NATIONAL CHEMISTRY OLYMPIAD 2023
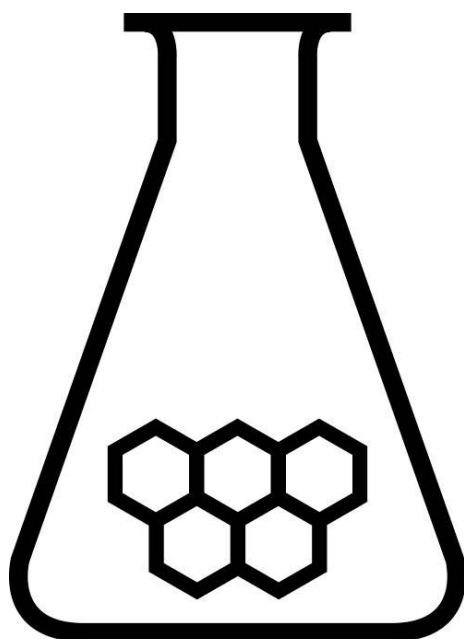
ASSIGNMENTS PRELIMINARY ROUND 2
To be conducted from March 20 until March 24 2023

- This preliminary round consists of 20 multiple choice questions divided over 8 topics and 3 problems with a total of 17 open questions as well as an answer sheet for the multiple choice questions.
- Use the answer sheet to answer the multiple choice questions.
- Use for each problem with open questions a separate answer sheet. Don't forget to write your name on it.
- The maximum score for this work is 94 points.
- The preliminary round lasts a maximum of 3 clock hours.
- Required materials: (graphic) calculator and BINAS 6th edition or ScienceData 1st edition or BINAS 5th edition, English version.
- For each question the number of points you can score are given.
- Unless otherwise stated, standard conditions apply: T = 298 K and $p = p_0$.

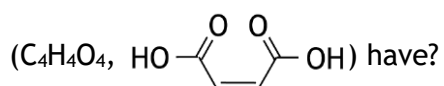## Problem 1 Multiple-choice questions   (total 40 points)

For each question, write your answer (letter) on the answer sheet. This answer sheet can be found at the end of this examination booklet.
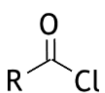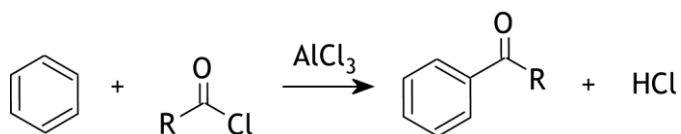**Score: 2 points for each correct answer.**

Carbon chemistry

1   How many σ bonds and how many π bonds does a molecule of maleic acid

$(C_4H_4O_4,$) have?

	number of σ bonds	number of π bonds
A	4	6
B	6	3
C	6	6
D	7	3
E	8	3
F	8	6
G	9	3
H	9	6
I	11	3
J	11	6

2

When an acyl chloride, , reacts with benzene

using $AlCl_3$ as a catalyst, the following reaction occurs:


What kind of reaction is this?

A   addition
B   condensation
C   elimination
D   substitution

3   Someone wants to make anisole (methoxybenzene). He has devised the following two methods for this:

Method I: a reaction of phenol (hydroxybenzene) with bromomethane in alkaline conditions. After the base has accepted a proton from a phenol molecule, the following reaction should occur:
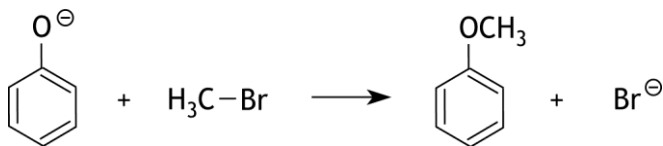
Method II: a reaction of bromobenzene with methanol under the influence of a very strong base. After the base has accepted a proton from a methanol molecule, the following reaction should occur:
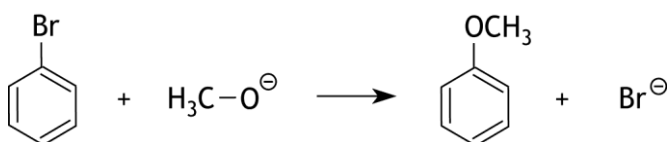
Which method(s) is(are) suitable?

A   neither method
B   method I only
C   method II only
D   both methods

Structures and formulae

4   What is the formal charge of the sulfur atom in the Lewis structure of SO_2 in which all atoms follow the octet rule?

A   4−
B   2−
C   1−
D   1+
E   2+
F   4+

5   The unit cell of the metal gold is a face-centered cube, FCC, see figure below.
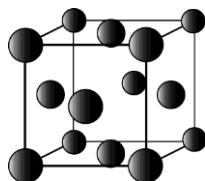
The density of gold is $19.3 \cdot 10^3$ kg m^{-3}.

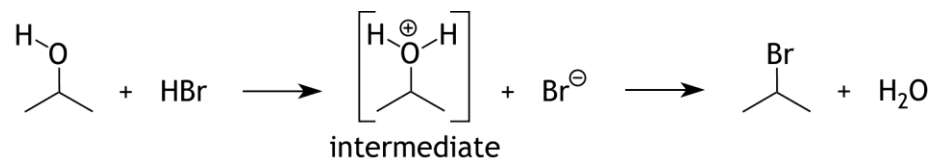What is the smallest distance between the nuclei of two gold atoms?

A $1.44 \cdot 10^{-10}$ m
B $2.88 \cdot 10^{-10}$ m
C $4.08 \cdot 10^{-10}$ m
D $5.77 \cdot 10^{-10}$ m

6   In the reaction between propan-2-ol and hydrogen bromide, 2-bromopropane is formed. First, an alcohol molecule is protonated, creating an intermediate:

What is the hybridization of the O atom in a molecule of propan-2-ol and in the intermediate?

	in a molecule of propan-2-ol	in the intermediate
A	sp	sp
B	sp	sp^2
C	sp	sp^3
D	sp^2	sp
E	sp^2	sp^2
F	sp^2	sp^3
G	sp^3	sp
H	sp^3	sp^2
I	sp^3	sp^3

7   Which set of quantum numbers can correspond to one of the valence electrons in an O atom in the ground state?

	n	l	m_l	m_s
A	1	0	0	$+\frac{1}{2}$
B	1	1	0	$-\frac{1}{2}$
C	2	0	-1	$+\frac{1}{2}$
D	2	1	-1	$-\frac{1}{2}$
E	3	0	0	$+\frac{1}{2}$
F	3	1	0	$-\frac{1}{2}$

Thermochemistry

8 In the water-gas shift reaction, carbon monoxide reacts with water vapor to form carbon dioxide and hydrogen:

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$
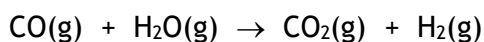
In this reaction the entropy change $\Delta S^0 = -42\ \text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$. For this question, assume that ΔH and ΔS are independent of temperature and that the reaction occurs under standard pressure.

Two statements are made:

I   This reaction is an exothermic reaction.
II   This reaction is spontaneous at temperatures above 1200 K.

Which of the above statements is/are true?

A neither
B only I
C only II
D both

9 When a solution of potassium iodide is added to a solution of iron(III) chloride, the following equilibrium is reached:

$$2\ Fe^{3+}(aq) + 3\ I^-(aq) \rightleftharpoons 2\ Fe^{2+}(aq) + I_3^-$$
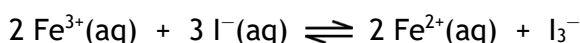
The change in the Gibbs energy can be calculated with: $\Delta G^0 = -nF\Delta E^0$.

What is the value of the equilibrium constant at 298 K and $p = p_0$?

A $1.7\cdot10^{-8}$
B $1.3\cdot10^{-4}$
C $7.8\cdot10^{3}$
D $6.0\cdot10^{7}$

Redox and electrochemistry

10 Given is the redox couple ethanol/ethanoate:
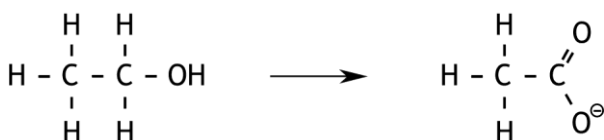
How many electrons (e^-) are in the equation of the half-reaction of this redox couple and on which side of the arrow are they?

A $2\ e^-$ to the left of the arrow
B $2\ e^-$ to the right of the arrow
C $4\ e^-$ to the left of the arrow
D $4\ e^-$ to the right of the arrow
E $6\ e^-$ to the left of the arrow
F $6\ e^-$ to the right of the arrow

11   A solution containing equal amounts of moles of $NiCl_2$ and $CuBr_2$ is electrolyzed. The voltage of the power source used for the electrolysis is slowly increased.

Which products are formed first?

	at the negative electrode	at the positive electrode
A	$Br_2(aq)$	$Cu(s)$
B	$Br_2(aq)$	$Ni(s)$
C	$Cl_2(aq)$	$Cu(s)$
D	$Cl_2(aq)$	$Ni(s)$
E	$Cu(s)$	$Br_2(aq)$
F	$Cu(s)$	$Cl_2(aq)$
G	$Ni(s)$	$Br_2(aq)$
H	$Ni(s)$	$Cl_2(aq)$

pH / acid-base

12   Amino acid molecules contain an amino group and a carboxylic acid group. The amino group can act as a base and the carboxylic acid group as an acid. For glycine, the pK_b of the amino group is 4.22 and the pK_a of the carboxylic acid group is 2.35.

In what form does glycine mainly exist in a solution where the pH has been adjusted to 4.60 with a solution of hydrochloric acid?

A $NH_2CH_2COO^-$

B NH_2CH_2COOH

C $^+NH_3CH_2COO^-$

D $^+NH_3CH_2COOH$

13   0.020 mol NaOH is added to 1.50 L of a solution containing 0.100 mol lactic acid (2-hydroxypropanoic acid, $CH_3CHOHCOOH$) and 0.120 mol sodium lactate (lactate is the conjugate base of lactic acid).

What will the pH be?

A   3.61

B   3.77

C   3.93

D   4.10

E   4.27

Chemical calculations

14 Weigh out 600 mg of iron(III) oxide. This reacts with hydrogen gas. Water vapor and a solid containing only iron ions and oxide ions are formed.

At a certain moment, 22.6 mg of water vapor was created.

What is the molar ratio between Fe and O in the remaining solid?

	Fe	:	O
A	1	:	1
B	3	:	4
C	4	:	5
D	5	:	6
E	6	:	7
F	7	:	8

15 Which gas has a density of 2.16 g dm^{-3} at 200 °C and 3.00 atm?

A argon

B krypton

C neon

D nitrogen

E hydrogen

F oxygen

Reaction rate and equilibrium

16 For the reaction

$2 H_2(g) + 2 NO(g) \rightarrow N_2(g) + 2 H_2O(g)$
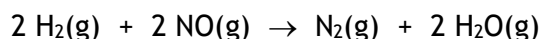
the rate equation is:

$rate = k[H_2][NO]^2$

The following mechanism is proposed:

Step 1 $2 NO(g) \rightleftharpoons N_2O_2(g)$

Step 2 $N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$

Step 3 $N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$
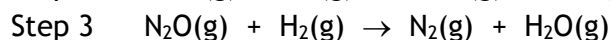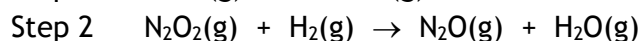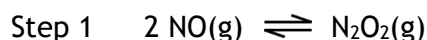
Which statement(s) about the rate equation and the proposed mechanism can be correct?

I   The mechanism is in agreement with the rate equation if step 1 is the rate determining step.

II   The mechanism is in agreement with the rate equation if step 2 is the rate determining step.

A neither

B only I

C only II

D both

17   0.015 M ZnF_2 solution is slowly added to 50 mL of a 0.010 M $BaCl_2$ solution. After adding 50 mL of this solution, a precipitate of BaF_2 forms for the first time.

What is the solubility product of BaF_2 according to these data?

A $2.8 \cdot 10^{-7}$
B $1.1 \cdot 10^{-6}$
C $9.0 \cdot 10^{-6}$
D $3.8 \cdot 10^{-5}$
E $7.5 \cdot 10^{-5}$
F $1.5 \cdot 10^{-4}$

18   A mixture of 1.00 mol bromine and 1.00 mol chlorine is heated to 190°C. The following equilibrium is reached:

$Br_2(g) + Cl_2(g) \rightleftharpoons 2\ BrCl(g)$

The equilibrium constant K_c for this equilibrium at 190°C is 6.80.

What is the mass percentage of BrCl in the equilibrium mixture at 190 °C?

A   28.3%
B   32.4%
C   36.1%
D   56.6%
E   64.8%
F   72.3%
G   77.2%

Analysis

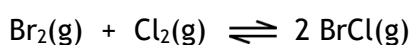**19**   A student is instructed to investigate whether a white solid is barium carbonate, zinc carbonate or calcium hydroxide.

The student proposes the following two designs:

Design 1:   Add an excess of hydrochloric acid to part of the white solid.
Design 2:   Add an excess of sulfuric acid solution to part of the white solid.

Which design(s) gives/give visible observations that enables the student to identify the white solid?

A   neither design
B   design 1 only
C   design 2 only
D   design 1 and design 2

20 A student determines the concentration of a colored salt solution by measuring the absorbance at the wavelength at which the absorbance is greatest (λ_{max}) and calculates the concentration using Lambert-Beer's law.

In which action(s) below does she find a higher concentration than the actual concentration?

I She rinses the cuvette with water and then fills it with the salt solution.

II She sets the spectrophotometer at a wavelength higher than (λ_{max}).

A in neither
B only in I
C only in II
D in both

▌Problem 2 Methylphenidate   (25 points)

Methylphenidate is the active ingredient of the medicine Ritalin®.

Methylphenidate was first synthesized in 1944 by Panizzon. The synthesis route is shown below.
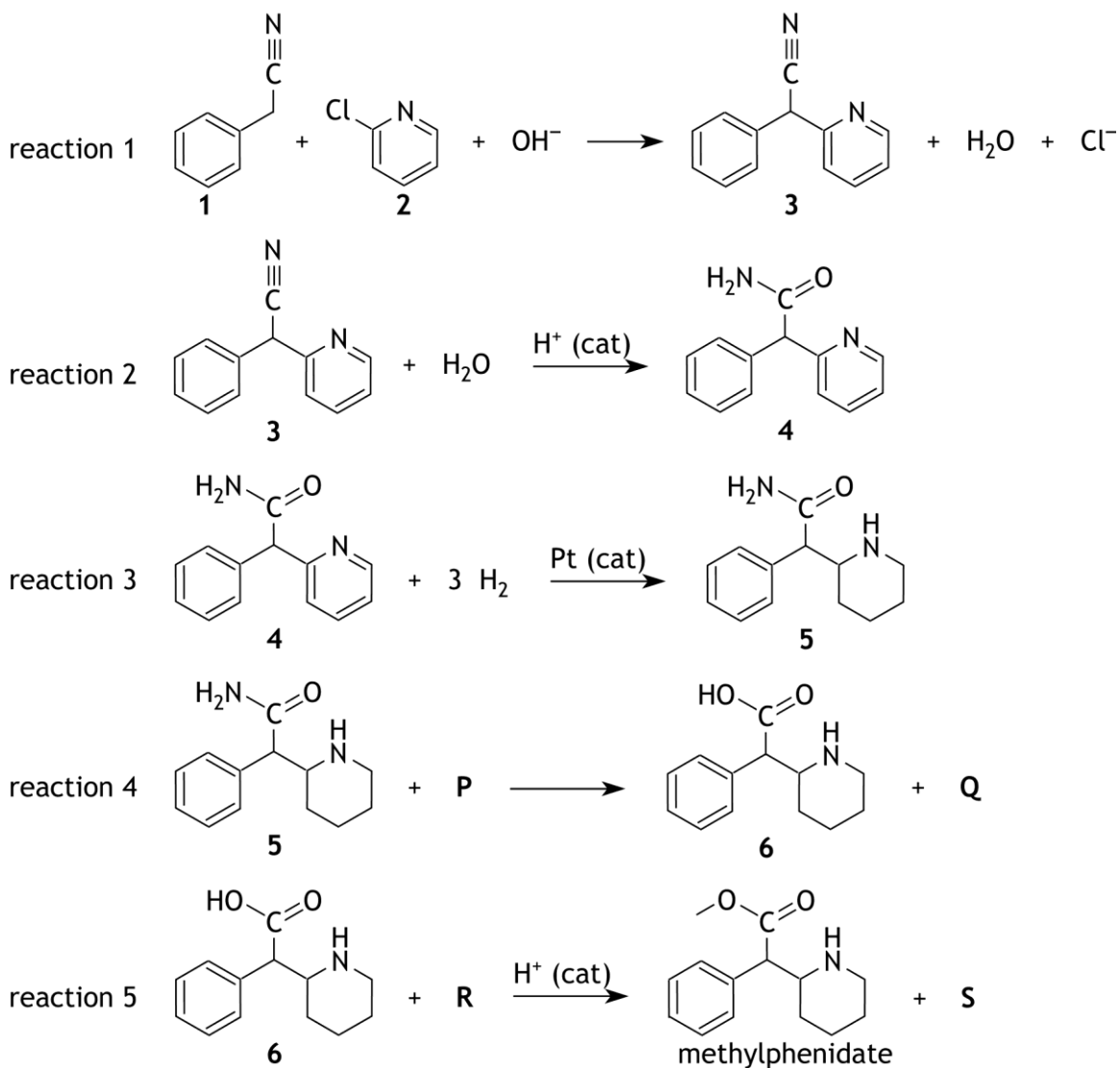
During this synthesis route reactions occur in which stereoisomers are formed. The mixtures of stereoisomers that are formed during this synthesis route, are not separated.

▢1   In which reaction(s) does the number of stereoisomers increase?   2

In reaction 1, first a hydroxide ion reacts with a molecule **1** to form the negative ion below.
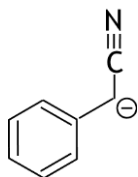
In this ion, the negative charge is not localized on one atom, but distributed over several atoms. This can be explained with the help of resonance (mesomerism).

☐2   Copy the structural formula of the negative ion and indicate with asterisks (*) which atoms, except the C atom in the formula shown above, are negatively charged.   2

The resultant negative ion reacts with a molecule **2**.

☐3   Copy the sentence below and choose the correct option between the alternatives in cursive:

The reaction of the negative ion of **1** with a molecule **2** to form molecule **3** is *an addition reaction / an elimination reaction / a substitution reaction* in which the negative ion of **1** functions as *electrophile / nucleophile*.   2

In reaction 2, the formed molecule **3** reacts with water, with sulfuric acid acting as catalyst. The mechanism of the reaction is described step by step below.

Step 1: the lone pair on the N atom of the CN group of **3** bonds to the H^+ of a H_3O^+ ion.
Step 2: a water molecule is bonded to the C atom of the CN group, while also a neutral NH group is formed.
Step 3: exchange of a proton takes place between the formed OH_2^+ group and the N atom.
Step 4: transfer of a proton takes place from the OH group to a water molecule, bonds also shift so that **4** is produced.

☐4   Show the steps 1 to 4 of the mechanism with structural formulas.

- Use the following notations for the side chains: = R_1 and = R_2 .
- Draw all bonding and non-bonding electron pairs.
- Use curved arrows ( ) to indicate how the electron pairs shift during the formation and breaking of bonds.
- Place all formal charges in the right place.   8

In reaction 3 the pyridine ring (R_2 in question 4) reacts with hydrogen. In this reaction, the benzene ring (R_1 in question 4) does not react with hydrogen. This is due to the so-called resonance energy (mesomeric energy) of both groups.

The resonance energy of the benzene ring ($1.50 \cdot 10^5$ J mol^{-1}) is the difference between the energy released during the complete hydrogenation of three moles of C = C bonds and the energy released during the complete hydrogenation of one mole of benzene rings.

The resonance energy of the pyridine ring ($1.07 \cdot 10^5$ J mol^{-1}) is the difference between the energy released during the complete hydrogenation of two moles of C = C bonds together with one mole of C = N bonds and the energy released during the complete hydrogenation of one mole of pyridine rings.

As an explanation for the fact that in reaction 3 the pyridine ring is hydrogenated and the benzene ring is not, Gerrit assumes that more energy is released in the reaction of the pyridine ring with hydrogen than in the reaction of the benzene ring with hydrogen.

5 Control by means of a calculation whether during the hydrogenation of one mole of pyridine rings more energy is released than in the hydrogenation of one mole of benzene rings.
   -   Use information from Binas table 58 or ScienceData table 9.3.
   -   The resonance energy of the pyridine ring is $1.07 \cdot 10^5$ J mol^{-1}.
   -   During the complete hydrogenation of one mole of benzene rings, $2.1 \cdot 10^5$ J is produced.   6

6 Give another possible explanation for the fact that the benzene ring in reaction 3 is not hydrogenated.   1

   In reaction 4, substance **5** reacts with a solution of hydrochloric acid.

7 Give the formulas of **P** and **Q**. Record your answers as follows:
   P is …
   Q is …   2

8 Give the formulas of **R** and **S**. Record your answers as follows:
   R is …
   S is …   2

Problem 3 The decomposition of azomethane (14 points)

Azomethane has the molecular formula $C_2H_6N_2$. In one molecule of azomethane, there are two nitrogen atoms bonded to each other and each nitrogen atom is bonded to a methyl group.

9 Give the Lewis structure of a molecule of azomethane. Indicate the methyl groups as CH_3. 2
10 Explain whether stereoisomers of azomethane are possible. 3

Azomethane decomposes readily to form ethane and nitrogen:

$C_2H_6N_2(g) \rightarrow C_2H_6(g) + N_2(g)$
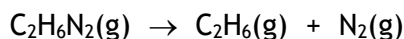
During an investigation into the kinetics of the reaction, a certain amount of azomethane was placed in a reaction vessel with a fixed volume and the pressure in the vessel was measured a number of times. The temperature remained constant during the experiment. The following results were obtained:

t	10.0 min	21.0 min	35.0 min	∞
p_{total}	$0.656 \cdot 10^5$ Pa	$0.732 \cdot 10^5$ Pa	$0.813 \cdot 10^5$ Pa	$1.144 \cdot 10^5$ Pa

At $t = \infty$ all azomethane has been converted.

11 Show that the decomposition of azomethane is a first order reaction and calculate the rate constant k for the reaction at this temperature. 7

12 Indicate what you need to do if you want to determine the activation energy of this reaction. 2

Problem 4 Superphosphate   (15 points)

The fertilizer superphosphate is a mixture of mostly calcium hydrogen phosphate $(Ca(H_2PO_4)_2)$ and calcium sulphate $(CaSO_4)$. Superphosphate is prepared by reacting an ore, consisting mainly of fluorapatite $(Ca_5(PO_4)_3F)$, with pure sulfuric acid at normal temperature and pressure. This reaction produces only gaseous hydrogen fluoride (HF), solid calcium dihydrogen phosphate and solid calcium sulfate.

▫13 Give the equation of the reaction between fluorapatite and sulfuric acid. Also indicate the states.   3

▫14 Calculate the mass percentage of calcium dihydrogen phosphate, rounded to a whole number, in superphosphate if it were prepared from pure fluorapatite and pure sulfuric acid.   3

Of the ingredients in superphosphate, only calcium dihydrogen phosphate is effective as fertilizer. Calcium dihydrogen phosphate is soluble in water at room temperature. The remaining ingredients of the superphosphate can be removed by adding water to the superphosphate and then filtering the obtained cloudy liquid at room temperature. When water is added to superphosphate, the following occurs:

$$Ca(H_2PO_4)_2 \rightarrow Ca^{2+} + 2\,H_2PO_4^-$$

and

$$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$$

Calcium sulfate is moderately soluble in water at room temperature. When water is added to superphosphate, less calcium sulfate dissolves per liter compared to adding water to calcium sulphate alone.

▫15 Explain why, when water is added to superphosphate, less calcium sulfate dissolves per liter compared to adding water to calcium sulphate alone.   2

Emmy wants to determine the amount of mmoles of calcium dihydrogen phosphate present in a small sample of superphoshate. Water is added to the sample until the volume of the solution is 100.0 mL. All calcium dihydrogen phosphate dissolves. After the non-dissolved components of the superphosphate have precipitated, two solutions are added in excess to 10.00 mL of the colourless solution: one of them is a solution of ammonia and the other is a solution of a molybdenum (Mo) complex. As a result, all $H_2PO_4^-$ ions in solution react forming solid $(NH_4)_3PMo_{12}O_{40}$. This solid compound is removed from the suspension by means of filtration. It is then added to a solution containing 10.0 mmol dissolved NaOH. This amount of NaOH is a small excess.

Upon adding the solid to the NaOH solution, all $(NH_4)_3PMo_{12}O_{40}$ reacts with OH^-. Only MoO_4^{2-}, HPO_4^{2-}, H_2O and NH_3 are formed. Finally, after adding a suitable indicator, the amount of unreacted OH^- is determined using a titration with a solution of hydrochloric acid. It turns out that 0.380 mmol H_3O^+ ions are needed. You can assume that H_3O^+ only reacts with OH^-.

To determine the amount of mmoles of calcium hydrogen phosphate in the sample of superphosphate one needs to know the molar ratio in which $(NH_4)_3PMo_{12}O_{40}$ and OH^- react. This (rather extreme) molar ratio can be found by setting up part of the reaction equation and looking at the charges left and right of the reaction arrow.

▢16 Set up part of the reaction equation and explain, based on charges left and right of the reaction arrow, how many moles of OH^- react with 1 mol $(NH_4)_3PMo_{12}O_{40}$.   3

▢17 Calculate the amount of mmoles of calcium hydrogen phosphate in the superphosphate sample.   4

44th National Chemistry Olympiad 2023 preliminary round 2

Answer sheet Multiple choice questions

name:

no.	choice letters	(score)
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