for definition of Health Statements**

[b] You will need to weigh the vial containing 3-pentanone right before using. The exact value can be calculated based on the information given on the label.

[c] The exact value is indicated on the label.

II. Equipment and labwares

Shared equipment	Quantity
Balance	Shared 12 per room
Water aspirator	Shared 2 per bench
Foam bucket filled with ice	Shared 1 per row (Refill could be requested)
Personal Equipment	**Quantity**
Hotplate stirrer with temperature probe	1
Stand	1
Clamps	2
100-cm^3 Round bottom flask	1
Measuring cylinder, 25 cm^3	1
Measuring cylinder, 50 cm^3	1
Air condenser	1
Crystallizing dish, 250 cm^3	1
125-cm^3 Erlenmeyer flask	2
Suction flask, 250 cm^3	1
Buchner funnel, 25 cm^3	1
Watch glass	1
Pasteur pipettes (droppers)	5
Rubber bulbs	2
Suction rubber	1
Rubber support ring	1
Magnetic bar	1
Filter papers	3 (pack in 1 zipped bag)
Spatula	1
Stirring Rod	1
Forceps	1
Plastic joint clips	1
Wash Bottle (filled with EtOH)	1 (can be refilled)
Nitrile gloves	2 (exchange size if needed)
Towels	2
Paper clip	1
“Waste Task 2”, 500 cm^3-glass bottle	1
Vial labeled “Student code” for submitting product.	1
Goggles	1

Task 2	a			b	Total
	a1	a2	a3	b1	
Total	2	2	2	18	24
Score					

Accounted for 14% of Total Score

Task 2: Elaborating Carbon Framework

The core structure of organic molecules is mostly based on carbon-carbon skeleton. Carbon-carbon bond formations have played a vital role in the construction of complex structures from smaller starting materials. Therefore, the synthetic transformations to efficiently achieve carbon-carbon bond formation has long been of interest. In this experiment, you are required to transform commercially available *p*-chlorobenzaldehyde and 3-pentanone to a more elaborated structure.

Important Notes:

- Ethanol can be refilled with no penalty.
- All weighing processes require verification from lab supervisor. The supervisor will need to sign in the student's answer sheet for grading. No mark will be given for unverified values.
- Total of 18 points of this exam score will be based on the quality and quantity of the product submitted. **We could not give any score on this part if the product is not submitted for grading.**
- ^{1}H-NMR and melting point determination techniques will be used by the grader to verify the quality of your product.

Part a

1. Take the vial containing 3-pentanone (**A**) (Code Axxx, For example: A305) and unwrap the parafilm. Weigh the vial with caps. Record the weight in the answer sheet question a1.
2. Setup a water bath by filling water in the 250 cm^3-crystallizing dish and heat to 55±2°C. Add paper clip into the water bath and let it stir so that the heat could be distributed evenly.
3. Ensure a magnetic stirring bar is in the 100-cm^3 round bottom flask. Transfer the pre-weighed 3-pentanone (labeled as **A**) and *p*-chlorobenzaldehyde (labeled as **B**) to the flask. Add 50 cm^3 ethanol to the mixture and swirl to dissolve.

4. Measure 15 cm^3 of 2 mol dm^{-3} NaOH (labeled as 2N NaOH) using a measuring cylinder and add to the reaction mixture. Be careful not to wet the ground joint with NaOH solution.

5. Setup the reaction as shown in **Figure 1**. The reaction flask is placed in the 55±2°C water bath. Attach the air condenser to the reaction flask with plastic joint clip. Heat the reaction mixture while stirring for 30 minutes using the water bath.

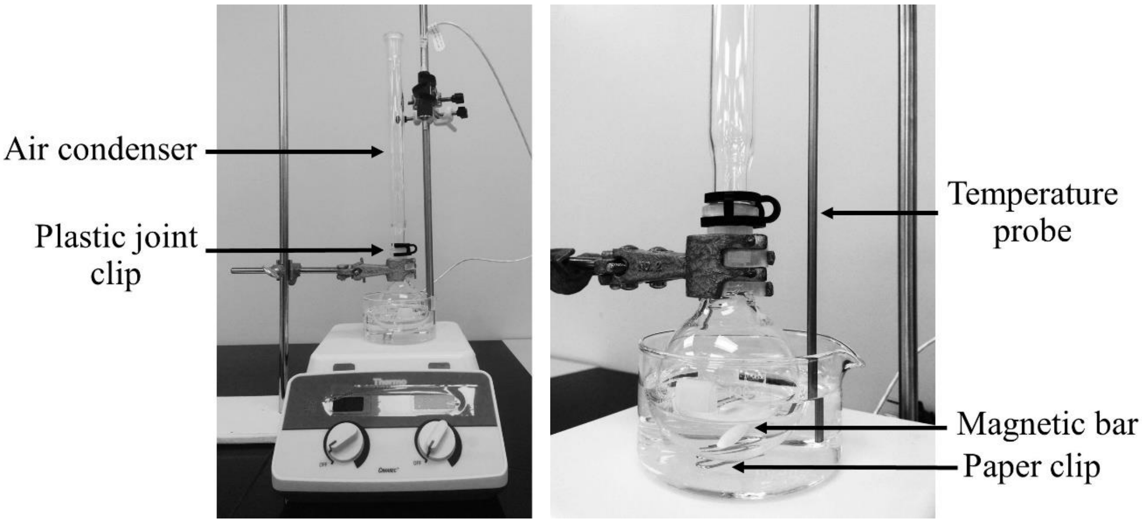


Figure 1: Set up needed for heating the reaction with water bath.

6. Remove the reaction flask from the water bath. **(Be careful! The flask might be hot.)** Place the flask on the rubber supporting ring.

7. **(Important)** Detach the probe from the hotplate/stirrer to avoid over-heating of the hotplate in the recrystallizing steps. After you detach the probe, inform the supervisor to check and submit the probe to the supervisor.

8. Prepare the ice bath by replacing the warm water in the 250 cm^3-crystalizing dish with ice and small amount of water. Place the reaction flask on the ice bath to cool down the reaction. Solid should be observed. (**Suggestion:** If you do not observe any solid within 5 minutes, you may use a stirring rod to scratch the side of the flask. This could induce precipitation.)

9. Keep the mixture cool for approximately 20 minutes to allow complete precipitation.

10. Set up the suction filtration equipment (**Figure 2**). Connect the suction flask to the water aspirator. Place a Buchner funnel fitted with a rubber adapter onto the suction flask. Place a filter paper at the center of the funnel. Filter the precipitate *via* suction filtration and wash the precipitate with small amount of cold ethanol. Let air suck through the precipitates for 2-3 minutes to dry the product.

Figure 2: Set up needed for suction filtration.

11. Disconnect the vacuum (before turning off the water aspirator). Bring your equipment back to your space and keep the common area clean. Collect the crude precipitates from the filter paper and transfer to the Erlenmeyer flask. **Careful not to scrape the paper too hard as you may obtain small pieces of paper as contaminant**. Student may use Ethanol to rinse the Buchner funnel.

12. Place ethanol in a separate Erlenmeyer flask and heat it gently on a hotplate. (Student may set the temperature mark at 100-120°C) **Before heating, please make sure that the temperature probe is detached from the hotplate.**

13. Recrystallize the product from hot ethanol. You can follow the procedure below.

    Add small amount of hot ethanol to the flask containing crude solid while swirling. Continue addition of hot ethanol (swirling after each addition) until the solid is completely dissolved. During the dissolution process, keep the flask hot at all times by resting it on the hotplate. **Be careful that the flask may be hot.** You may use paper towels or towels provided to wrap around the flask while swirling. Once the dissolution is complete, set the flask containing the dissolved compound on a benchtop and let the flask cool down to room temperature without disturbance. The crystalline product should be observed. If not, you may use the stirring rod to scratch the side of the flask to induce crystallization. Place the flask into the ice bath to complete crystallization.

14. Filter the recrystallized product *via* suction filtration (See step 10 for suction filtration protocol) and wash the product with small amount of cold ethanol. Let air suck through the precipitates for 2-3 minutes. Disconnect the vacuum. Let the purified product air-dry on the benchtop for at least 15 minutes.

15. Weigh the vial (without cap) labeled with your student code provided. Record the value in the answer sheet question a1.

16. Transfer the recrystallized product to the pre-weighed vial. Determine and record the mass of the purified product in the answer sheet question a1.

17. Fill the information on the label of the product vial. Place the product-containing vial on the benchtop. The supervisor will pick up your vial and sign on your answer sheet question b after the "Stop command". The student also must sign the answer sheet question b for grading. Once both supervisor and student sign, place the vial into a zipped bag and submitted for grading.

These following items should be left on your bench:

- The exam/answer booklet (this booklet) placed in an exam envelope
- The vial labeled "Student Code" with filled information

Supervisor will place a label here
when randomly distributed the compounds:

Axxx (For example: A567) =	Code of vial containing 3-pentanone
Tared (w/caps):	Mass of (vial + label + caps) **before** adding 3-pentanone
Bxxx (For example: B567) =	Code of vial containing *p*-chlorobenzaldehyde
Net:	Mass of *p*-chlorobenzaldehyde

a1) Use the information provided in the label above along with your experimental data for your calculation. Write down all the results in this Table.

Mass of 3-pentanone in the vial provided (must weigh with caps) = ________________

*Signature of the supervisor is required for grading

Mass of pentan-3-one = ______________________________

Mass of *p*-chlorobenzaldehyde (copy from the label):__________________________

Mass of the empty vial for product:_____________________________

*Signature of the supervisor is required for grading

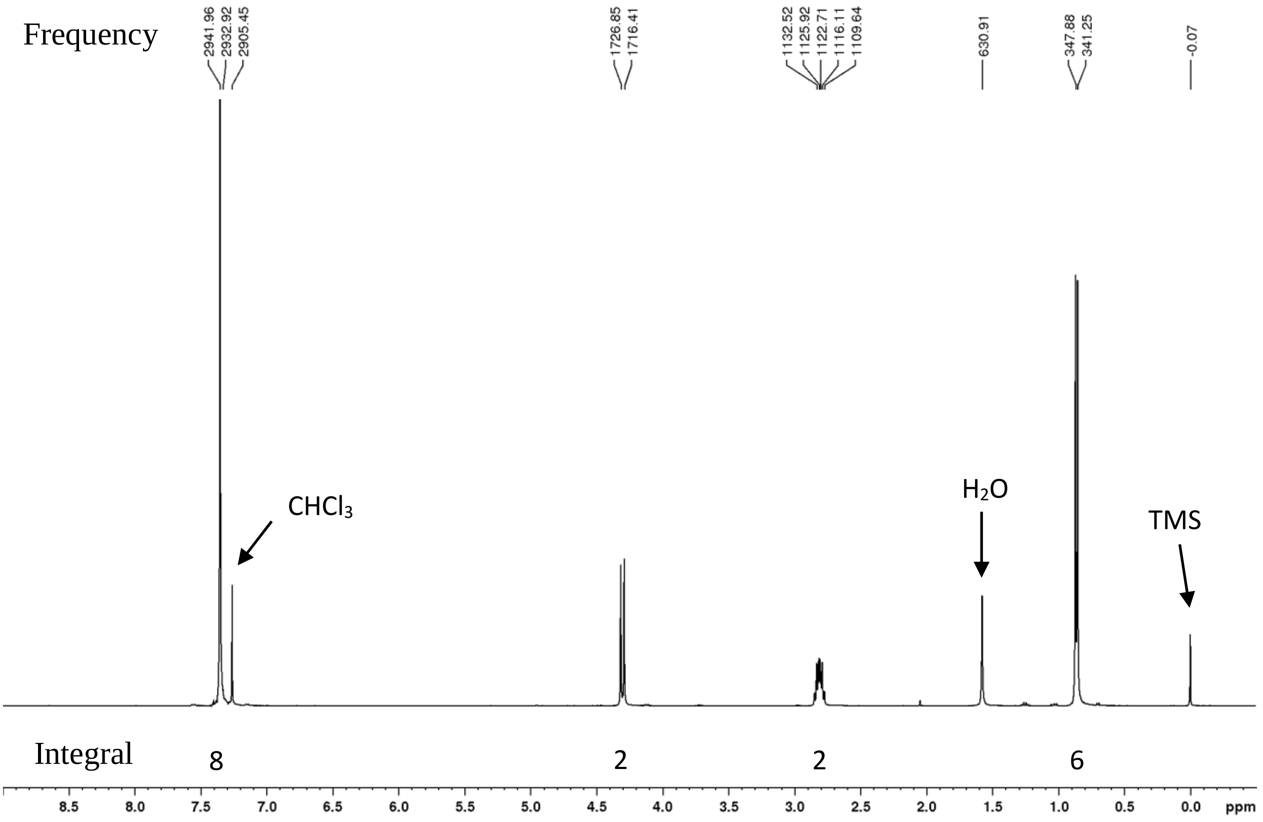
Mass of the vial with the recrystallized product:______________________________

*Signature of the supervisor is required for grading

Mass of the recrystallized product:_____________________

a2) Write 4 plausible aromatic compounds that may occur from this reaction. Stereoisomers are excluded.

a3) Given the 400MHz ^{1}H-NMR (in $CDCl_3$) of the product below, write the structure of the product.



Integrals are for all protons presented in the molecule.

Part b

b1) Your submitted product will be characterized and graded for its %yield and purity. Provide information of the product you submitted.

Status: ☐ Solid ☐ Liquid

Signature of Supervisor: ____________________________(Signed when submitted)

Signature of Student: ______________________________ (Signed when submitted)

Student Code **AAA-1**

Task 2	**a**			**b**	**Total**
	a1	a2	a3	b1	
Total	2	2	2	18	24
Score					

Accounted for 14% of Total Score

a1) Use the information provided in the label above along with your experimental data for your calculation. Write down all the results in this Table.

Mass of 3-pentanone in the vial provided (must weigh with caps) = ________________

*Signature of the supervisor is required for grading ☐

Mass of pentan-3-one = ______________________________1 point

Mass of *p*-chlorobenzaldehyde (copy from the label):__________________________

Mass of the empty vial for product:_____________________________

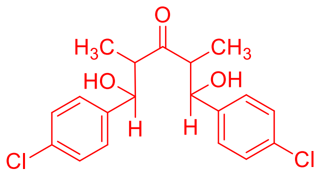
*Signature of the supervisor is required for grading ☐

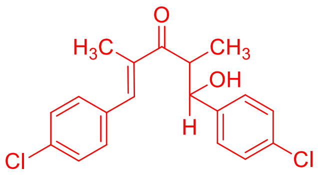
Mass of the vial with the recrystallized product:______________________________

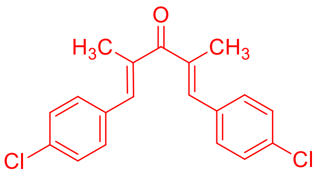
*Signature of the supervisor is required for grading ☐

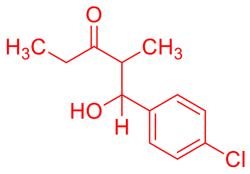
Mass of the recrystallized product:______________________ 1 point

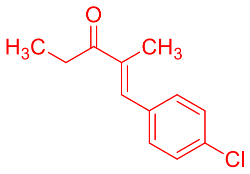
a2) Write 4 plausible aromatic compounds that may occur from this reaction. Stereoisomers are excluded.

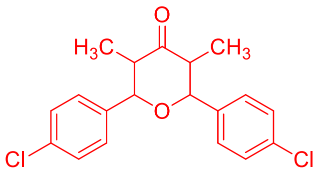






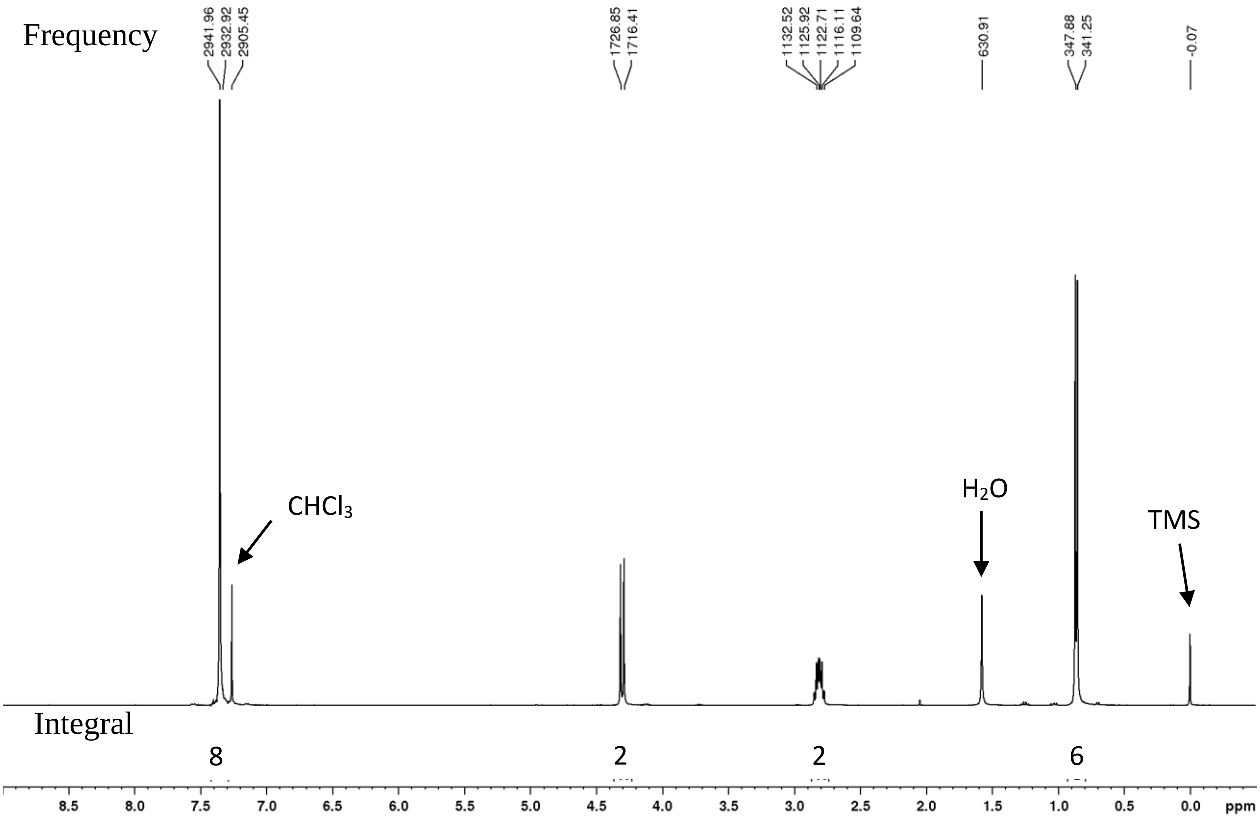






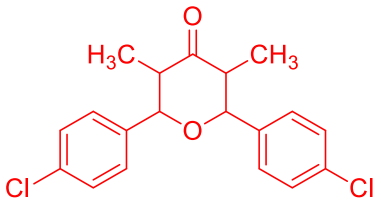
0.5 point each, maximum 2 points

a3) Given the 400MHz ^{1}H-NMR (in $CDCl_3$) of the product below, write the structure of the product.



Integrals are for all protons presented in the molecule.

2 points.



Sintesi inorganica

IChO

International Chemistry Olympiad

PRACTICAL PROBLEMS

Introduction:

The experimental assignment consists of the synthesis and subsequently, the analysis of amminenickel(II) chloride: $NiCl_x(NH_3)_y$.

The synthesis proceeds in three steps:

a) Preparation of a solution of nickel nitrate from nickel and concentrated nitric acid (green solution), time required about 20 min.

b) Preparation of amminenickel(II) nitrate (blue crystals)

c) Preparation of amminenickel(II) chloride (blue-violet crystals)

The analysis encompasses the determination of the percentages of the three components (ammonia, nickel and chlorine) of the salt, according to the instructions given in 2.

PROBLEM 1 (practical)

Synthesis of the nickel(II) salt:

All work on the synthesis must be carried out in the fume hood. Use of (safety) glasses is obligatory. If necessary use other safety equipment, such as rubber gloves and pipetting balloons.

a) Put a "dubbeltje" (Dutch coin of 10 c, containing 1.5 g of nickel), in a 100 ml conical flask (Erlenmeyer flask) and add 10 ml of concentrated nitric acid (65 %). Fit the flask with an "air cooled" condenser (no water) and heat the contents on a hot plate until a violent reaction occurs. Continue heating carefully until all metal is dissolved. Cool the green solution in an ice-water mixture.

Write in the report form the equation of the chemical reaction that has occurred.

b) Add, under continuous cooling, in small portions 25 ml of ammonia solution (25 %) to the ice cold solution. As soon as about 15 ml has been added, salt crystals start to precipitate. Having added all ammonia solution, filter the cold solution through a sintered glass filtering crucible by applying a vacuum with an aspirator. Wash the crystals three times with small portions of a cold ammonia solution (25 %). Remove as much liquid as possible from the crystalline mass by maintaining the vacuum.

c) Dissolve the moist crystalline mass in 10 ml of hydrochloric acid (18 %). Cool the blue solution in an ice-water mixture and then add slowly 30 ml of a solution of 30 g ammonium chloride in 100 ml of ammonia solution (25 %). This yields a blue-violet coloured crystalline mass. Cool the mixture and filter as in b). Wash with ammonia solution (25 %), then with ethanol and finally with diethyl ether. Leave the crystals on air until all ether has evaporated. Determine the mass of the dry product and record this on the report form.

PROBLEM 2 (Practical)

Preparation of cis-Copper-bis-Glycinate Hydrate [$Cu(gly)_2 \bullet xH_2O$]

Copper(II) amino acidate coordination compounds are monometric units for synthesizing important biopolymers such as metalloenzymes like ceruloplasmin, on which every living organism depends. In laboratory cis-copper-bis-glycinate hydrate can be produced by the reaction of cupric hydroxide with glycine at a temperature of ca. 70 °C.

Reagents:

$CuSO_4 \cdot 5\ H_2O$(s)
NH_3 (aq) (3 mol dm^{-3})
glycine(s)
95% ethanol,
acetone
NaOH (2 mol dm^{-3})
$BaCl_2$ (0.5 mol dm^{-3})

1. *Preparation of $Cu(OH)_2$*

Procedure:

(1) Dissolve your pre-weighted sample of $CuSO_4 \cdot 5\ H_2O$ (6.0 g) in 40 cm^3 of water with a 250 cm^3 beaker as a container.
(2) Add slowly 3 mol dm^{-3} ammonia solution to the $CuSO_4$ solution, gently stirring, until the precipitate is completely dissolved and the solution is turning blue-violet.
(3) Add 2 mol dm^{-3} NaOH solution to the above solution until no more precipitate formed.
(4) Filter the precipitate over a Büchner funnel under reduced pressure. Wash the precipitate with water until no SO_4^{2-} ion is detected in the filtrate.
(5) Collect $Cu(OH)_2$ for the preparation of $Cu(gly)_2 . x\ H_2O$.

Write the equations for the main chemical reactions having taken place in the above procedure.

2. *Preparation of cis-Copper-bis-Glycinate Hydrate*

Procedure:

(1) Dissolve a pre-weighted sample of glycine (3.6 g) in 130 cm^3 of water and then warm the solution in a hot water bath (70 ℃). Add the $Cu(OH)_2$ to the solution, stir gently until the precipitate is dissolved. Perform a hot filtration and add 10 cm^3 of 95 % ethanol.

(2) Cool the solution and when needle-like crystals appear, place it in the ice water bath for 10 min.

(3) Filter the crystals over a Büchner funnel under reduced pressure, wash once with 10 cm^3 of ethanol-water mixing solvent and then twice with 10 cm^3 acetone, squeeze the crystals as dry as possible on the funnel.

(4) Collect the crystals to a watch glass and dry it (consult your supervisor).

(5) Half an hour later weigh the product. Write the mass of product and the percentage of yield on your student's report. Give the expressions for calculation to show how you calculate.

SOLUTION

The following values were required to be written on the Answer Sheet :

- Mass of the product.
- The calculated theoretical yield in g.
- The yield obtained as a percentage of the theoretical yield.

Tasks:

Write down the balanced chemical equations used in the preparation.

Solution of the tasks:

1. $Cu^{2+} + 2\ NH_3 + 2\ H_2O \rightarrow Cu(OH)_2 + 2\ NH_4^+$

   $Cu(OH)_2 + 4\ NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 2\ OH^-$

2. $Cu(OH)_2 + 2\ NH_2CH_2COOH \rightarrow Cu(NH_2CH_2COO^-)_2 + 2\ H_2O$

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 sufficient 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.

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.

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)

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).

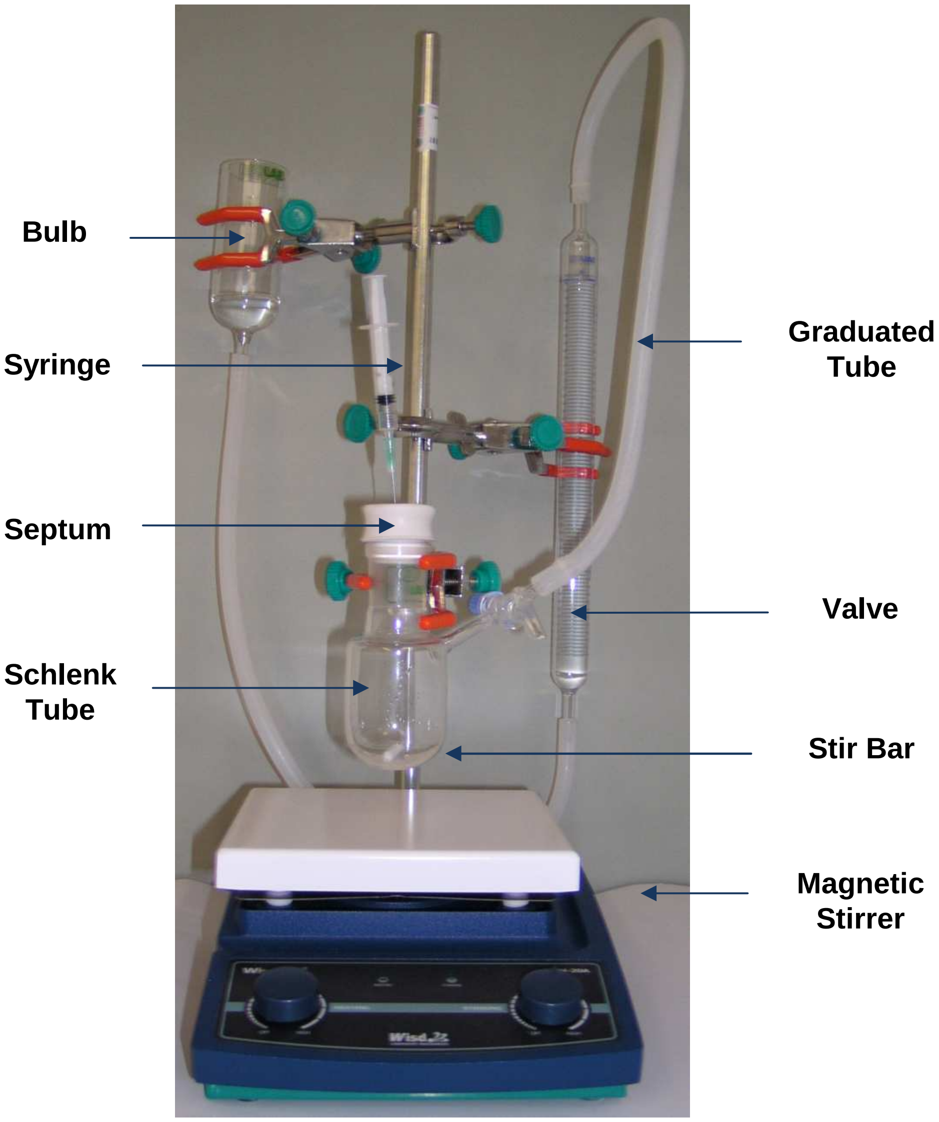
In this experiment, the catalytic hydrolysis of ammonia borane will be carried out starting with potassium tetrachloropalladate(II) in a solution containing poly(4-styrenesulfonic acid-co-maleic acid). Potassium tetrachloropalladate(II) will be used as precatalyst, which will be reduced by ammonia borane 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_o 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 °C. 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 °C. 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 tetrachloropalladate(II) is 98 % w/w.

SOLUTION

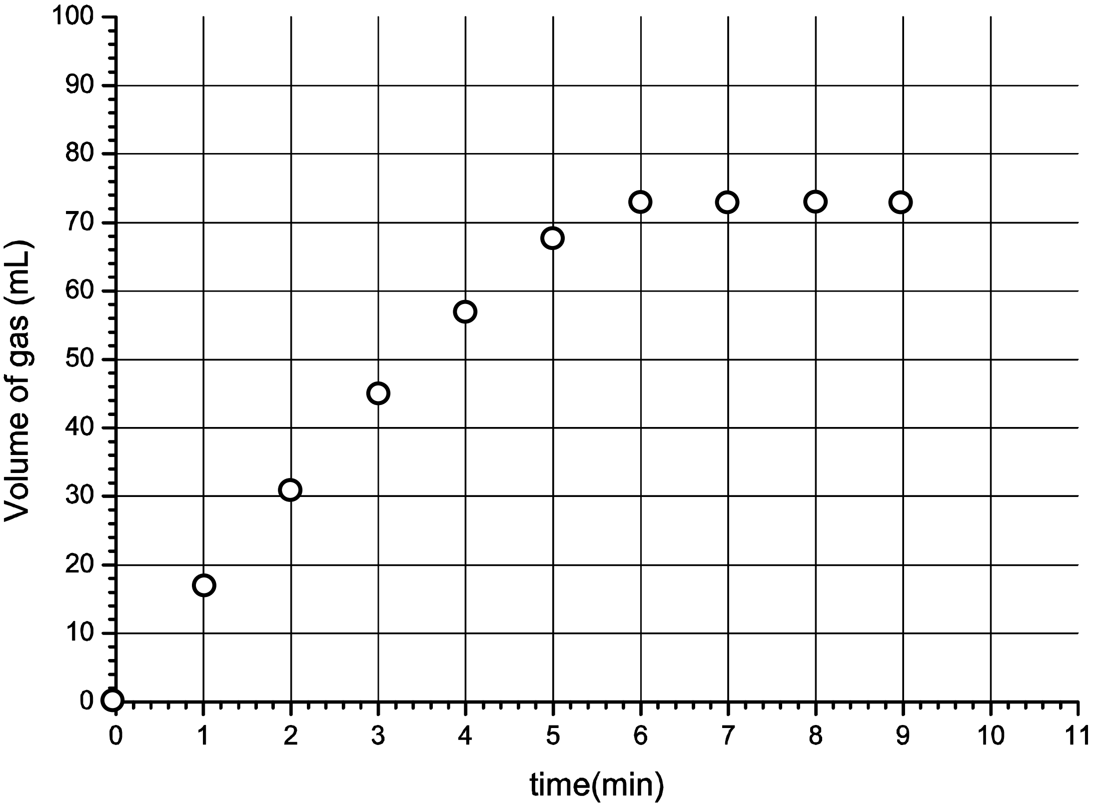
2.1 **Part A.** The volume of the gas evolved stays within a range of 0 – 2 cm^3 (maximum).

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:



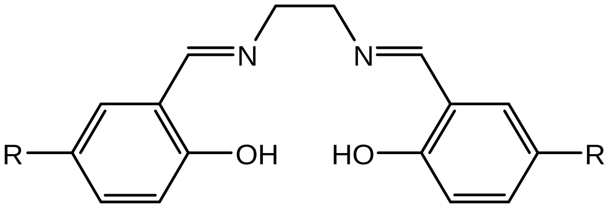
2.4 – 2.6

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 2 (Practical)

Synthesis of a Salen Manganese Complex and Determining Formula of the Product

Transition metal complexes of the 3*d*-block elements derived from the bis(salicylidene)ethylenediamine (salen) ligand have proven to be efficient catalysts of various redox reactions in organic synthesis.



(salen)H$_2$, R = H

(salen*)H$_2$, R = H, COOH, or SO_3H

The ability of the salen ligand to stabilize higher oxidation states of 3*d*-block elements is important in this sphere of chemistry. In particular, compounds of manganese in oxidation states from II to V could be generated depending on the reaction conditions when the manganese salen complex is prepared. In this task you are required to prepare a manganese salen complex by reacting (salen)H$_2$ with Mn(II) acetate in ethanol in the air in the presence of lithium chloride. Under these conditions, you might have obtained a complex of the formula (salen)MnCl$_x$, where x = 0, 1, 2, or 3.

You are expected to:

i) determine the mass of the product,

ii) characterize the purity of the material prepared using thin-layer chromatography (TLC),

iii) determine the metal oxidation state in the complex using an iodometric redox titration.

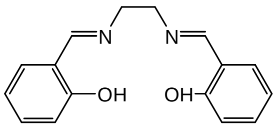
For the redox titration, you will be given a solution of a previously prepared analogue of your compound, (salen*)MnCl$_x$, where manganese has the same oxidation state as in the product and the substituent R on the benzene ring is either H, COOH, or SO_3H.

Please read the whole description of this task and plan your work before you begin. Some operations have to be performed in parallel in order to complete it in time.

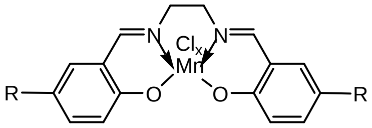
Chemicals

Note: The exact values of masses and concentrations of the particular chemicals are indicated on the labels.

- **(salen)H$_2$**, ~1.0 g in a vial



- $Mn(OOCCH_3)_2 \cdot 4\ H_2O$, ~1.9 g in a vial
- Lithium chloride, solution in ethanol, c = 1 mol dm^{-3}
- Ethanol
- Acetone
- (salen*)MnCl$_x$, ~32 cm^3 of a solution with a mass concentration of ~3.5 mg cm^{-3}



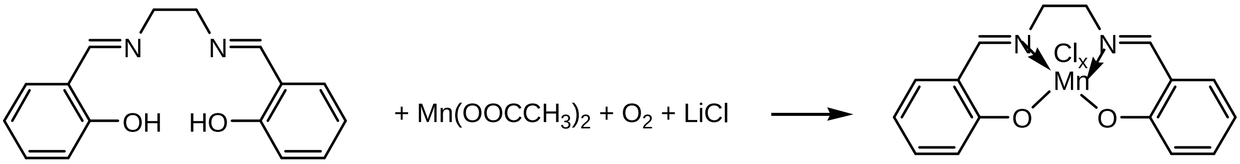
Both R groups are equal and can be either H, or COOH or SO_3H.

- KI_3, 50 cm^3 of an aqueous solution in a bottle, labelled "I$_2$", c = ~0.010 mol dm^{-3}.
- Ascorbic acid, 20 cm^3 of an aqueous solution, c = ~0.030 mol dm^{-3}.
- Starch, w = 0.01, 2 cm^3 solution in water,

Procedure:

A. Synthesis of (salen)MnCl$_x$

B.



(salen)MnCl$_x$

(1) Place 2-3 crystals of (salen)H$_2$ aside in a small vial to be used for the TLC experiment later.

(2) Transfer the pre-weighed ~1.0 g sample of (salen)H_2 provided into a 250 cm^3 Erlenmeyer flask charged with a stirring bar. Combine the reagent with 35 cm^3 of absolute ethanol.

(3) Place the flask on a hot plate/stirrer. Heat the contents with constant stirring until the solid dissolves (usually, dissolution is complete when the ethanol is about to boil). Then decrease the temperature setting to maintain the mixture close but below its boiling point. Do not boil the mixture so that the neck of the flask remains cool. If the flask is too hot to hold with bare hands, use a folded paper towel.

(4) Remove the flask from the hotplate and add to its content a pre-weighed ~1.9 g sample of $Mn(OAc)_2 \cdot 4\ H_2O$. A dark brown colour will develop. Return the flask to the hotplate immediately and continue heating and stirring for 15 min. Do not boil the mixture so that the neck of the flask remains cool.

(5) Remove the flask from the hotplate and add to its contents the provided solution of LiCl (c = 1 mol dm^{-3}) in ethanol (12 cm^3, an excess). Return the flask to the hotplate and continue heating and stirring for 10 min. Do not boil the mixture so that the neck of the flask remains cool.

(6) After this time remove the flask from the hotplate and place it in an ice bath for crystallization for 30 min. Every 5 min gently scratch the walls of the flask from inside under the liquid level with a glass rod to accelerate crystallization of (salen)$MnCl_x$. The first crystals may appear immediately upon cooling or after a period of only 10 – 15 minutes.

(7) Use vacuum line located inside the hood (the corresponding valve is labelled “Vacuum”) and suction filter the crystalline solid formed using the small Hirsch funnel and a suction flask. Use a transfer pipette to wash the solid with few drops of acetone without disconnecting the flask from the vacuum line, and leave it on the filter (with the suction on) for 10 – 15 min to air-dry.

(8) Transfer the solid product into a pre-weighed vial labelled “Product”, then determine and record its mass, m_p, in the box below. Record also the mass of the following reagents used in the synthesis: (salen)H_2, m_S, and $Mn(OOCCH_3)_2 \cdot 4\ H_2O$, m_{Mn}.

(9) Place the labelled vial with product into a zipper bag.

You are required to fill in the following table:

Mass of the empty vial for the product: ________________ g

Mass of the vial with the dried product: ________________ g

Mass of the product, m_p: ________________ g

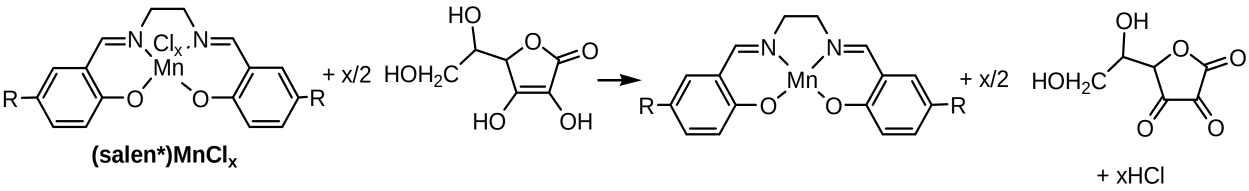
Mass of (salen)H_2 from label on the vial (copy from the label), m_S:

________________ g

Mass of $Mn(OOCCH_3)_2 \cdot 4\ H_2O$ from label on the vial (copy from the label), m_{Mn}:

________________ g

B. Volumetric analysis of a sample of (salen*)$MnCl_x$ provided



R = H, COOH, or SO_3H

Procedure:

(1) Dispense 10.00 cm^3 of the provided (salen*)$MnCl_x$ solution into a 125 cm^3 Erlenmeyer flask using the volumetric pipette.

(2) Add 5.00 cm^3 of the ascorbic acid solution to this solution and mix well. Allow the solution to stand for 3 – 4 minutes.

(3) To avoid oxidation of ascorbic acid with O_2 do not delay and titrate the solution immediately with the KI_3 solution using 5 drops of a 1 % starch solution as indicator. The blue or blue-green endpoint should persist for at least 30 sec.

(4) If time permits, perform 1 – 2 replicate titrations to improve the accuracy of your determination.

Place results of your titration experiment(s) in table 2.1.

Table 2.1. Results of the titration experiment(s).

#	Initial volume reading in burette of KI_3 solution, cm^3	Final volume reading in burette of KI_3 solution, cm^3	Volume of KI_3 solution consumed, cm^3
1			
2			

2.1 Indicate the volume (selected or averaged) of KI_3 solution consumed in cm^3 that you will use for calculations of molar mass of (salen*)$MnCl_x$.

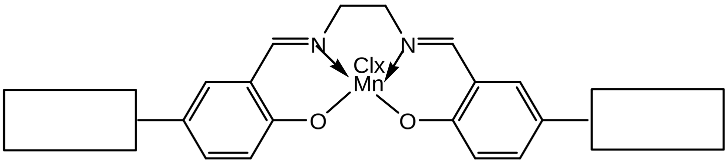
Concentrations of (salen*)$MnCl_x$ (in mg cm^{-3}) and ascorbic acid (in mol dm^{-3}) are given on the labels of the particular bottles.

2.2 From your titration data and referring to the table 2.2 deduce:

i) the value of *x*,

ii) oxidation state of manganese,

iii) the identity of the substituent on the salen ligand (R = H, COOH, SO_3H). Show them in the template below.



x = ________

Manganese oxidation state: ______________

Table 2.2

R	x	(Theoretical molar mass)/x, g mol^{-1}
H	1	357
H	2	196
H	3	143
COOH	1	445
COOH	2	240

Table 2.2 continued

COOH	3	172
SO_3H	1	517
SO_3H	2	276
SO_3H	3	196

C. TLC characterization of (salen)MnCl$_x$

(1) Dissolve a few crystals of the (salen)MnCl$_x$ that you have prepared in a few drops of absolute ethanol using a small vial and a plastic transfer pipette for ethanol.

(2) Dissolve a few crystals of (salen)H$_2$ in few drops of absolute ethanol using another small vial.

(3) If necessary, use scissors (available from lab assistant upon request) to trim the TLC plate so it is an appropriate height for the TLC chamber.

(4) Fold or trim a large circle of filter paper, and place it in the beaker so that it takes almost the full height of the beaker. This is required to saturate the chamber with ethanol vapour. Add ethanol to the beaker to wet the filter and cover the bottom with a 3 – 4 mm thick layer of the solvent. Close the beaker with watch glass.

(5) Mark the start.

(6) Using the capillary tubes provided spot the TLC plate with both solutions.

(7) Run a TLC in the beaker covered with a watch glass for 10 – 15 min.

(8) Mark the solvent front as well as the coloured spots on the TLC plate using a pencil.

(9) Dry the TLC plate in air and place it back into a zipper bag.

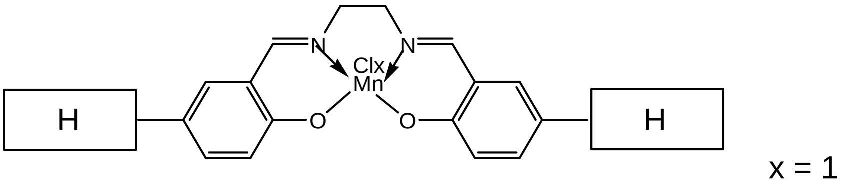
2.3 Calculate the R_f for both (salen)H$_2$ and (salen)MnCl$_x$.

2.4 Sketch the TLC plate on your answer sheet.

2.5 Determine and record the R_f values for (salen)H$_2$ and (salen)MnCl$_x$.

SOLUTION

2.2



Manganese oxidation state: 3

2.4 Evaluation of the TLC plate:

Maximum points:

- for the appearance of two spots on the start line,
- for the start and solvent front lines,
- for the clearly visible spots.

2.5 The relevant R_F values:

Compound	R_f
(salen)H_2	0.58 – 0.68
(salen)$MnCl_x$	0.30 – 0.40

Altre tecniche

PROBLEM 2 (Practical)

Allow to react 10 cm^3 of a 3 N HCl solution with the metal sample (competing pupils were given precisely weighed samples of magnesium, zinc or aluminium) and collect the hydrogen evolved in the reaction in a measuring cylinder above water. Perform the task by means of available device and procedure.

In order to simplify the problem, calculate the mass of your metal sample from the volume of hydrogen on the assumption that it was measured at STP conditions.

PROBLEM 2 (Practical)

Determination of the formation (stability) constants of the complex ions $[Cu(NH_3)_4]^{2+}$ and $[Zn(NH_3)_4]^{2+}$

Equipment:

Two dry beakers with copper and zinc electrodes,
three bottles with aqueous solutions of $CuSO_4$, $ZnSO_4$ and NH_3, respectively,
one beaker with strips of filter paper for making a salt bridge,
one beaker with an aqueous solution of KNO_3,
three pipettes for delivering $CuSO_4$, $ZnSO_4$ and NH_3 solutions,
digital voltmeter for the EMF measurements,
red and blue leads (conductors) for connecting cell electrodes to the digital voltmeter,
rubber pipette filler,
appropriately marked glass stirring rods.

a) Procedure for setting up the Daniell cell:

1. Into the dry beakers containing Cu and Zn electrodes deliver 20 cm^3 of $CuSO_4$ and 20 cm^3 of $ZnSO_4$ using marked pipettes in order to get Cu/Cu^{2+} and Zn/Zn^{2+} half-cells.
2. Wet the filter paper strip with KNO_3 solution. The strip should only be moisten with the solution. Then place the strip ends into the $CuSO_4$ and $ZnSO_4$ solutions.
3. Connect the leads to the electrodes (red to Cu electrode and blue to Zn electrode).

   a)

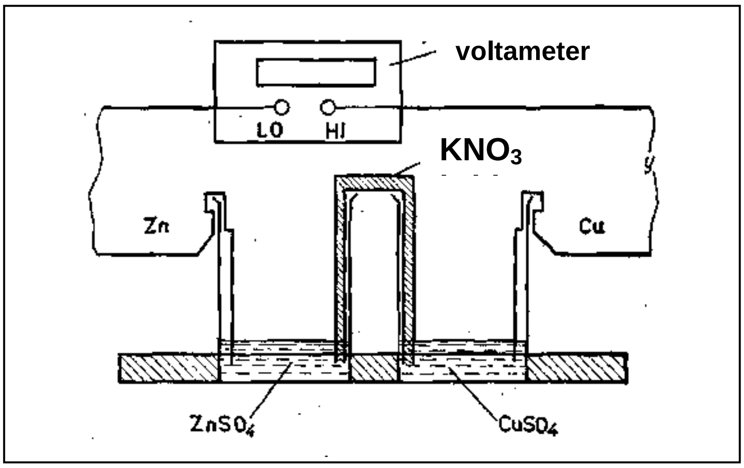


Fig. 1

b) Procedure for the EMF measurement of the Daniell cell (E_A):

Put the appropriately marked glass rods (red - Cu, blue - Zn) into the $CuSO_4$ and $ZnSO_4$ solutions. Having stirred the solutions gently with the rods, the rods should be left in the solutions throughout the course of the experiment. Start the EMF measurement of the cell by connecting the red lead to the voltmeter terminal (HI) and the blue one to the negative terminal (LO). If the EMF value changes by no more than 0.001 V, record the EMF (E_A).

c) Procedure for the EMF measurement of the cell (E_B) after the addition of the complexing agent (NH_3 solution) into the Cu/Cu^{2+} half-cell:

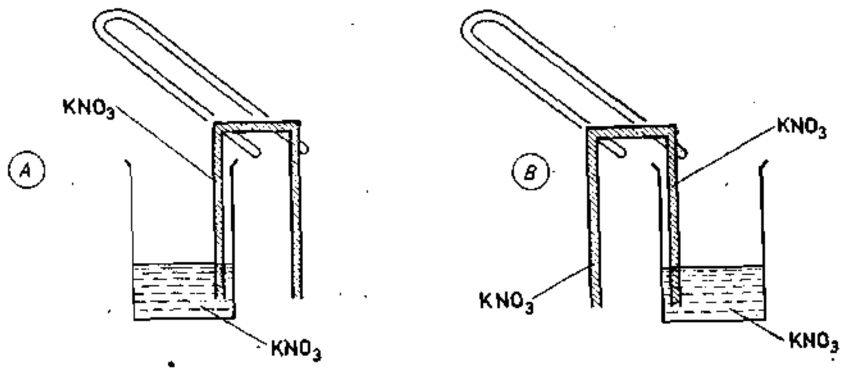


Fig. 2

Pipette 20 cm^3 of aqueous NH_3 solution into the $CuSO_4$ solution. Stir the solution with a glass rod gently until it becomes a clear dark blue. Leave the rod in the solution. Measure and record the new EMF (E_B), in the way described in part b).

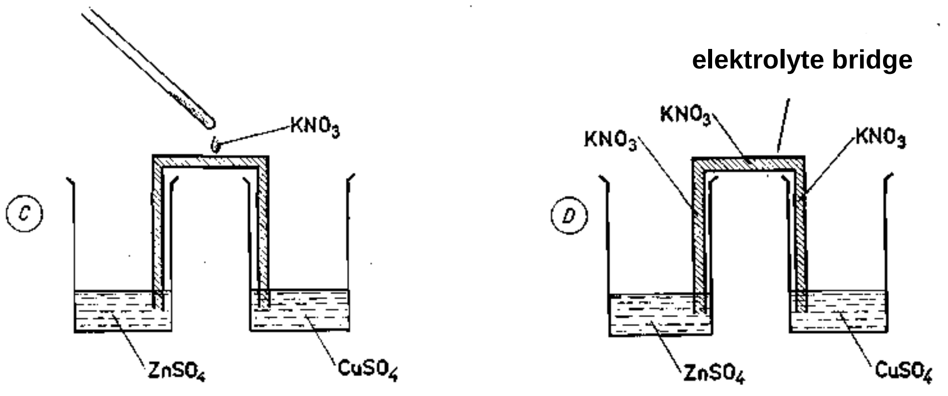


Fig. 3

d) Procedure for the EMF measurement of the cell (E_C) after the addition of the complexing agent (NH_3 solution) to the Zn/Zn^{2+} half-cell:

Leave the $Cu/[Cu(NH_3)_4]^{2+}$ half-cell unchanged. Add 20 cm^3 of NH_3 solution to the $ZnSO_4$ half-cell. Carry out the EMF measurement of the cell in the way described in part b). Write down the result (E_C).

Theoretical considerations:

Gas constant R = 8.314 J K^{-1} mol^{-1}
Faraday constant F = 96 487 C mol^{-1}

i) The concentrations of $CuSO_4$, $ZnSO_4$ and NH_3 aqueous solutions written on the bottles are expressed in mol kg^{-1}. Therefore they must be converted into appropriate concentrations expressed in mol dm^{-3}. The densities (d) of the solutions as functions of temperature are respectively:

$CuSO_4$: d_1 = 1.0923 (kg dm^{-3}) **–** 0.0002700 (kg $dm^{-3}K^{-1}$) T
$ZnSO_4$: d_2 = 1.0993 (kg dm^{-3}) **–** 0.0002900 (kg $dm^{-3}K^{-1}$) T
NH_3 : d_3 = 1.0740 (kg dm^{-3}) **–** 0.0002800 (kg $dm^{-3}K^{-1}$) T

ii) In order to convert concentrations (c_i) into ionic activities (a_i), we need to calculate activities of the ions using the equation $a_i = f_i{*}c_i$. The activity coefficient values, f_i, of the ions involved are given in the answer sheet. The activity coefficient of ammonia should be assumed to be 1.

iii) To simplify the calculations it should be assumed that after the addition of the excess of complexing agent (NH_3) only Cu^{2+}_{aq}, Zn^{2+}_{aq}, $[Cu(NH_3)_4]^{2+}$, $[Zn(NH_3)_4]^{2+}$ ions exist in the respective solutions.

iv) Any diffusion potential occurring between both half-cells when the salt bridge is applied may be neglected in practice.

Questions:

2.1 Calculate the values of the concentrations of Cu^{2+} and Zn^{2+} ions in the Daniell cell before the introduction of the complexing agent (NH_3).

2.2 Calculate the standard EMF value E^o of your Daniell cell using the Nernst equation.

2.3 Calculate the concentrations of $[Cu(NH_3)_4]^{2+}$ and NH_3 in the B type cell, i.e. after the addition of NH_3 to the Cu/Cu^{2+} half-cell.

2.4 Determine the values of the thermodynamic formation (stability) constants K_B and ln K_B for the $[Cu(NH_3)_4]^{2+}$ ions.

2.5 Calculate the concentrations of $[Zn(NH_3)_4]^{2+}$ and NH_3 in the type C cell, i. e. after the addition of NH_3 to the Zn/Zn^{2+} half-cell.

2.6 Determine the values of the thermodynamic formation (stability) constant K_C and ln K_C for $[Zn(NH_3)_4]^{2+}$ ions.

SOLUTION

2.1 The mass of the solutions (kg) can be transformed to volumes of the solutions (dm^3) using the given densities. The concentrations are then given in units mol dm^{-3}.

2.2 $$E = \left(E^0(\mathrm{Cu^{2+}/Cu}) + \frac{RT}{2F}\ln([\mathrm{Cu^{2+}}]\times f_{Cu^{2+}})\right) - \left(E^0(\mathrm{Zn^{2+}/Zn}) + \frac{RT}{2F}\ln([\mathrm{Zn^{2+}}]\times f_{Zn^{2+}})\right) - E_{dif}$$

For E_{dif} = 0 :

$$E_A = E^0(\mathrm{Cu^{2+}/Cu}) - E^0(\mathrm{Zn^{2+}/Zn}) + \frac{RT}{2F}\ln\frac{[\mathrm{Cu^{2+}}]\times f_{Cu^{2+}}}{[\mathrm{Zn^{2+}}]\times f_{Zn^{2+}}}$$

E_A can be measured. All other data required are given in the text of the problem or in the answer sheet.

2.3 Concentrations after the addition of NH_3:

$$[\mathrm{Cu(NH_3)_4^{2+}}] = \frac{c(\mathrm{Cu^{2+}})\times V}{V+V_1}$$

$$[\mathrm{NH_3}] = \frac{(c(\mathrm{NH_3})\times V_1) - (4\,c(\mathrm{Cu^{2+}})\times V)}{V+V_1}$$

2.4 After the addition of NH_3 the following complex equilibrium is established:

$$\mathrm{Cu^{2+} + 4\ NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}}$$

$$\beta_4 = \frac{[\mathrm{Cu(NH_3)_4^{2+}}]\times f_{\mathrm{Cu(NH_3)_4^{2+}}}}{[\mathrm{Cu^{2+}}]\times f_{\mathrm{Cu^{2+}}} \times [\mathrm{NH_3}]^4}$$

Then the Nernst equation has the form:

$$E_1^{'} = E^0(\mathrm{Cu^{2+}/Cu}) = \frac{RT}{2F}\ln\frac{[\mathrm{Cu(NH_3)_4^{2+}}]\times f_{\mathrm{Cu(NH_3)_4^{2+}}}}{\beta_4\times[\mathrm{NH_3}]^4}$$

$$E_B = E'_1 - E_2 = E^0(\mathrm{Cu^{2+}/Cu}) - E^0(\mathrm{Zn^{2+}/Zn}) + \frac{RT}{2F}\ln\frac{[\mathrm{Cu(NH_3)_4^{2+}}]\times f_{\mathrm{Cu(NH_3)_4^{2+}}}}{[\mathrm{Zn^{2+}}]\times f_{Zn^{2+}}\times\beta_4\times[\mathrm{NH_3}]^4}$$

From the above equation β_4 or lnβ_4 can be calculated since E_B can be measured, and all other data required are given in the text of the problem or in the answer sheet.

2.5 and **2.6**

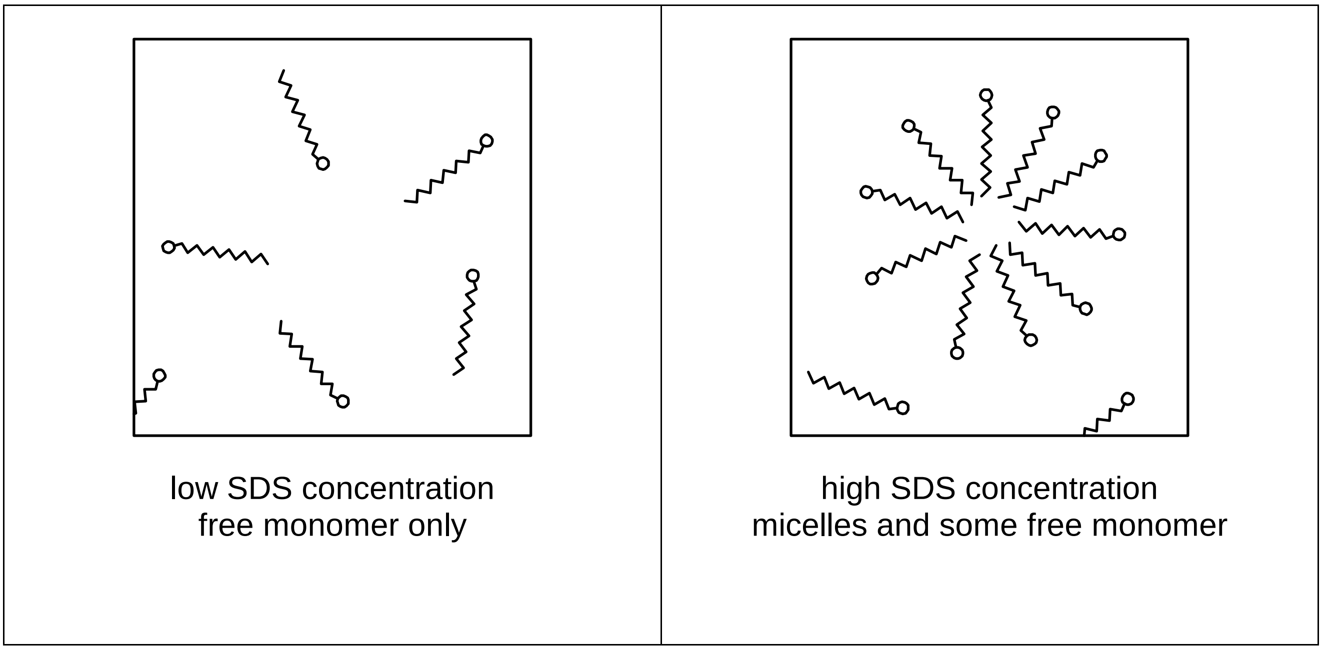
The procedure in the calculation of β_4 or lnβ_4 for complex $\mathrm{Zn(NH_3)_4^{2+}}$ is analogical as that shown in parts (2.3) and (2.4) for complex $\mathrm{Cu(NH_3)_4^{2+}}$.

PROBLEM 3 (Practical)

The Critical Micelle Concentration of a Surfactant

Surfactants are used extensively in many everyday cleaning products, such as shampoos or detergents for washing clothes. One such surfactant is SDS, sodium *n*-dodecyl sulfate, $CH_3(CH_2)_{11}OSO_3Na$ (Relative Molecular Mass: 288.37).

Very dilute aqueous solutions consist of solvated individual molecules of SDS. However, if the concentration is gradually increased beyond a specific concentration, the concentration of monomeric SDS does not change, but instead the surfactant begins to form clusters known as *micelles*. It is these micelles that assist in the removal of grease and dirt. The concentration at which the micelles form is called the *critical micelle concentration*. This process is shown schematically in the figure below.



low SDS concentration
free monomer only

high SDS concentration
micelles and some free monomer

In this experiment, you will determine the critical micelle concentration of SDS by measuring the conductivity of different concentrations of SDS.

Chemicals

- Sodium dodecyl sulphate, (99%), approximately 4.3 g, accurately pre-weighed in vial labelled ‘SDS’.
- Conductivity solution ‘HI 70031’, 20 cm^3 in pouch.

Procedure

(a) You are provided with approximately 4.3 g SDS, accurately pre-weighed in a vial, a 250 cm^3 volumetric flask, a 50 cm^3 burette, 50 cm^3 bulb pipette, a conductivity meter, conductivity solution (used only for calibration), and a tall plastic vessel.

(b) You need to measure the conductivity (σ, in μS cm^{-1}) of various concentrations of aqueous SDS (c, up to 30 mmol dm^{-3}). [Note: You may assume that all volumes are additive.]

3.1 Give the concentration of your stock SDS solution.

3.2 Use the table given in the answer booklet to record your results and plot a suitable graph to determine the critical micelle concentration (CMC) on the paper provided.

3.3 State the concentration at which micelles begin to form (the critical micelle concentration).

Notes

1) Solutions of SDS readily form bubbles if shaken.

2) The conductivity meter needs at least 50 cm^3 of solution to be inside the plastic vessel in order to work correctly.

3) To calibrate the conductivity meter:
   - Switch the meter on by pressing the ON/OFF button once.
   - Press and hold the ON/OFF button again, this time for about 3 seconds, until you see the letters 'CAL' on the screen, indicating that the calibration mode has been entered. Let go of the ON/OFF button and '1413' will start blinking on the display. To calibrate, carry out the next step immediately, before the meter has reverted back to reading '0' on the screen (meaning you have exited the calibration mode)
   - Immerse the probe in the pouch containing the 'HI 70031' calibration solution, without exceeding the maximum immersion level.
   - Stir gently and wait for about 20 seconds to confirm the reading.
   - Once the display stops blinking, the meter is calibrated and ready for use.
   - Rinse the meter with distilled water and dry before making measurements.

4) To record the reading:
   - Switch the meter on by pressing the ON/OFF button.
   - Immerse the probe in the sample without exceeding the maximum immersion level and being above the minimum immersion level.

- Stir gently and wait for the reading to stabilize. The meter automatically compensates for temperature variations.
- The conductivity value of the sample will be shown on the LCD.

SOLUTION

3.1 Correct concentration with correct units is expected - full points.

Correct concentration but with missing or incorrect units - 1/2 points.

Note:

The evaluation of the graphs, constructed by competitors in this practical problem, differs from that used for grading especially titration results in the other practical problems. That is the reason why the evaluation in this particular case is given here more in detail.

3.2 Number and spread of data points

The graph should show two distinct gradients and the point at which the gradients change is the critical micelle concentration (CMC). The region where the concentrations are lower than the point at which the gradients change is referred to as "Region 1"; "Region 2" refers to the region where the concentrations are higher than this point. The gradient change will be taken from the data presented. If no gradient change is obvious the literature value of 8.3 mmol dm^{-3} will be used to distinguish between the two Sections.

Maximum marks are allotted if:

a) in Region 1 at least three points are distributed with a spacing of approx CMC/(n+1) mmol (where n is the number of points).

b) in Region 2 at least three points are distributed through a range of at least 10 mmol with a spacing of approx c/(n+1) mmol (where n is the number of points and c the concentration range and $c \geq$ 10 mmol dm^{-3}).

Indicating gradients

Straight lines plotted through experimental points with different gradients and extended to identify crossing points are expected.

Alternative graphs with marks allotted are shown below.

Accuracy of data

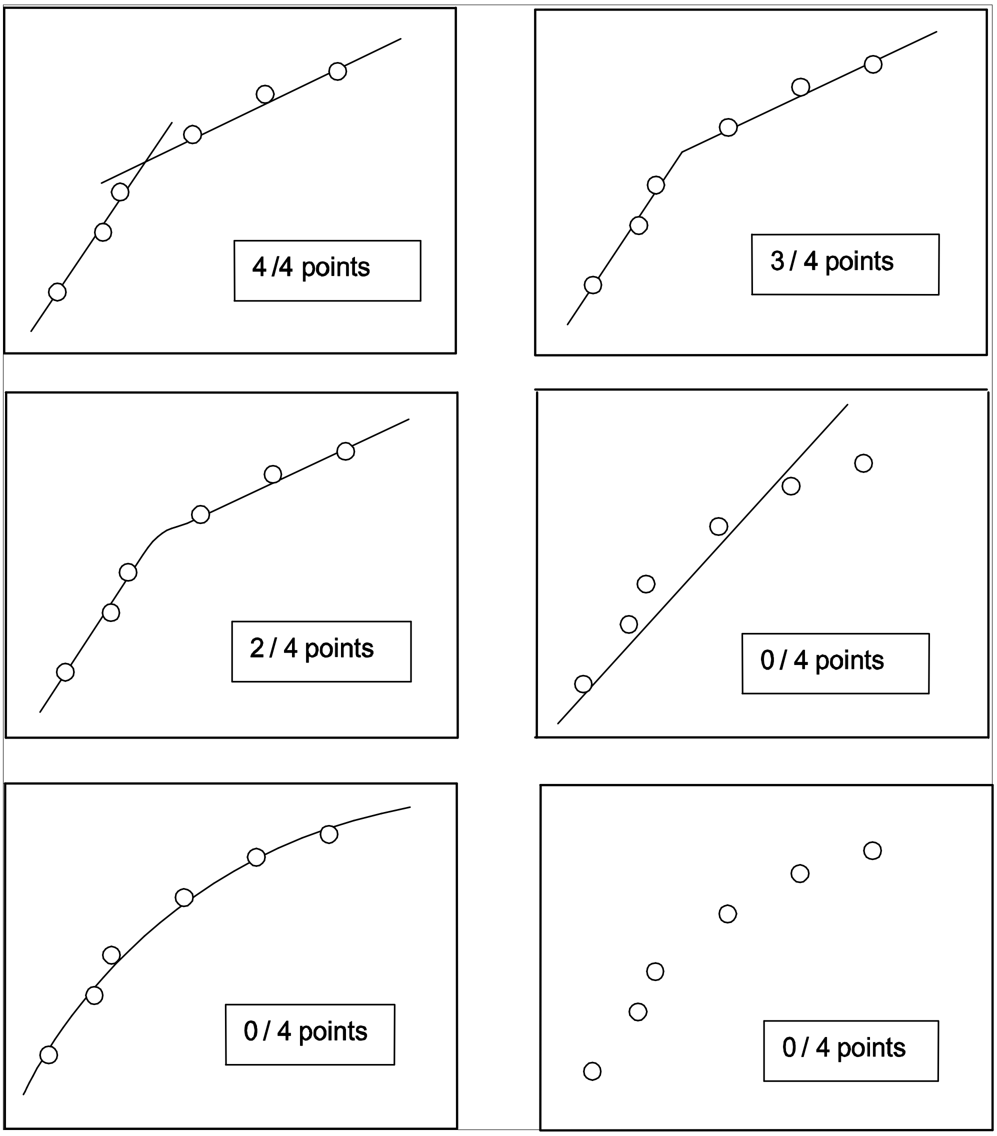
A transparent overlay will be used to judge the accuracy of the experimental measurements as plotted on the graph. If a systematic error in calculation can be determined from the table of data the graph will be re-plotted by the organisers for the purposes of this part of the marking.

The overlay has a number of bands marked and the marking scheme has been devised to reward careful experimental technique. There is one set of bands for Region 1 and another for Region 2. The bands are numbered from the innermost (band 1) to the outermost (band 5) (see Fig. 3.1).

The maximum number of points for each band is shown in the following table:

Band	1	2	3	4	5	Outside 5
Maximum number of points	10	8	6	4	2	0

Alternative graphs with marks allotted

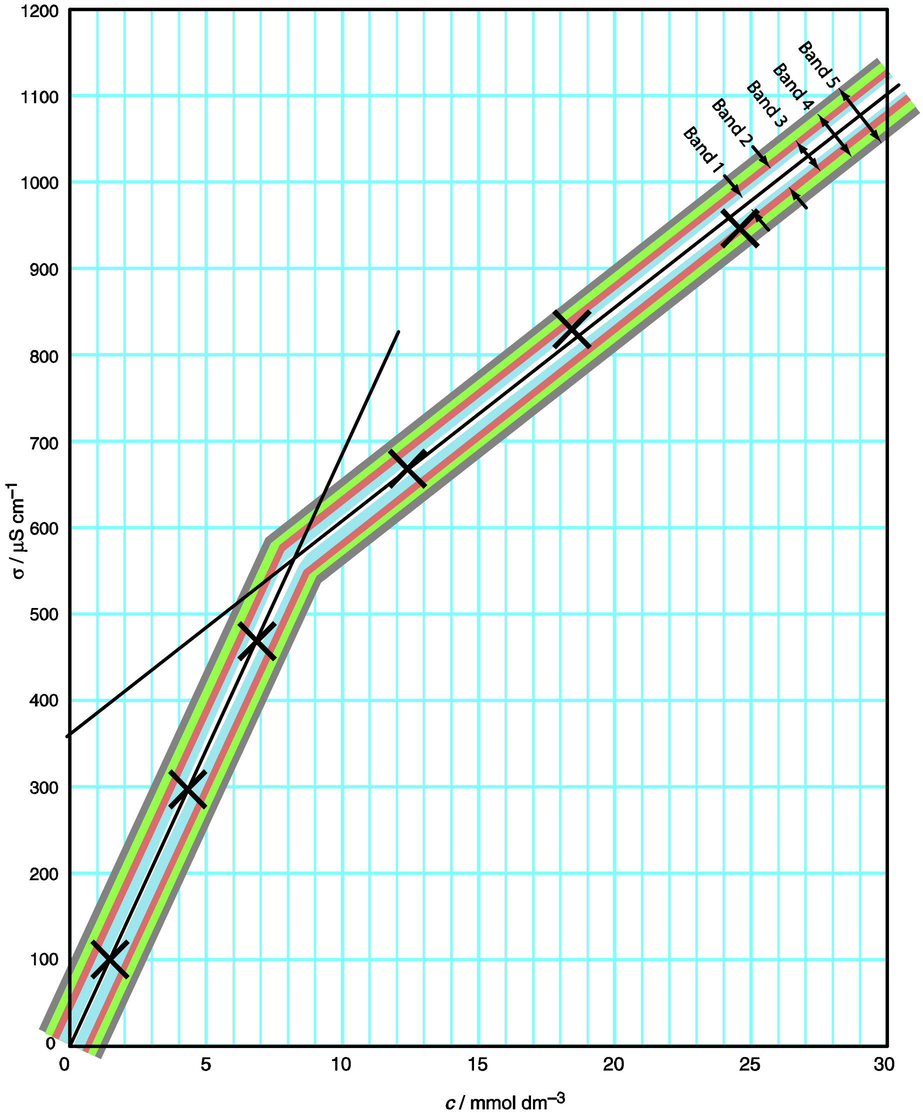


Points will be awarded as follows:

If there are three or more points in a Region and 50 % are in band *m* (where *m* is the number of the band) with none falling in band *m*+2 or beyond, the full marks for band *m* are awarded.

If *n*, the number of points in the Region, is less than 3, only (*n*/3) of the relevant band marks will be given (and rounded up to the nearest half-integer when necessary).

Fig. 3.1. Examples



In Region 1 all of the datapoints lie in Band 1 (cross hatched) so 10 points scored for that Region.

In section 2 one of the three datapoints lies in Band 1 (not 50%) but two lie in band 2. The remaining point does not lie in Band 4 (*m*+2) so full 8 points are scored.

3.3 Correct concentration as read from graph with correct units is expected.

PROBLEM 2 (practical)

Determination of the content of phosphoric acid in a cola drink

Apparatus:

500 ml round-bottom flask with stirrer, reflux condenser, heating mantle, magnetic stirrer, water bath.

Preparation of the sample:

The content of a cola drink bottle is stirred for two or three minutes in a round-bottom flask. Afterwards, 6.0 g powdered active charcoal are added. The entire suspension is carefully heated to reflux and is maintained there for ten minutes. The glass joint of the reflux condenser must not be greased!

The heating mantle is then exchanged with an ice water bath. After the sample has been cooled to 20 °C, it is filtered through a double fluted filter paper. The initial filtrate should be recycled several times.

Adjustment of the pH-meter:

The pH-meter is adjusted to the working electrode by using two buffer solutions.

Titration:

150 ml of the unknown solution are titrated using pH indication with a standardized sodium hydroxide solution ($c(\text{NaOH}) = 0.0500 \text{ mol dm}^{-3}$).

The first equivalence point of the phosphoric acid is reached after about 6 ml of the NaOH solution have been consumed. The titration is to be continued until more than about 12 ml of sodium hydroxide solution have been added.

Results of the experiment:

a) Draw the titration curve and determine the first equivalence point.

b) Determine the pH value of the heated cola drink and the pH value at the first equivalence point.

c) Calculate the concentration of phosphoric acid in the cola drink. Write the calculation and the result in your report.

Interpretation of the experiment:

1. Describe and explain your observations during the titration.
2. Is it possible that the active charcoal could have influenced your titration result? Give reasons for your presumption.

Chemicals:

Powdered active charcoal
Sodium hydroxide solution; c(NaOH) = 0.0500 mol dm^{-3}
Buffer solutions

PROBLEM 2 (practical)

By thermometric titration of a hypochlorite solution with a solution of propanone you will find the equivalent amounts of the reactants and consequently, the reaction products.

Procedure:

For the reaction of a hypochlorite solution with a propanone use solutions tempered at laboratory temperature (check). Put 100,0 cm^3 of a hypochlorite solution into a thermobeaker, insert a thermometer and keep adding a 4-molar solution of propanone in 1,0 cm^3 portions from burette, stirring the reaction mixture continuously by means of the thermometer (carefully, do not break!). Stir the reaction mixture thoroughly after each addition and read the highest temperature reached. Keep on adding the propanone solution as long as the temperature rises. Then add three more portions and finish the experiment. Keep the reaction mixture for possible later use.

Problems:

2.1 Draw a titration curve from the data of the temperature changes and consumption of propanone solution. Read the end point of the titration from the curve. Express the equivalent amounts of the reactants in moles.

2.2 Write equation for the chemical reaction and name the product that is formed.

2.3 Suggest a calculation for the approximate value of the reaction heat from the data obtained.

2.4 Consider the procedure of isolation of the product from the reaction mixture and give the method of its identification.

2.5 The exact concentration of a hypochlorite solution can also by determined by measuring the volume of oxygen released after catalytic decomposition of hypochlorite. Illustrate the principle of this method by means of a chemical equation and show schematically the procedure for the calculation.

SOLUTION

2.2 $$CH_3COCH_3 + 3\ ClO^- \rightarrow \underset{\text{chloroform}}{CHCl_3} + 2\ OH^- + CH_3COO^-$$

2.3 Calculation of heat evolved in the course of the reaction:

$Q = m\, c\, \Delta t$

Q – reaction heat,

m – mass of the solution,

c – specific heat capacity of the solutions taking part in the reaction,

Δt – temperature difference (elevation of temperature)

On the basis of the data obtained in the task, it is possible to calculate Q value per one mole of reactant.

2.4 The mixture contains:

reactants – (excess of about 3 cm^3 of the 4-molar propanone solution),

products – $CHCl_3$, OH^-, CH_3COO^-.

Acetone and chloroform are separated from other substances in the aqueous solution by means of a separatory funnel and a subsequent distillation.

Identification of chloroform: smell, density.

2.5 $2\ ClO^- \rightarrow O_2$

$2\text{ mol} \rightarrow 1\text{ mol} = 22.4\text{ dm}^3$

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Four aqueous solutions are available on the laboratory desk. These are solutions of HCl, NaOH, NH_3, and CH_3COOH whose concentrations are approximately 1 mol dm^{-3}. The concentration of HCl solution is the only one that is exactly determined and known.

Using the volumetric solution of HCl, determine the exact concentrations of the other solutions. A burette, pipette, titration flasks and indicators methyl orange and phenolphthalein are at your disposal. Perform twice each titration and calculate the mean value for concentration. The third determination is needed to be carried out only in such a case when the results of the previous two titrations differ more than by 2 %.

Now you will perform the following thermochemical measurements of neutralisation heat evolved in the reactions of the above given solutions of acids and bases:

a) Measure quantitatively exactly 50.0 cm^3 of the hydrochloric acid solution into a beaker. Measure into another equal beaker a volume of NaOH solution that contains such a number of moles of NaOH as that of HCl being present in the first beaker. Then measure the temperatures of both solutions with a precision of 0.2 K. Pour quickly the content of the first beaker into the other using the thermometers as a glass stick and stir the resulting solution with the thermometer. Determine the final highest temperature of the mixture.

b) Perform analogous measurement with the following pairs of acids and bases:
HCl – NH_3, CH_3COOH – NaOH, CH_3COOH – NH_3.

Problems:

1.1 What indicators have been used for the individual determinations? Give approximately pH regions in which the mentioned indicators show colour transitions. Give reasons for the use of the individual indicators using only ionic equations for the reactions which are characteristic of specific properties of salts being formed in the individual neutralisation reactions. Calculate the concentrations of all solutions under investigations.

1.2 Write the calorimetric equation in its general form by means of which the neutralisation heat can be calculated. Calculate the thermal effect for each neutralisation reaction under investigation and give the value in relation to one mole of the water formed.

Densities of the solutions are as follows:

$\rho(HCl) = 1.02$ g cm^{-3}
$\rho(NaOH) = 1.04$ g cm^{-3}
$\rho(NH_3) = 0.99$ g cm^{-3}
$\rho(CH_3COOH) = 1.01$ g cm^{-3}

In the calculations consider the specific heat capacity value for the solutions equal to 4.19 J g^{-1} K^{-1} whereas the heat capacity of glass and thermometer may be neglected.

1.3. Have you obtained equal results in all four cases? If not, order the particular reaction systems according to the decreasing value of reaction heat. What reactions cause the above mentioned differences? Express the reactions by means of chemical equations.

1.4 The exact methods showed that neutralisation heat in the reaction of the strong acid with a strong base (i. e. the reaction heat when 1 mole of water is formed from H^+ and OH^- ions) is equal to 57.57 kJ mol^{-1}. Calculate the relative error of your determination.

SOLUTION

1.1. In titrating a strong acid with a strong base, both phenolphthalein and methyl orange can be used as acid-base indicators. The drop on the titration curve covers the colour changes of both indicators (pH values from 4 – 10).

Only phenolphthalein can be used in the case when a weak acid is titrated with a strong base because the neutralisation occurs at higher pH values (the colour transition of phenolphthalein is in the region of pH = 8 – 10). A salt formed undergoes hydrolysis (more precisely its anion) and the solution exhibits a basic reaction:

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

In titrating a strong acid with a weak base or vice versa, methyl orange is used (pH = 3 – 4.5) and due to hydrolysis the resulting solution shows an acidic reaction:

$$NH_4^+ + 2\,H_2O \rightleftharpoons NH_3\,.\,H_2O + H_3O^+$$

The exact concentrations of the aqueous solutions of sodium hydroxide and ammonia are determined by titrations with the volumetric solution of hydrochloric acid. The exact concentration of the acetic acid solution is then determined by a titration with the sodium hydroxide solution.

1.2 When the specific heat capacities of glass and thermometer are neglected the neutralisation heat can be then calculated according to a simple relation:

$\Delta H_{neutr.} = (m_1 + m_2)\, c\, (T_2 - T_1)$

m_1 – mass of the first solution,

m_2 – mass of the second solution,

c – specific heat capacity of the solutions,

T_1 – temperatures of the solutions before mixing,

T_2 – temperatures of the solutions after mixing.

If the temperatures of the solutions before mixing are not equal then T_1 will be the mean temperature of both. Finally, the neutralisation heat value should be related to 1 mole of water formed.

1.3 The results obtained for the neutralisation of a strong base with a weak acid and vice versa, as well as for the reaction of a weak acid with a weak base, are lower than those obtained for the neutralisation of a strong acid with a strong base. A part of the heat is consumed for ionisation of a weak electrolyte:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

A similar equation can be written for $NH_3.H_2O$.

PROBLEM 2 (practical)

You are required to estimate the heat (enthalpy) change on mixing a series of 5 liquids to produce equimolar mixtures and to explain the temperature changes.

Procedure:

1. A mixture of trichloromethane (chloroform) and propanone (acetone)

Measure 0.5 mol of trichloromethane in the measuring cylinder labelled A_1 and measure its temperature. Dry the thermometer with a piece of tissue paper. Measure 0.5 mol of propanone using measuring cylinder B_1, pour it into a beaker and measure its temperature. Record the average of the two temperatures as temperature t_1 (to 0.1 °C). Leave the thermometer in the beaker. Add the trichloromethane to the propanon, stir the mixture carefully and follow the temperature changes until a maximum or minimum is reached. Record this extreme temperature as temperature t_2. Dispose the mixture into a special bottle labelled "waste solution", dry the reaction beaker and the thermometer and proceed to the next part of the experiment.

2. A mixture of methanol and propanone (acetone)

Measure 0.5 mol of propanone in measuring cylinder B_1 and 0.5 mol of methanol in measuring cylinder A_2, and continue as in part 1.

3. A mixture of methanol and n-hexane

Measure 0.5 mol of methanol into measuring cylinder A_2 and 0.5 mol of hexane into measuring cylinder B_2, and continue as in part 1.

4. A mixture of methanol and water

Measure 0.5 mol of methanol into measuring cylinder A_2, measure its temperature and pour it into the beaker. Rinse the cylinder thoroughly with distilled water and then measure 0.5 mole of water using this measuring cylinder. Continue as instructed in the above part 1.

Tasks:

Calculate the enthalpy (heat) changes involved in the mixings on the basis of the temperature changes observed. In your calculations you should neglect heat exchanges with the surroundings as well as the heat capacity of the beaker and thermometer. Briefly explain your results in terms of the molecular interactions in the pure liquids and in the mixture, preferably using sketches.

Data:

Substance	Relative molecular mass	Density (g cm^{-3})	Molar heat capacity (J K^{-1} mol^{-1})
methanol	32.04	0.79	80.61
chloroform	119.38	1.49	114.94
acetone	58.08	0.79	124.96
n-hexane	86.18	0.66	190.10
water	18.02	1.00	75.35

PROBLEM 3 (Practical)

Determination of molecular mass by viscometry

Viscosity coefficient is a measure of fluid resistance to flow. It can be determined by measuring the rate of liquid flow through a thin capillary. Polymer solution viscosity grows with increasing concentration. At constant concentration, stronger solvent-polymer interactions result in more expanded polymer coils and, therefore, in higher viscosity. Provided the density of the diluted solution of a polymer is equal to that of the solvent, the reduced viscosity η_{red} of the polymer solution with concentration c (g cm^{-3}) is defined as follows:

$$\eta_{\text{red}} = \frac{t - t_0}{t_0 c} \quad \left[\text{cm}^3\ \text{g}^{-1}\right],$$

where t and t_0 are the flow times of the solution and pure solvent, respectively.

Reduced viscosity for dilute polymer solutions depends on concentration as follows:

$$\eta_{red}(c) = [\eta] + kc\ ,$$

with k, a parameter and $[\eta]$, intrinsic viscosity (cm^3 g^{-1}). The intrinsic viscosity $[\eta]$ is determined by extrapolation of the reduced viscosity to zero polymer concentration. In general, the intrinsic viscosity is related to the molecular mass M of the polymer according to the Mark-Kuhn-Houwink equation:

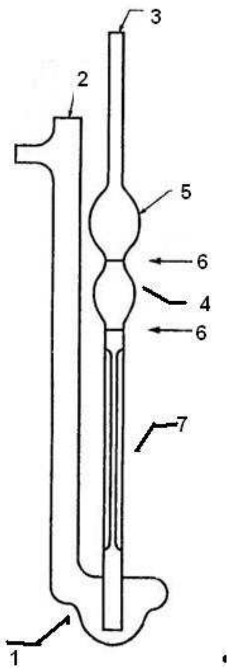
$$[\eta] = K\,M^{\alpha}\ ,$$

where K and α are the constants for a particular solvent–polymer pair at a certain temperature. Thus, M can be derived from the Mark-Kuhn-Houwink equation using experimentally determined $[\eta]$ and reference data for K and α.

How to work with viscometer

a) Mount the viscometer (see the picture below) attached so that its tubing (3) is vertical, and the collection vessel (1) stands on the lab stand basement. Adjust the fixing clamp as low as possible.

b) Put 10 cm^3 of the liquid to be analyzed into the collection vessel (1) through the tubing (2) using a pipette.



1 – collection vessel
2 – supplementary tubing
3 – supplementary tubing
4 – measurement vessel
5 – collection vessel
6 – the match marks
7 - capillary

c) Place the pipette filler or rubber bulb on top of the tubing (3) and suck the liquid into the measurement vessel (4) so that the liquid is drawn into the collection vessel (5). When sucking the liquid, avoid the air bubbles in the capillary (7) and the vessels (4, 5), as these can cause significant experimental errors. The liquid meniscus should be about 10 mm above the upper mark (6).

d) Zero the stopwatch, and remove the pipette filler or bulb out of the tube (3). The liquid starts flowing down to the collection vessel (1).

e) Measure the flow time: start the stopwatch when the liquid meniscus passes the upper match mark (6) and stop the stopwatch when the liquid meniscus passes the lower match mark (6).

ATTENTION: Handle the viscometer with great care!
There will be no replacement if you have broken your viscometer!
If you break your viscometer tell the lab assistant. You may then attempt to do the experiment using the 25 mL pipette and beaker in place of viscometer.

Clean the viscometer three times with tap water and once with distilled water before you pass over to a new polymer sample. To do this, first wash it with tap water, and then rinse with distilled water. There is no need to wash it with the polymer solution, the error can occur but it is negligible.

You are NOT requested to fill in all table cells in the Answer Boxes. Perform as many measurements as you prefer for accurate averaging.

Chemicals

- Poly(vinyl) alcohol, 40 cm^3 each, 5 vials

Procedure

You are provided with a set of aqueous solutions of polymers (0.01 g cm^{-3}, stock solutions). Three of P1-P4 are solutions of poly(vinyl alcohol), whereas the fourth one is that of a partially hydrolyzed poly(vinyl acetate) containing *ca*. 10 % of non-hydrolyzed units. It is unknown which of the P1 – P4 solutions is partially hydrolyzed poly(vinyl acetate). Molecular masses of the polymers P1 – P4 are given in the Table.

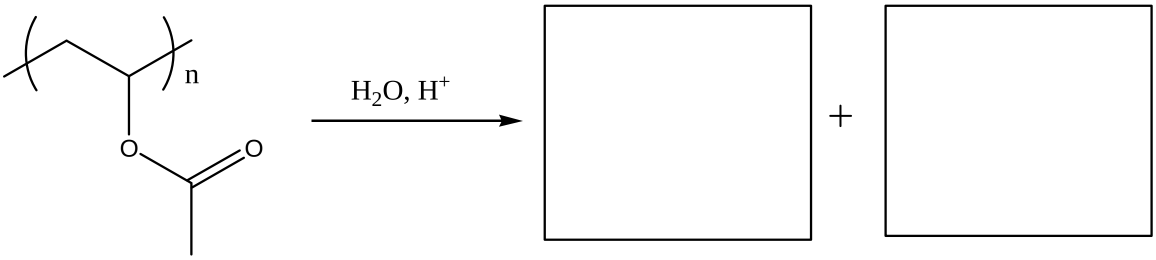
Approximate molecular mass	Sample code
26650	P2
50850	P1
65300	P4
91900	P3

Sample X is poly(vinyl alcohol) of an unknown molecular mass.

In this task you will have to identify which of P1 – P4 is the solution of partially hydrolyzed poly(vinyl acetate) and determine the molecular mass of polymer X.

3.1 Write down the reaction scheme of poly(vinyl alcohol) preparation by hydrolysis of poly(vinyl acetate).

Reaction scheme:



3.2 Choose (tick appropriate box) which polymer shows the stronger interaction with water and compare the viscosities of aqueous solutions of fully and partially hydrolyzed poly(vinyl acetates). Assume that the concentration of the solutions and the molecular masses of the polymers are the same.

Poly(vinyl alcohol) ☐

Partially hydrolyzed poly(vinyl acetate) ☐

Compare the viscosities:

η (poly(vinyl alcohol) _____ η (partially hydrolyzed poly(vinyl acetate)

(put either <. >, or ≈)

3.3 Measure the flow time of the pure solvent (distilled water). You are not requested to fill all the boxes in the answer sheet.

3.4 Measure the flow times of the stock solutions of P1 – P4, and that of X. Calculate the reduced viscosities. You are NOT requested to fill in all table cells in the Answer Boxes. Perform as many measurements as you prefer for accurate averaging.

3.5 Encircle the solution out of P1, P2, P3, P4 which is the sample of partially hydrolyzed poly(vinyl acetate). Hint: Take into account the given molecular masses of the polymers P1 – P4.

Do not use this polymer in the next part of the experiment.

3.6 To determine the parameters of the Mark-Kuhn-Houwink equation and calculate the unknown molecular mass of X choose and encircle two most appropriate solutions of poly(vinyl alcohol) with different molecular masses. Assume that the absolute error of intrinsic viscosity determination does not depend on the sample molar mass.

3.7 Using appropriate measuring glassware to prepare the solutions, measure the flow time of a number of diluted solutions of three poly(vinyl alcohol) samples: that of an unknown molecular mass (X), and the pair of poly(vinyl alcohols) chosen in 3.6, and calculate the corresponding reduced viscosities. When calculating the diluted solutions concentration, assume that density of the polymer solutions is equal to that of water. Determine the intrinsic viscosities for each of the examined samples. Submit the graph paper with your plots together with the booklet. **Note:** if you would like to plot the data referring to different samples on the same plot, make sure you use clearly distinguishable symbols for each dataset. You are NOT requested to fill in all table cells in the answer booklet.

Summary of experimental results (only fill in the measured values)

Sample	P__	P__	X
Concentration (c), g cm^{-3}:	0.01	0.01	0.01
Reduced viscosity (η_{red}), cm^3 g^{-1}			
c (1st dilution), g cm^{-3}:			
η_{red}, cm^3 g^{-1}			
c (2nd dilution), g cm^{-3}:			
η_{red}, cm^3 g^{-1}			
c (3rd dilution), g cm^{-3}:			
η_{red}, cm^3 g^{-1}			
c (4th dilution), g cm^{-3}:			
η_{red}, cm^3 g^{-1}			
c (5th dilution), g cm^{-3}:			
η_{red}, cm^3 g^{-1}			

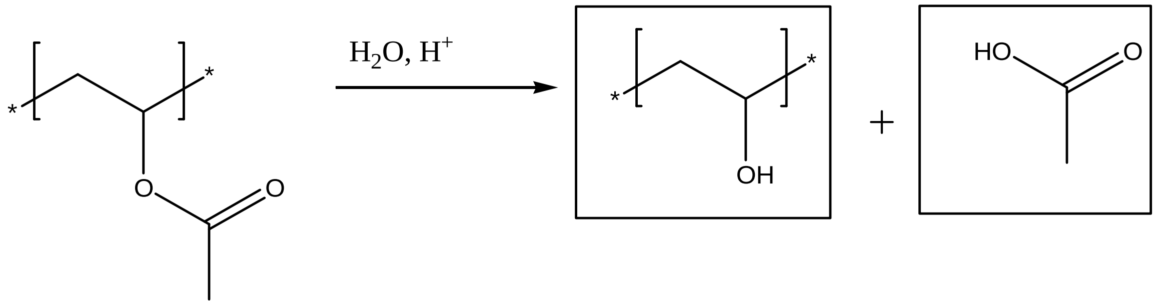
3.8 Write down the form of equation you would use to determine K and α.

Derive the K and α values for the aqueous solution of poly(vinyl alcohol).

3.9 By using the obtained K and α values, as well as the intrinsic viscosity of the X solution, calculate the molecular mass of the polymer X. If you have failed to determine K and α, use K = 0.1 cm^3 g^{-1} and α = 0.5.

SOLUTION

3.1



3.2

Poly(vinyl alcohol) ☑

η (poly(vinyl alcohol) > η (partially hydrolyzed poly(vinyl acetate)

3.8 $\log[\eta] = \log K + \alpha \log M$

3.9 Sample calculation:

$$23.7 = 0.1 \times M^{0.5} \Rightarrow 237 = M^{0.5}$$
$$M = 237^2 = 56169 \approx 56200$$

Sommario