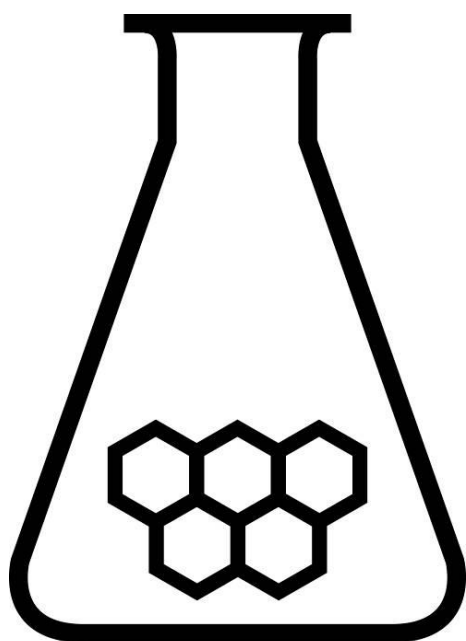# NATIONAL CHEMISTRY OLYMPIAD 2023

MARKING SCHEME PRELIMINARY ROUND 2

To be conducted from March 20 until March 24 2023

SCHEIKUNDE OLYMPIADE

Universiteit Leiden

- This preliminary round consists of 20 multiple choice questions divided over 8 topics and 3 problems with a total of 17 open questions.
- The maximum score for this work is 94 points.
- 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.
- While assigning scores for the work, this marking scheme has to be used. Moreover the general rules for the Dutch Central Exams apply.
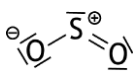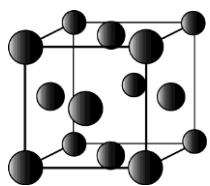
Problem 1 Multiple-choice questions (total 40 points)

For every correct answer: 2 points

Carbon chemistry

1	I	The single bonds between the C atoms and the H atoms are σ-bonds, as are the single bonds between two C atoms, between the C atoms and the O atoms of the OH groups, and between de O atoms and the H atoms.
		The double bond between the C atoms consists of a σ-bond and a π-bond. The double bonds between the C atoms and the O atoms consist of a σ-bond and a π-bond.
2	D	An H atom is replaced by a $\overset{O}{\underset{R}{\overset{\|}{\diagdown}}}$ group.
3	B	Method I is a nucleophilic substitution reaction of the phenolate on the bromomethane. Method II would also be a nucleophilic substitution reaction, of methanolate on the benzene ring, but in a benzene ring only electrophilic substitution would occur.

Structures and formulas

4	D	$^{\ominus}\!\ddot{O}\!-\!\overset{\oplus}{\overset{..}{S}}\!=\!\ddot{O}$
5	B	The structure of the FCC unit cell is: The unit cell contains $8\times\dfrac{1}{8}+6\times\dfrac{1}{2}=4$ atoms. When the edge of the unit cell is set to a m, the density is $\dfrac{4\times197.0\times1.66\cdot10^{-27}}{a^3}=19.3\cdot10^3$ kg m^{-3}. That gives $a = 4.08\cdot10^{-10}$ m. The smallest distance between two gold nuclei is half of the diagonal of one face of the cube, so $\dfrac{4.08\cdot10^{-10}}{\sqrt{2}}=2.88\cdot10^{-10}$ m.
6	I	The oxygen atom in the alcohol molecule has two bonds and two lone pairs, so it is sp^3 hybridised. The oxygen atom in the intermediate has three bonds and one lone pair, so it is also sp^3 hybridised.
7	D	Oxygen is in period 2, so $n = 2$ and $l = 0$ or $l = 1$. If $l = 0$ m_l can't be -1.

Thermochemistry

8	B	$\Delta H = -(-1.105 \cdot 10^5) - (-2.42 \cdot 10^5) + (-3.935 \cdot 10^5) = -0.41 \cdot 10^5$ J mol^{-1}, this is negative so the reaction is exothermic. When the reaction occurs spontaneously, it must be that $\Delta G < 0$, so $\Delta H - T\Delta S < 0$. At 1200 K $\Delta H - T\Delta S = -0,41 \cdot 10^5 - 1200 \times (-42) = 9,4 \cdot 10^3$ J mol^{-1}. This is greater than zero and at even higher temperatures ΔG becomes even greater.
9	D	$\Delta G^0 = -nF\Delta E^0 = -RT\ln K$; $n = 2$ and $\Delta E^0 = (0.77 - 0.54) = 0.23$ V, so $K = e^{\frac{nF\Delta E^0}{RT}} = e^{\frac{2 \times 9.649 \cdot 10^4 \times 0.23}{8.314 \times 298}} = 6.0 \cdot 10^7$.

Redox and electrochemistry

10	D	The equation of the half-reaction is:

11	E	The strongest oxidising agent (Cu^{2+}) and the strongest reducing agent (Br^-) will react first.

pH / acid-base

12	C	At very high pH, glycine occurs as $H_2NCH_2COO^-$. As the pH drops, a H^+ binds to the most basic group, which is the NH_2 group ($pK_b = 4.22$, while the pK_b of the COO^- group is equal to $14.00 - 2.35 = 11.65$). At pH = 4.60 there is the following equilibrium: $^+NH_3CH_2COOH \rightleftharpoons {}^+NH_3CH_2COO^- + H^+$ $pK_z = pH - \log \dfrac{\text{number of moles of } ^+NH_3CH_2COO^-}{\text{number of moles of } ^+NH_3CH_2COOH}$, filled out: $2.35 = 4.60 - \log \dfrac{\text{number of moles of } ^+NH_3CH_2COO^-}{\text{number of moles of } ^+NH_3CH_2COOH}$, so $\log \dfrac{\text{number of moles of } ^+NH_3CH_2COO^-}{\text{number of moles of } ^+NH_3CH_2COOH} = 4.60 - 2.35 = 2.25$ So, the number of moles of $^+NH_3CH_2COO^- \gg$ the number of moles of $^+NH_3CH_2COOH$. At even lower pH values, the COO^- group is also protonated. At pH < 2.35, glycine occurs primarily as $^+NH_3CH_2COOH$.

13	D	0.020 moles of OH^- react with 0.020 moles of $CH_3CHOHCOOH$ to form 0.020 moles of $CH_3CHOHCOO^-$.
		After the reaction there are $0.100 - 0.020 = 0.080$ moles of $CH_3CHOHCOOH$ present and $0.120 + 0.020 = 0.140$ moles of $CH_3CHOHCOO^-$, so a buffer solution has formed.
		So, $[H_3O^+] = K_z \times \dfrac{\text{number of moles of } CH_3CHOHCOOH}{\text{number of moles of } CH_3CHOHCOO^-} = 1.4 \cdot 10^{-4} \times \dfrac{0.080}{0.140} = 8.0 \cdot 10^{-5}$
		and pH $= -\log 8.0 \cdot 10^{-5} = 4.10$.

Chemical calculations

14	B	600 mg Fe_2O_3 is $\dfrac{600}{159.69}$ mmol which contains $2 \times \dfrac{600}{159.69} = 7.51$ mmoles of Fe and
		$3 \times \dfrac{600}{159.69} = 11.27$ mmoles of O.
		In 22.6 mg H_2O there is $\dfrac{22.6}{18.015} = 1.25$ mmoles of O,
		so there is $11.27 - 1.25 = 10.02$ mmoles of O remaining in the solid.
		Therefore, the ratio Fe : O is $7.51 : 10.02 = 3 : 4$.
15	D	200 °C is 473 K, 3.00 atm is $3.00 \times 1.01 \cdot 10^5$ Pa and 2.16 g dm^{-3} is $2.16 \cdot 10^3$ g m^{-3}.
		Setting the molar mass to M g mol^{-1}, it follows that 1.00 m^3 of the gas contains
		$\dfrac{2.16 \cdot 10^3}{M}$ mol.
		The ideal gas law states that $pV = nRT$ or $3.03 \cdot 10^5 \times 1.00 = \dfrac{2.16 \cdot 10^3}{M} \times 8.314 \times 473$ or
		$M = \dfrac{2.16 \cdot 10^3}{3.03 \cdot 10^5 \times 1.00} \times 8.314 \times 473 = 28.0$ g mol^{-1}.
		This is the molar mass of nitrogen, N_2.

Reaction rate and equilibrium

16	C	When step 2 is rate determining, $rate = k_2[N_2O_2][H_2]$.
		From the equilibrium condition $\dfrac{[N_2O_2]}{[NO]^2} = K$ for step 1, it follows that $[N_2O_2] = K[NO]^2$.
		So $rate = k_2K[NO]^2[H_2]$, which is in agreement with the stated rate equation for $k = k_2K$.
17	B	$[Ba^{2+}] = \dfrac{50 \times 0.010}{50 + 50} = 0.0050$ mol L^{-1} and $[F^-] = \dfrac{2 \times 50 \times 0.015}{50 + 50} = 0.015$ mol L^{-1}
		$K_s = [Ba^{2+}][F^-]^2 = 0.0050 \times (0.015)^2 = 1.1 \cdot 10^{-6}$

18	D	

	Br$_2$	+	Cl$_2$	$\rightleftharpoons$	2 BrCl
start	1.00 mol		1.00 mol		0.00
converted/produced	x mol		x mol		2 x mol
equilibrium	$(1.00 - x)$ mol		$(1.00 - x)$ mol		2 x mol

$$K = \frac{[BrCl]^2}{[Br_2][Cl_2]} = \frac{\left(\dfrac{2x}{V}\right)^2}{\left(\dfrac{1.00 - x}{V}\right)^2} = 6.80 \text{, or } \frac{(2x)^2}{(1,00 - x)^2} = 6.80 \text{, it follows that } x = 0.566.$$

So, 2×0.566 moles of BrCl are produced, which is $2 \times 0.566 \times 115.35$ g BrCl.

The total mass is $1.00 \times 2 \times 79.90 + 1.00 \times 2 \times 35.45 = 230.7$ g, so the mass percentage

BrCl is $\dfrac{2 \times 0.566 \times 115.35}{230.7} \times 100 = 56.6\%$.

Analysis

19	C	Adding hydrochloric acid causes gas production with the carbonates but not with the hydroxide. There is no precipitation when a solution of hydrochloric acid is added to barium carbonate or zinc carbonate. The negative SO_4^{2-} ion of sulphuric acid forms a precipitate with Ba^{2+} and Ca^{2+} but not with Zn^{2+}. Sulphuric acid causes gas formation with barium carbonate, while with calcium hydroxide it does not.
20	A	Because the cuvette is not rinsed with the solution that will be measured, dilution will cause a lower extinction to be measured and thus a lower concentration to be found. At a wavelength higher than λ_{max}, the extinction is lower. When calculations are then performed with the smaller ε (molar extinction coefficient), belonging to that higher wavelength, the student will find a similar concentration to the real one. If calculations are performed with the ε that belongs to λ_{max}, the student will find a lower concentration than the real one.

Open questions (total 54 points)

▌ Problem 2 Methylphenidate 25 points

▢1 Maximum score 2

· in reaction 1   1
· in reaction 3   1

Note
When an incorrect reaction is listed, deduct 1 point – the minimum score for this question is 0 points.

▢2 Maximum score 2

A correct answer might look as follows:
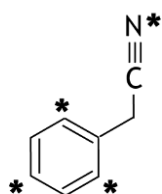
· asterisks at the three carbon atoms of the benzene ring correct   1
· asterisk at the N atom of the cyanide group   1

Notes
- *When an asterisk is placed at an incorrect atom of the benzene ring, the first partial score is not to be assigned.*
- *When an asterisk is placed at the C atom of the cyanide group, the second partial score is not to be assigned.*
- *When an asterisk is placed at the C atom where the negative charge was drawn in the given structural formula, do not penalize this.*

▢3 Maximum score 2

The reaction of the negative ion of **1** with a molecule **2** to form molecule **3** is *a substitution reaction* in which the negative ion from **1** functions as *nucleophile*.

· substitution reaction   1
· nucleophile   1

◻4 Maximum score 8

Examples of a correct answer are:

step 1

step 2

step 3

step 4
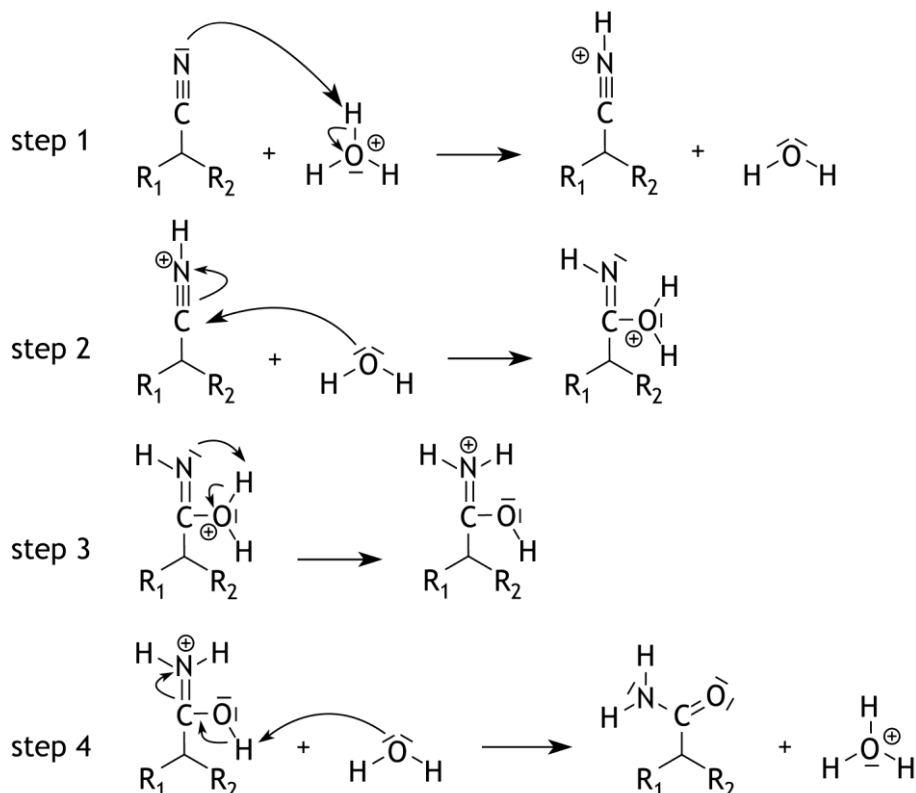
and
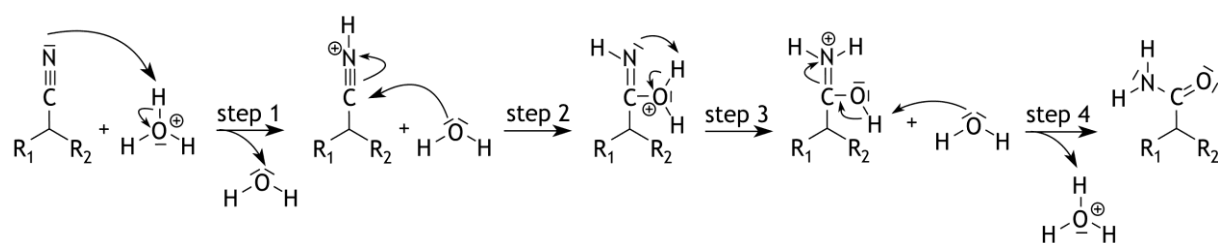
· in step 1, correctly drawn arrows   1
· in step 1, the Lewis structures and charges correct   1
· in step 2, correctly drawn arrows   1
· correct Lewis structure and charge after step 2   1
· in step 3, correctly drawn arrows   1
· correct Lewis structure and charge after step 3   1
· in step 4, correctly drawn arrows   1
· correct Lewis structure and charge after step 4   1

If, in an otherwise correct answer, one or more arrows are drawn 'wrong way around'   7

Note
When H₂O is not listed to the right of the arrow in step 1 and/or H₃O⁺ is not listed to the right of the arrow in step 4, do not penalize this.

▫5　Maximum score 6

A correct answer might look as follows:

The change in energy for the hydrogenation of 2 moles of $C=C$ bonds and 1 mole of $C=N$ bonds is:
$2 \times (-BE_{C=C} - BE_{H-H} + BE_{C-C} + 2 \times BE_{C-H}) + (-BE_{C=N} - BE_{H-H} + BE_{C-N} + BE_{C-H} + BE_{N-H})=$
$2 \times \{-(-6.1 \cdot 10^5) - (-4.36 \cdot 10^5) + (-3.5 \cdot 10^5) + 2 \times (-4.1 \cdot 10^5)\} + \{-(-6.2 \cdot 10^5) - (-4.36 \cdot 10^5) + (-2.8 \cdot 10^5) + (-4.1 \cdot 10^5) + (-3.9 \cdot 10^5)\} = -2.7 \cdot 10^5$ J.
So, the hydrogenation energy of one mole of pyridine rings is
$-2.7 \cdot 10^5 + 1.07 \cdot 10^5 = -1.6 \cdot 10^5$ J.
This is less than the $2.1 \cdot 10^5$ J released in the hydrogenation of a mole of benzene rings.

· notion that 2 moles of $C=C$ bonds and 1 mole of $C=N$ bonds are broken	1
· notion that 3 moles of $H-H$ bonds are broken	1
· notion that 2 moles of $C-C$ bonds and 1 mole of $C-N$ bonds are formed	1
· notion that 5 moles of $C-H$ bonds and 1 mole of $N-H$ bonds are formed	1
· correct summation of bond energies	1
· calculation of the hydrogenation energy of a mole of pyridine rings and conclusion	1

▫6　Maximum score 1

Examples of a correct answer are:

- The activation energy for the hydrogenation of benzene rings is greater than that for the hydrogenation of pyridine rings.
- The catalyst is specific for the hydrogenation of the pyridine ring.

▫7　Maximum score 2

· **P** is H_3O^+	1
· **Q** is NH_4^+	1

If the answer **P** is H_2O and **Q** is NH_3 is given | 1

▫8　Maximum score 2

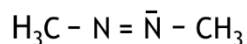|	
· **R** is CH_3OH	1
· **S** is H_2O	1

Problem 3 The decomposition of azomethane   14 points

▫9   Maximum score 2

A correct answer might look as follows:

$$H_3C - \underline{N} = \overline{N} - CH_3$$

· single bonds between the N atoms and C atoms and double bond between both N atoms   1
· non-bonding electron pairs on both N atoms   1

Note
When the answer $CH_3 - \underline{N} = \overline{N} - CH_3$ *is given, give full marks.*

▫10   Maximum score 3

The nitrogen atoms have a trigonal planar geometry.
There is no free rotation around the double bonds between the N atoms / the double bond
is rigid, so there are two *cis-trans* isomers.

· the nitrogen atoms have a trigonal planar geometry   1
· there is no free rotation around the double bond between the N atoms / the double bond
  is rigid   1
· conclusion   1

Note
An answer like the following is also correct: „There are two stereoisomers / cis-trans
isomers namely $\begin{array}{c} H_3C \\ \diagdown \\ N=N \\ \diagdown \\ CH_3 \end{array}$ *and* $\begin{array}{c} H_3C \quad CH_3 \\ \diagdown \quad \diagup \\ N=N \end{array}$ *.”*

▫11 Maximum score 7

An example of a correct calculation is as follows:

For a first order reaction $\ln\dfrac{[C_2H_6N_2]_0}{[C_2H_6N_2]_t} = kt$.

For gases, the partial pressure is proportional to the concentration, therefore

$\ln\dfrac{(p_{C_2H_6N_2})_0}{(p_{C_2H_6N_2})_t} = kt$ or $k = \dfrac{\ln\dfrac{(p_{C_2H_6N_2})_0}{(p_{C_2H_6N_2})_t}}{t}$.

From 1 mole of gas, 2 moles of gas are produced, therefore

$(p_{C_2H_6N_2})_0 = \dfrac{(p_{C_2H_6N_2})_\infty}{2} = \dfrac{1.144\cdot10^5}{2} = 0.572\cdot10^5$ Pa.

If at time t during the reaction the partial pressure of $C_2H_6N_2$ has decreased by x Pa, the partial pressures of C_2H_6 and N_2 have increased by x Pa, and the total pressure is then $(0.572\cdot10^5 + x)$ Pa, thus

$(p_{C_2H_6N_2})_t = 0.572\cdot10^5 - x$.

After 10.0 min, $p_{total} = 0.656\cdot10^5$ Pa, thus $x = 0.656\cdot10^5 - 0.572\cdot10^5 = 0.084\cdot10^5$ Pa and

$(p_{C_2H_6N_2})_{10.0} = 0.572\cdot10^5 - 0.084\cdot10^5 = 0.488\cdot10^5$ Pa and

$\dfrac{\ln\dfrac{(p_{C_2H_6N_2})_0}{(p_{C_2H_6N_2})_{10.0}}}{10.0} = \dfrac{\ln\dfrac{0.572\cdot10^5}{0.488\cdot10^5}}{10.0} = 0.0159$.

After 21.0 min, $p_{total} = 0.732\cdot10^5$ Pa, thus $x = 0.732\cdot10^5 - 0.572\cdot10^5 = 0.160\cdot10^5$ Pa and

$(p_{C_2H_6N_2})_{21.0} = 0.572\cdot10^5 - 0.160\cdot10^5 = 0.412\cdot10^5$ Pa and

$\dfrac{\ln\dfrac{(p_{C_2H_6N_2})_0}{(p_{C_2H_6N_2})_{21.0}}}{21.0} = \dfrac{\ln\dfrac{0.572\cdot10^5}{0.412\cdot10^5}}{21.0} = 0.0156$.

After 35.0 min, $p_{total} = 0.813\cdot10^5$ Pa, thus $x = 0.813\cdot10^5 - 0.572\cdot10^5 = 0.241\cdot10^5$ Pa and

$(p_{C_2H_6N_2})_{35.0} = 0.572\cdot10^5 - 0.241\cdot10^5 = 0.331\cdot10^5$ Pa and

$\dfrac{\ln\dfrac{(p_{C_2H_6N_2})_0}{(p_{C_2H_6N_2})_{35.0}}}{35.0} = \dfrac{\ln\dfrac{0.572\cdot10^5}{0.331\cdot10^5}}{35.0} = 0.0156$.

Three times (almost) the same result for $\dfrac{\ln\dfrac{(p_{C_2H_6N_2})_0}{(p_{C_2H_6N_2})_t}}{t}$ is obtained, so this is a first order reaction.

$k = \dfrac{0.0159 + 0.0156 + 0.0156}{3} = 0.0157$ min^{-1} .

In SI units: $k = \dfrac{0.0157}{60} = 2.62\cdot10^{-4}$ s^{-1} .

· notion that holds for the first order reaction $\ln\dfrac{(p_{C_2H_6N_2})_0}{(p_{C_2H_6N_2})_t} = kt$ or $k = \dfrac{\ln\dfrac{(p_{C_2H_6N_2})_0}{(p_{C_2H_6N_2})_t}}{t}$ 1

· calculation of $(p_{C_2H_6N_2})_0$: $1.144\cdot10^5$ Pa divided by 2   1

· notion that the increase in total pressure equals the decrease in $(p_{C_2H_6N_2})$ 1

· calculation of $(p_{C_2H_6N_2})_{10.0}$, $(p_{C_2H_6N_2})_{21.0}$ and $(p_{C_2H_6N_2})_{35.0}$ 1

· calculation of $\dfrac{\ln\dfrac{(p_{C_2H_6N_2})_0}{(p_{C_2H_6N_2})_t}}{t}$ for t = 10.0 min, t = 21.0 min and t = 35.0 min and concluding

that it is a first order reaction   1

· calculation of k: the average of the results of $\dfrac{\ln\dfrac{(p_{C_2H_6N_2})_0}{(p_{C_2H_6N_2})_t}}{t}$ for t = 10.0 min, t = 21.0 min

and t = 35.0 min   1
· correct unit of k provided   1

If in an otherwise correct answer k is calculated for only one moment (so not is proven that
it is a first order reaction)   5

Notes
-   *If the unit is given in min^{-1}, do not penalize this.*
-   *When by using the data at two points it is shown that the reaction is of the first*

    order, and for the calculation of k the average of the two results of $\dfrac{\ln\dfrac{(p_{C_2H_6N_2})_0}{(p_{C_2H_6N_2})_t}}{t}$ is

    used, do not penalize this.

▫12   Maximum score 2

An example of a correct answer is:

The rate constant should be determined at one more temperature, and Arrhenius' law
applied.

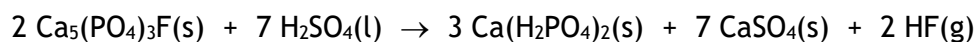· the rate constant should be determined at one more temperature   1
· apply Arrhenius' law   1

Problem 4 Superphosphate   15 points

□13   Maximum score 3

$$2\ Ca_5(PO_4)_3F(s)\ +\ 7\ H_2SO_4(l)\ \rightarrow\ 3\ Ca(H_2PO_4)_2(s)\ +\ 7\ CaSO_4(s)\ +\ 2\ HF(g)$$

· correct formulas with correct state symbols at the correct side of the arrow   1
· P and F balanced correctly   1
· Ca, H, S and O balanced correctly   1

□14   Maximum score 3

An example of a correct calculation is:

$$\frac{3 \times 234.05}{3 \times 234.05 + 7 \times 136.14} \times 10^2 = 42\ (mass\%)$$

· calculation of the molar mass of $Ca(H_2PO_4)_2$: 234,05 g mol^{-1} 1
· calculation of the sum of the masses of 3 moles of $Ca(H_2PO_4)_2$ and 7 moles of $CaSO_4$ 1
· rest of the calculation and answer rounded to the nearest whole number   1

Notes
- *When an incorrect answer to question 14 is a direct consequence of an incorrect answer to question 13 and the molar ratio $Ca(H_2PO_4)_2$: $CaSO_4$ was not equal to 1:1, do not penalize this.*
- *When the molar ratio $Ca(H_2PO_4)_2$: $CaSO_4$ = 1 : 1 was used in the answer to question 14, the second partial score is not to be assigned.*

□15   Maximum score 2

A correct answer can be formulated as follows:
By dissolving $Ca(H_2PO_4)_2$, the $[Ca^{2+}]$ increases. Hence, the solution equilibrium of $CaSO_4$ shifts to the left (and less $CaSO_4$ dissolves).

· due to dissolving $Ca(H_2PO_4)_2$, the $[Ca^{2+}]$ increases   1
· so the solution equilibrium of $CaSO_4$ shifts to the left   1

If an answer is given such as: „Due to the dissolving of $Ca(H_2PO_4)_2$, the solution already contains many ions so that less Ca^{2+} and SO_4^{2-} can be added/dissolved."   1

◻16 Maximum score 3

A correct answer can be formulated as follows:

$(NH_4)_3PMo_{12}O_{40} + OH^- \rightarrow 12\ MoO_4^{2-} + HPO_4^{2-}$
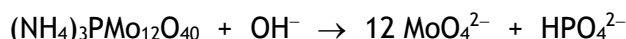
The amount of negative charges to right of the arrow is $12 \times 2 + 2 = 26$.
So 26 moles of OH^- react with 1 mole of $(NH_4)_3PMo_{12}O_{40}$.

· each mole of $(NH_4)_3PMo_{12}O_{40}$ forms 12 moles of MoO_4^{2-} and 1 mole of HPO_4^{2-} 1
· calculation of the amount of negative charges to the right side of the arrow   1
· number of OH^- made equal to the amount of negative charges on the right side of the
arrow   1

If an answer is given like: „To the right of the arrow MoO_4^{2-} and HPO_4^{2-} are listed, these
have 4 negative charges, so 4 (moles of) OH^- react."   1

Note
When the complete and correct reaction equation is given, give full marks.

◻17 Maximum score 4

An example of a correct calculation is:

$$\frac{(10.00 - 0.380)}{26} \times \frac{1}{2} \times \frac{100.0}{10.00} = 1.85\ (mmol)$$

· calculation of the amount of mmoles of OH^- that reacted with $(NH_4)_3PMo_{12}O_{40}$:
$10.00 - 0.380\ (mmol)$ 1
· calculation of the amount of mmoles of $(NH_4)_3PMo_{12}O_{40}$: dividing the amount of mmoles of
OH^- by 26   1
· calculation of the amount of mmoles of $Ca(H_2PO_4)_2$ present in 10.00 mL solution: dividing
the amount of mmoles of $(NH_4)_3PMo_{12}O_{40}$ by 2   1
· calculation of the amount of mmoles of $Ca(H_2PO_4)_2$ present in 100.0 mL solution: dividing
the amount of mmoles of $Ca(H_2PO_4)_2$ by 10.00 (mL) and multiplying by 100.0 (mL)   1

Notes
– *When an incorrect answer to question 17 is a direct consequence of an incorrect*
   answer to question 16 and the answer to question 16 was not equal to 1 mol OH^-, do
   not penalize this
– *When the following molar ratio is used in question 17: „one mole of $(NH_4)_3PMo_{12}O_{40}$*
   reacts with one mole of OH^- (as answer to question 16)", the second partial score is
   not to be assigned.