

Name:

Code: XXX-

# Task 1

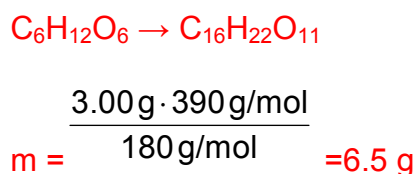
# 10% of the total

|    |    |    |    |        |
|----|----|----|----|--------|
| 1a | 1b | 1c | 1d | Task 1 |
| 30 | 2  | 12 | 4  | 48     |
|    |    |    |    |        |

a) Yield of the product in g, measured by the organizer:

The samples are dried by the organisers. Full pts for a 60-100% yield, linear scale between 0-60% yield. 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.  
If there is a considerable (easily visible) amount of insoluble material or impurity on the TLC plate, then 0 point is received for the yield (only possible in case of intentional contamination).  
5 points off if filter disc is submitted.

b) Calculate the theoretical yield of your product in g.



Theoretical yield:

c) Sketch your developed TLC plate and leave on your desk to be evaluated,

If both standards and all samples are present and labeled: 5 pts  
If any sample is missing: 2 pts, if more than one is missing: 0 pt.  
Loading of the plate: if over- or underloading does not interfere with the evaluability: 4 pts, if interfering, but evaluation is still possible: 2 pts, if evaluation is not possible: 0 pt  
If the development is appropriate (minor tilting is acceptable): 3 pts. If erratically developed, but still evaluable (the two isomers separate): 1 pt, otherwise 0 pt.

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d) **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  $\beta$ -D-glucopyranose pentaacetate can be used for the preparation of pure  $\alpha$ -D-glucopyranose pentaacetate.

- a) Yes
- b) No
- c) Cannot be decided based on these experiments

Solutions: a, a (2 pts. each)

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## Task 2

15 % of the total

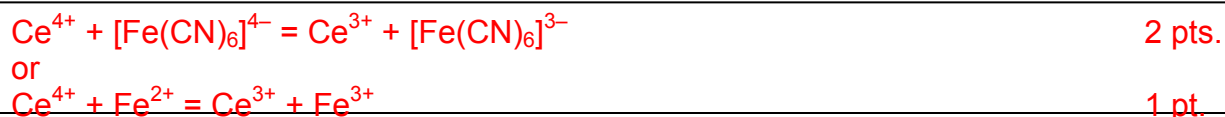
|    |    |    |    |    |        |
|----|----|----|----|----|--------|
| 2a | 2b | 2c | 2d | 2e | Task 2 |
| 25 | 4  | 25 | 6  | 5  | 65     |
|    |    |    |    |    |        |

a)  $\text{Ce}^{4+}$  consumptions:

Full marks (25 pts.) if  $V_1$  is within  $0.15 \text{ cm}^3$  of the expected value recalculated from the  $\text{K}_4[\text{Fe}(\text{CN})_6]$  mass. Zero marks if deviation is more than  $0.50 \text{ cm}^3$ . Linear scale is applied in between.

Average volume consumed ( $V_1$ ):

b) The titration reaction:



Calculation of sample mass:

$$m = c_{\text{Ce}} V_1 10 \cdot M \quad 2 \text{ pts.}$$

Actual sample masses will be distributed with the exam copies.

$\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  mass ( $m$ ):

c) Zinc consumptions:

Full marks (25 pts.) if  $V_2$  is within  $0.15 \text{ cm}^3$  of the expected value recalculated from  $\text{K}_4[\text{Fe}(\text{CN})_6]$  mass, zinc concentrations and empirical ratio. Zero marks if the deviation is more than  $0.50 \text{ cm}^3$ . Linear scale is applied in between.

Average volume consumed ( $V_2$ ):

d) Mark the correct answer.

The diphenyl amine indicator changes in colour at the end point

- a) because the concentration of the  $\text{Zn}^{2+}$  ions increases.
- b) because the concentration of the  $[\text{Fe}(\text{CN})_6]^{4-}$  ions decreases.
- c) because the concentration of the  $[\text{Fe}(\text{CN})_6]^{3-}$  ions increases.
- d) because the indicator is liberated from its complex.

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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

Solutions: b, b, a (2 pts. each)

e) Determine the formula of the precipitate. Show your work.

The mole ratio of the zinc:hexacyanoferrate(II) in the precipitate can be evaluated as:

$$n_{\text{Zn}}/n_{\text{Fe(CN)}_6} = \frac{10c_{\text{Zn}}V_2M}{m}$$

Values for  $c_{\text{Zn}}$  are distributed according to country color (found on seating plan)  
Red/Pink: 0.0500    Green: 0.0450    Blue: 0.0475    Yellow/Ivory: 0.0525

The empirical ratio obtained from the experiments is 1.489.

Calculating the zinc/hexacyanoferrate(II) ratio:

3 pts.

Cations are needed to make the precipitate neutral and only potassium is present.

The precipitate is  $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ .

2 pts.

Any other reasonable calculation giving the same result is accepted.

Hydrogen instead of potassium ( $\text{H}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$  or  $\text{KHZn}_3[\text{Fe}(\text{CN})_6]_2$ ) is also acceptable.

Mistakes in units, dilution factors, significant figures (not 3 or 4 in 2b) carry a penalty of 1 pt. in each calculation.

The formula of the precipitate:

Items replaced or refilled:

Student signature:

Supervisor signature:

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**Task 3****15 % of the total**

|        |
|--------|
| Task 3 |
| 108    |
|        |

Only fill out this table when you are ready with all your assignments.

|        | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|--------|---|---|---|---|---|---|---|---|
| Cation |   |   |   |   |   |   |   |   |
| Anion  |   |   |   |   |   |   |   |   |

6 pts for each correctly identified ion except for  $\text{HCO}_3^-$  and  $\text{HS}^-$  which are worth 12 pts, bringing up the total to 108 points.

Partial points will be awarded in the following cases:

Anions:

$\text{AgNO}_3$ : Full points if  $\text{NO}_3^-$  is the only anion shown. 3 pts for  $\text{ClO}_4^-$  only. 3 pts if fluoride appears together with nitrate and/or perchlorate. Otherwise 0 pt.

$\text{Pb}(\text{CH}_3\text{COO})_2$ : 3 pts if  $\text{NO}_3^-$  and/or  $\text{ClO}_4^-$  appear together with  $\text{CH}_3\text{COO}^-$ . 1 pt for nitrate and/or perchlorate on their own. Otherwise 0 pt.

3 pts for  $\text{CO}_3^{2-}$  instead of  $\text{HCO}_3^-$ , and for  $\text{S}^{2-}$  instead of  $\text{HS}^-$ .

Cations:

In the case of all alkali metal compounds, 2 pts for an incorrect alkali metal.

1 pt for  $\text{Ca}^{2+}$  or  $\text{Sr}^{2+}$  instead of  $\text{Ba}^{2+}$ .

# Solution

The solutions received by the students contain the following compounds. The country colours can be found on the laboratory seating plan.

| Country colour | 1                                | 2                                | 3                                | 4                                | 5                                | 6                                | 7                                | 8                                |
|----------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| Blue           | AgNO <sub>3</sub>                | KHCO <sub>3</sub>                | NH <sub>4</sub> ClO <sub>4</sub> | NaOH                             | NaHS                             | Pb(OAc) <sub>2</sub>             | BaI <sub>2</sub>                 | MgSO <sub>4</sub>                |
| Green          | Pb(OAc) <sub>2</sub>             | NH <sub>4</sub> ClO <sub>4</sub> | NaOH                             | NaHS                             | MgSO <sub>4</sub>                | KHCO <sub>3</sub>                | AgNO <sub>3</sub>                | BaI <sub>2</sub>                 |
| Ivory          | NH <sub>4</sub> ClO <sub>4</sub> | Pb(OAc) <sub>2</sub>             | KHCO <sub>3</sub>                | BaI <sub>2</sub>                 | AgNO <sub>3</sub>                | MgSO <sub>4</sub>                | NaHS                             | NaOH                             |
| L.Blue         | NaHS                             | MgSO <sub>4</sub>                | BaI <sub>2</sub>                 | NH <sub>4</sub> ClO <sub>4</sub> | Pb(OAc) <sub>2</sub>             | AgNO <sub>3</sub>                | NaOH                             | KHCO <sub>3</sub>                |
| L.Green        | BaI <sub>2</sub>                 | NaHS                             | MgSO <sub>4</sub>                | AgNO <sub>3</sub>                | NaOH                             | NH <sub>4</sub> ClO <sub>4</sub> | KHCO <sub>3</sub>                | Pb(OAc) <sub>2</sub>             |
| Pink           | MgSO <sub>4</sub>                | NaOH                             | AgNO <sub>3</sub>                | Pb(OAc) <sub>2</sub>             | KHCO <sub>3</sub>                | BaI <sub>2</sub>                 | NH <sub>4</sub> ClO <sub>4</sub> | NaHS                             |
| Red            | NaOH                             | BaI <sub>2</sub>                 | Pb(OAc) <sub>2</sub>             | KHCO <sub>3</sub>                | NH <sub>4</sub> ClO <sub>4</sub> | NaHS                             | MgSO <sub>4</sub>                | AgNO <sub>3</sub>                |
| Yellow         | KHCO <sub>3</sub>                | AgNO <sub>3</sub>                | NaHS                             | MgSO <sub>4</sub>                | BaI <sub>2</sub>                 | NaOH                             | Pb(OAc) <sub>2</sub>             | NH <sub>4</sub> ClO <sub>4</sub> |

The problem can be approached in many ways. Intuition is very helpful in the tentative assignment of some compounds in the early phases of the work. A systematic solution is given here for the blue Country colour.

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<sup>3+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and MnO<sub>4</sub><sup>-</sup>. (In principle we should also exclude Mn<sup>2+</sup> 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<sup>+</sup>, Sn<sup>2+</sup>, Sn<sup>4+</sup>, Sb<sup>3+</sup>, Bi<sup>3+</sup>, and HSO<sub>4</sub><sup>-</sup> 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<sub>4</sub><sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Sr<sup>2+</sup>, Ag<sup>+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>.

Anions: OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, HPO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, S<sup>2-</sup>, HS<sup>-</sup>, Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>.

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

|  | <b>1</b><br>AgNO <sub>3</sub>                              | <b>2</b><br>KHCO <sub>3</sub>                       | <b>3</b><br>NH <sub>4</sub> ClO <sub>4</sub>                              | <b>4</b><br>NaOH   | <b>5</b><br>NaHS   | <b>6</b><br>Pb(OAc) <sub>2</sub> | <b>7</b><br>BaI <sub>2</sub> | <b>8</b><br>MgSO <sub>4</sub> |
|--|--|---|---|--------------------|--------------------|----------------------------------|------------------------------|-------------------------------|
| <b>1</b><br>AgNO <sub>3</sub>                | —  | —   | —   | —                  | —                  | —                                | —                            | —                             |
| <b>2</b><br>KHCO <sub>3</sub>                | $\downarrow$ light yellow<br>$\uparrow$ neutral, odourless | —   | —   | —                  | —                  | —                                | —                            | —                             |
| <b>3</b><br>NH <sub>4</sub> ClO <sub>4</sub> | no change  | $\downarrow$ white crystals (*)                     | —   | —                  | —                  | —                                | —                            | —                             |
| <b>4</b><br>NaOH                             | $\downarrow$ brown-black                                   | no change   | boiling:<br>$\uparrow$ basic, odour of ammonia                            | —                  | —                  | —                                | —                            | —                             |
| <b>5</b><br>NaHS                             | $\downarrow$ black solution turns acidic                   | no change   | boiling:<br>$\uparrow$ basic, odour of NH <sub>3</sub> , H <sub>2</sub> S | no change          | —                  | —                                | —                            | —                             |
| <b>6</b><br>Pb(OAc) <sub>2</sub>             | $\downarrow$ white crystals                                | $\downarrow$ white<br>$\uparrow$ neutral, odourless | no change   | $\downarrow$ white | $\downarrow$ black | —                                | —                            | —                             |
| <b>7</b><br>BaI <sub>2</sub>                 | $\downarrow$ yellow  | $\downarrow$ white<br>$\uparrow$ (**)               | no change   | no change          | no change          | $\downarrow$ yellow              | —                            | —                             |
| <b>8</b><br>MgSO <sub>4</sub>                | $\downarrow$ white crystals                                | no change (***)                                     | no change   | $\downarrow$ white | no change (****)   | $\downarrow$ white               | $\downarrow$ white           | —                             |

(\*): upon boiling, the formation of NH<sub>3</sub> is detectable by its odour and by pH paper.

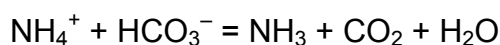
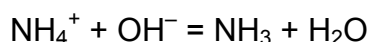
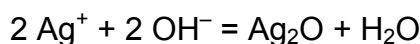
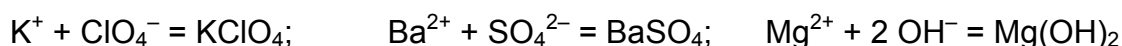
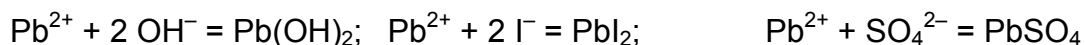
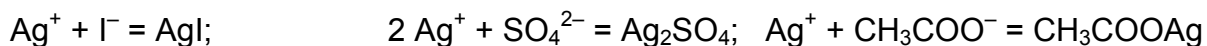
(\*\*): gas bubbles are usually not observed when **2** is in excess.

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

(\*\*\*\*): upon boiling, a white precipitate forms and the odour of H<sub>2</sub>S appears.



$\text{Mg}^{2+} + 2 \text{HCO}_3^- = \text{MgCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$  (more accurately, basic carbonates of variable composition are formed)



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  $\text{CO}_2$ . Thus **2** contains  $\text{CO}_3^{2-}$  or  $\text{HCO}_3^-$ .

Second, there are only 3 dark precipitates that can form from the given ions:  $\text{Ag}_2\text{O}$ ,  $\text{Ag}_2\text{S}$ , and  $\text{PbS}$ . This fact, together with the pH of the solutions, instantly identifies the cation of **1** as  $\text{Ag}^+$ , the cation of **6** as  $\text{Pb}^{2+}$ , the anion of **4** as  $\text{OH}^-$ , 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  $\text{HS}^-$ .

The evolution of  $\text{CO}_2$  in the reaction with  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  also identifies the anion of **2** as  $\text{HCO}_3^-$ . (in accord with the moderately basic pH)

The reaction of **3** and **4** yields ammonia. **4** is obviously not a solution of  $\text{NH}_3$  itself. Thus the cation of **3** is  $\text{NH}_4^+$ .

**2+4** do not form either a precipitate or ammonia. The cations of **2** and **4** are  $\text{Na}^+$  or  $\text{K}^+$ .

**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  $\text{Ag}^+$ . Accordingly, it can be ammonium nitrate, fluoride, or perchlorate. But it does give a precipitate with **2**, a hydrocarbonate of  $\text{Na}^+$  or  $\text{K}^+$ . Thus the anion of **3** is  $\text{ClO}_4^-$  and the cation of **2** is  $\text{K}^+$ .

**4** does not give a precipitate with  $\text{NH}_4\text{ClO}_4$ . The cation of **4** is  $\text{Na}^+$ .

**5** does not give a precipitate either with  $\text{NH}_4\text{ClO}_4$  ( $\text{K}^+$ ) or with a mixture of  $\text{KHCO}_3$  and  $\text{NaOH}$  ( $\text{Li}^+$ ). The cation of **5** is  $\text{Na}^+$ .

**7** forms no precipitate or ammonia with  $\text{NaOH}$  but gives a precipitate with  $\text{KHCO}_3$ . **7** cannot be an alkali metal perchlorate because it forms yellow precipitates with **1** and **6**. Thus the cation of **7** is  $\text{Ba}^{2+}$  and the anion of **7** is  $\text{I}^-$ .

At room temperature **8** gives a precipitate with  $\text{OH}^-$  but not with  $\text{HS}^-$  which means it can only be a salt of a Group 2A metal. Thus the reaction of **8** with  $\text{BaI}_2$  is obviously one



between  $\text{Ba}^{2+}$  and the anion of **8**. The latter is very likely  $\text{SO}_4^{2-}$  but  $\text{HCO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  are also theoretically possible. The solution of **8** is unchanged upon boiling and gives a white precipitate with  $\text{Ag}^+$ . This excludes both  $\text{HCO}_3^-$  and  $\text{H}_2\text{PO}_4^-$ . Thus the anion of **8** is  $\text{SO}_4^{2-}$ . This instantly identifies the cation of **8** as  $\text{Mg}^{2+}$ .

**6** is a soluble compound of lead. The anion could be  $\text{CH}_3\text{COO}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , or  $\text{ClO}_4^-$ . The slight odour of acetic acid might give a clue. Unlike **1**, the reaction of an excess of **6** with  $\text{HS}^-$  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  $\text{Ag}^+$ . It would also react with  $\text{NH}_4\text{ClO}_4$  upon heating with the evolution of  $\text{N}_2$  (and nitrogen oxides from the reaction with  $\text{HS}^-$  would also be noticeable). The absence of these reactions indicates that the anion of **6** is  $\text{CH}_3\text{COO}^-$ .

Soluble salts of silver are even less numerous, the only choices are  $\text{NO}_3^-$ ,  $\text{F}^-$ , and  $\text{ClO}_4^-$ . The anion can be examined if one removes the silver ions from the solution of **1** with an excess of  $\text{NaOH}$ . The  $\text{Ag}_2\text{O}$  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  $\text{BaI}_2$  which rules out  $\text{F}^-$ . The solubility of  $\text{KClO}_4$  is quite significant; therefore the absence of a precipitate with  $\text{KHCO}_3$  is inconclusive. The anion of **1** is therefore either  $\text{NO}_3^-$  or  $\text{ClO}_4^-$ .