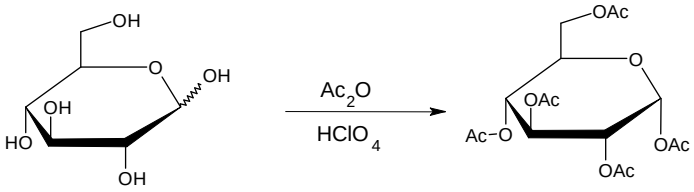
PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis of α-D-glucopyranose pentaacetate

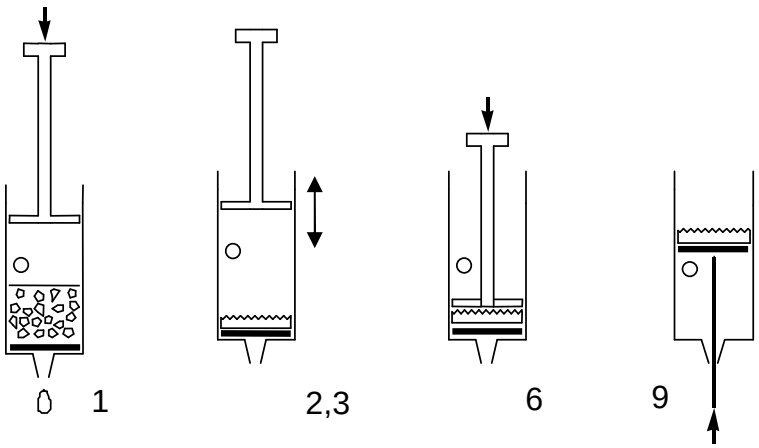


Caution: Use gloves while manipulating acetic acid and acetic anhydride. Let the lab supervisors know if any is spilled.

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



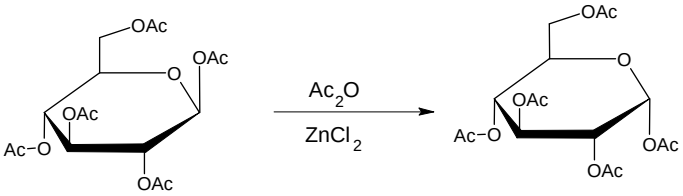
1. Pull out the piston. Fill the syringe from above with the suspension to be filtered. The syringe can be filled to the level of the hole. Replace piston.
2. Cover the hole with your finger and press in the piston as far as the hole.
3. Open the hole and draw the piston back. Do not draw in air through 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).

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:

$$\frac{n(\mathrm{Zn})}{n(\mathrm{Fe(CN)_6})} = \frac{10\, c(\mathrm{Zn})\, V_2\, M}{m}$$

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 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 °C. 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.

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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 ammo-nia	—	—	—	—	—
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^-**.