CHEMISTRY OLYMPIAD 2024

MARKING SCHEME PRELIMINARY ROUND 2

To be conducted from 19 until 22 March 2024

SCHEIKUNDE OLYMPIADE

Maastricht Science Programme

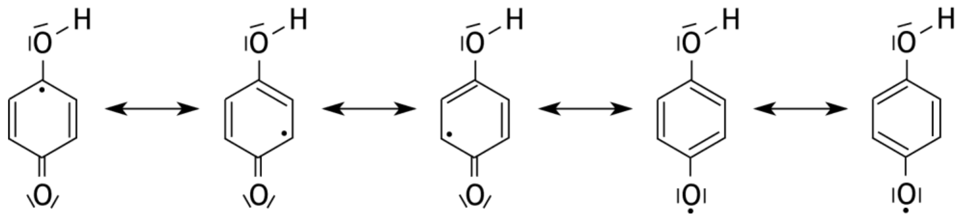
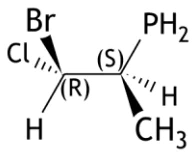
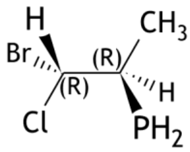
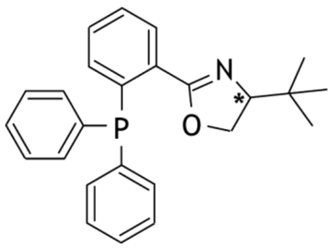
Maastricht University

- This preliminary round consists of 20 multiple choice questions divided over 8 topics and 3 problems with a total of 15 open questions.
- The maximum score for this work is 95 points (no bonus points).
- Required materials: (graphic) calculator and BINAS 6th or 7th edition or ScienceData 1st edition or BINAS 5th edition, English version.
- For each question the number of points you can score are given.
- The attached marking scheme must be used when grading the work. In addition, 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	**E**	
2	**A**	Below the absolute configurations of both molecules are given.   One stereocenter is different, so they are diastereomers.
3	**B**	The five-membered ring with O and N contains a chiral C atom, indicated below with an asterisk. The P atom and the N atom are not chiral. 

Reaction rate and equilibrium

4	**C**	The second step determines the rate, for which the following applies: $s = k[HOOBr][HBr]$. The equilibrium constant expression of step 1 is $K = \frac{[HOOBr]}{[O_2][HBr]}$. So $[HOOBr] = K[O_2][HBr]$. The rate expression becomes $s = kK[O_2][HBr][HBr] = k'[O_2][HBr]^2$.

5	B	The following applies: $K_p = \dfrac{p_Y \times p_Z}{p_X}$ and $p_X + p_Y + p_Z = p$ and $p_Y = p_Z$ so $p_Y = p_Z = \dfrac{p - p_X}{2} = \dfrac{3}{7}p$ and $K_p = \dfrac{\frac{3}{7}p \times \frac{3}{7}p}{\frac{1}{7}p} = \dfrac{9}{7}p$

Structures and formulas

6	F	In the molecule Cl – N = C = O, the N atom also has a non-bonding electron pair. N therefore has 3 electron domains and ∠ ClNC will be (approximately) 120°. C has 2 electron domains and ∠ NCO is therefore 180°.
7	C	The electron configuration of $_{32}$Ge in the ground state is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^2$. The set of quantum numbers $n = 4$, $l = 1$, $m_l = 1$, $m_s = +½$ corresponds to an electron in a 4*p* orbital. The first three quantum numbers at C indicate that this electron would be in the same 4*p* orbital as the mentioned electron. This is not possible because the second electron must be in a different 4p orbital A corresponds to an electron in a 3*d* orbital. B corresponds to an electron in the 4*s* orbital. D corresponds to the second electron in the 4p level, which is in another 4p orbital.
8	E	The bond between the two C atoms is a σ-bond and each of the triple bonds consists of one σ-bond and two π-bonds.

pH / acid-base

9	B	The graph shows a titration of a weak base with a strong acid (the initial pH is higher than 7 and the pH at the equivalence point is lower than 7).
10	B	The following reaction occurs: $H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$. For the buffer solution that is created: pH = pK_a – log $\dfrac{\text{moles of } H_2PO_4^-}{\text{moles of } HPO_4^{2-}}$ or 6.90 = 7.21 – log $\dfrac{\text{moles of } H_2PO_4^-}{\text{moles of } HPO_4^{2-}}$ log $\dfrac{\text{moles of } H_2PO_4^-}{\text{moles of } HPO_4^{2-}}$ = 7.21 – 6.90 = 0.31 or $\dfrac{\text{moles of } H_2PO_4^-}{\text{moles of } HPO_4^{2-}}$ = $10^{0.31}$ = 2.0. Suppose that *a* mL of 1.0 M NaOH solution was added, then $\dfrac{500 \times 0.200\ -\ a \times 1.0}{a \times 1.0}$ = 2.0; solving this equation gives *a* = 33 (mL).

Redox and electrochemistry

11	**F**	Zn^{2+} is a stronger oxidising agent than H_2O. Zn is a stronger reducing agent than H_2O.
12	**D**	In the Nernst equation for half-reaction I $[H^+]$ is present, and in the Nernst equation for half-reaction II $[OH^-]$ is present. Both concentrations are determined by the pH of the solution.
13	**D**	The half-reaction at the negative electrode can be represented as: $CO_2 + 6\,H^+ + 6\,e^- \rightarrow CH_3OH + H_2O$. The maximum amount that can be formed is: $\dfrac{0.370\,(\text{C s}^{-1}) \times 200\,(\text{min}) \times 60\,(\text{s min}^{-1})}{9.649 \cdot 10^4\,(\text{C mol}^{-1})} \times \dfrac{1}{6} = 0.0767\ \text{mol } CH_3OH$. So $\dfrac{0.0530}{0.0767} \times 10^2\,\% = 69.1\%$ of the current is used for the conversion of CO_2 into CH_3OH.

Analysis

14	**A**	Al^{3+} and SO_4^{2-} are both oxidising agents. (I^-, $H_2C_2O_4$ and Sn^{2+} are reducing agents and can be oxidised by dichromate, forming Cr^{3+}.)
15	**D**	In the resulting solution, $[MnO_4^-] = \dfrac{0.100}{0.600} \times 3.00 \cdot 10^{-4} = 5.00 \cdot 10^{-5}\ \text{mol L}^{-1}$. The volume of the resulting solution is 100.0 mL. So, $50.0 \times 3.00 \cdot 10^{-4} - 100.0 \times 5.00 \cdot 10^{-5} = 1.00 \cdot 10^{-2}$ mmol MnO_4^- was converted. This has reacted with $\dfrac{5}{2} \times 1.00 \cdot 10^{-2} = 2.50 \cdot 10^{-2}$ mmol SO_3^{2-}. Therefore, the molarity of the sodium sulphite solution was $\dfrac{2.50 \cdot 10^{-2}}{50.0} = 5.00 \cdot 10^{-4}\ \text{mol L}^{-1}$.

Chemical calculations

16	**C**	900 °C is 1173 K, 2.00 atm is $2.02 \cdot 10^5$ Pa and 0.826 g dm^{-3} is $0.826 \cdot 10^3$ g m^{-3}. Let the molar mass be M g mol^{-1}, then 1.00 m^3 of the gas contains $\dfrac{0.826 \cdot 10^3}{M}$ moles. According to the ideal gas law, $pV = nRT$ or $2.02 \cdot 10^5 \times 1.00 = \dfrac{0.826 \cdot 10^3}{M} \times 8.314 \times 1173$ or $M = \dfrac{0.826 \cdot 10^3}{2.02 \cdot 10^5 \times 1.00} \times 8.314 \times 1173 = 39.9\ \text{g mol}^{-1}$. That is the molar mass of Ar.

17	**C**	Part of the Zn has been converted into $Zn(OH)_2$ in the block . The extra mass is all OH^-: 140.2 g – 113.0 g = 27.2 g OH^-, and that is $\frac{27.2}{17.008} = 1.60$ mol OH^-. That corresponds to $\frac{1.60}{2} = 0.800$ moles of Zn^{2+} and that much Zn(0) has also been converted. There were originally $\frac{113.0}{65.38} = 1.728$ moles of Zn(0); in the final block the amount of Zn(0) is therefore 1.728 – 0.800 = 0.928 mol Zn(0). The ratio Zn(0) : Zn(II) is therefore 0.928 : 0.800 = 1.16 : 1.00.

Thermochemistry and Green Chemistry

18	**D**	*E*-factor = $\frac{\text{total mass of all reactants} - \text{mass of desired product}}{\text{mass of desired product}} = 6.5$ If the percentage yield is η, then: $6.5 = \frac{2 \times 183.52 + 5 \times 32.00 + 2 \times 60.09 - 2 \times 63.55 \times \eta}{2 \times 63.55 \times \eta}$. This results in η = 0.68, so the percentage yield is 68%.
19	**D**	$2\ H_2S + 3O_2 \rightarrow 2\ SO_2 + 2\ H_2O$ $CS_2 + 2\ H_2O \rightarrow 2\ H_2S + CO_2$ $\cancel{2\ H_2S} + 3\ O_2 + CS_2 + \cancel{2\ H_2O} \rightarrow 2\ SO_2 + \cancel{2\ H_2O} + \cancel{2\ H_2S} + CO_2$ So $\Delta_r H_3 = 2 \times \Delta_r H^0{}_1 - \Delta_r H^0{}_2 = 2 \times (-518.2) - 67.8 = -1104.2$ kJ mol^{-1}.
20	**B**	$\Delta G^0 = \Delta H^0 - T\Delta S^0$ At B, 2 moles of gas are formed from 2 moles of gas. In the other reactions the amount of moles of gas increases. So for B, ΔS^0 will be much closer to zero than for the other reactions.

Open questions — total 55 points

Problem 2 Hydrogen for a fuel cell — 15 points

□1 Maximum score 3

An example of a correct calculation is:

$$\frac{0.100}{24.5}\times\frac{1}{92}\times 101.1\cdot 10^3 = 4.5 \text{ (mg)}$$

- conversion from 0.100 dm^3 H_2 to moles: divide 0.100 (dm^3) by 24.5 ($dm^3\,mol^{-1}$) 1
- calculation of the amount of moles of Ru: divide the amount of moles of H_2 by 92 ($mol\,mol^{-1}$) 1
- conversion from the amount of moles of Ru to mg: multiply the amount of moles of Ru by 101.1 ($g\,mol^{-1}$) and by 10^3 ($mg\,g^{-1}$) 1

□2 Maximum score 4

An example of a correct calculation is:

$(1.0 \times 0.100) \times 4 \times 24.5 : 0.100 = 98$ (min)

- calculation of the amount of moles of $NaBH_4$: multiply 1.0 ($mol\,L^{-1}$) by 0.100 (L) 1
- calculation of the amount of moles of H_2: multiply the amount of moles of $NaBH_4$ by 4 1
- conversion from moles of H_2 to dm^3: multiply the amount of moles of H_2 by 24.5 ($dm^3\,mol^{-1}$) 1
- calculation of the amount of minutes: divide the amount of dm^3 of H_2 by 0.100 ($dm^3\,min^{-1}$) 1

Note

When in the answer to question 1 a wrong value is used for V_m and in the answer to question 2 that same wrong value is used for V_m, do not penalize this again.

□3 Maximum score 4

An example of a correct calculation is:

(At the temperature T that is needed, applies that:)

$k_T = 2 \times k_{298}$

$$E_a = R \times \frac{T_1 \times T_2}{T_1 - T_2} \ln \frac{k_{T_1}}{k_{T_2}}$$

$$4.2 \cdot 10^4 = 8.314 \times \frac{298 \times T}{298 - T} \ln \frac{k_{298}}{k_T} = 8.314 \times \frac{298 \times T}{298 - T} \ln \frac{1}{2}$$

$$\frac{298 \times T}{298 - T} = \frac{4.2 \cdot 10^4}{8.314 \times \ln \frac{1}{2}} = -7.29 \cdot 10^3$$

$T = 311$ K

- Arrhenius equation was written down and potentially filled in (partially) 1
- notion that by the temperature used for the calculation, T, applies that $k_T = 2 \times k_{298}$ 1
- Arrhenius equation filled in (almost complete) 1
- calculation of temperature needed 1

□4 Maximum score 4

An example of a correct calculation is:

$\Delta E^0 = E^0_{ox} - E^0_{red} = +0.40 - (-0.83) = +1.23$ V

$\Delta G^0 = -nF\Delta E^0 = -2 \times 9.649{\cdot}10^4 \times 1.23 = -2.37{\cdot}10^{\ 5}$ J (mol^{-1} H_2O)

- calculation of ΔE^0 1
- notion that n = 2 mol e^- per mol of H_2O 1
- rest of the calculation correct 1
- correct unit of ΔG^0 1

Problem 3 A high-temperature superconductor 24 points

□5 Maximum score 3

$2\ Y_2(CO_3)_3\ +\ 8\ BaCO_3\ +\ 12\ CuCO_3\ +\ (1-2x)\ O_2\ \rightarrow\ 4\ YBa_2Cu_3O_{(7-x)}\ +\ 26\ CO_2$

- all formulas before and after the arrow are correct 1
- correct coefficients for $Y_2(CO_3)_2$, $BaCO_3$, $CuCO_3$, $YBa_2Cu_3O_{(7-x)}$ and CO_2 1
- correct coefficient for O_2 1

Note

If the following equation is given:

$Y_2(CO_3)_3\ +\ 4\ BaCO_3\ +\ 6\ CuCO_3\ +\ \tfrac{1}{2}(1-2x)\ O_2\ \rightarrow\ 2\ YBa_2Cu_3O_{(7-x)}\ +\ 13\ CO_2$

accept it as correct.

□6 Maximum score 4

An example of a correct answer:

Per mol YBCO, $0.20 \times 3 = 0.60$ mol Cu^{3+} is formed, and $3 - 0.60 = 2.40$ mol Cu^{2+} remains.

The total amount of positive charges is $3 + 2 \times 2 + 2.40 \times 2 + 0.60 \times 3 = 13.6$.

This should be equal to the total amount of negative charges: $(7 - x) \times 2$.

From this follows that $x = 0.20$.

- calculation of the amount of moles of Cu^{3+} that is produced 1
- calculation of the amount of moles of Cu^{2+} that remains 1
- calculation of the total amount of moles of positive and negative charges 1
- calculation of x 1

□7 Maximum score 2

$Cu^{3+}\ +\ e^-\ \rightarrow\ Cu^{2+}$ $\times 4$

$2\ H_2O\ \rightarrow\ O_2\ +\ 4\ H^+\ +\ 4\ e^-$ $\times 1$

$4\ Cu^{3+}\ +\ 2\ H_2O\ \rightarrow\ 4\ Cu^{2+}\ +\ O_2\ +\ 4\ H^+$

- the equations of both half-reactions are correct 1
- correct combination of the equations of both half-reactions 1

□8 Maximum score 7

An example of a correct calculation is:

21.8 mL 0.0332 M sodium thiosulfate solution contains 21.8 × 0.0332 mmol $S_2O_3^{2-}$.

This has reacted with $\frac{1}{2} \times 21.8 \times 0.0332$ mmol I_2, so the iodide has reacted with

$2 \times \frac{1}{2} \times 21.8 \times 0.0332$ mmol Cu^{2+}.

This is the total amount of Cu^{2+} and Cu^{3+} in the 160 mg $YBa_2Cu_3O_{(7-x)}$,

therefore 160 mg $YBa_2Cu_3O_{(7-x)}$ is $\frac{1}{3} \times 2 \times \frac{1}{2} \times 21.8 \times 0.0332$ mmol.

The molar mass of $YBa_2Cu_3O_{(7-x)}$ is {554.2 + (7 − x) × 16.00} g mol^{-1}, therefore 160 mg is

$\frac{160}{554.2 + (7 - x) \times 16.00}$ mmol.

Thus $\frac{160}{554.2 + (7 - x) \times 16.00} = \frac{1}{3} \times 2 \times \frac{1}{2} \times 21.8 \times 0.0332$. Consequently x = 0.19.

- calculation of the amount of mmoles of $S_2O_3^{2-}$: multiply 21.8 (mL) by 0.0332 (mmol mL^{-1}) 1
- calculation of the amount of mmoles of iodide that reacted: divide the amount of mmoles of $S_2O_3^{2-}$ by 2 1
- calculation of the amount of mmoles of Cu^{2+} that reacted: multiply the amount of mmoles of iodide that reacted by 2 1
- calculation of the amount of mmoles of $YBa_2Cu_3O_{(7-x)}$ that follows from that: divide the amount of mmoles of Cu^{2+} that reacted by 3 1
- calculation of the molar mass of $YBa_2Cu_3O_{(7-x)}$: 554.2 + (7 − x) × 16.00 (mg mmol^{-1}) 1
- calculation of the amount of mmoles of $YBa_2Cu_3O_{(7-x)}$ in 160 mg: divide 160 (mg) by the molar mass of $YBa_2Cu_3O_{(7-x)}$ (in mg mmol^{-1}) 1
- rest of the calculation 1

□9 Maximum score 4

Examples of a correct answer are:

Suppose there are p oxide ions on the edges and q on exterior faces, then $p + q = 20$ and

$\frac{1}{4}p + \frac{1}{2}q = 7$.

Solving this system of two equations with two unknowns yields p = 12 en q = 8.

- notion that oxide ions on the edges contribute one fourth each 1
- notion that oxide ions in the exterior faces count for one half each 1
- setting up two equations with two unknowns 1
- solving the system of two equations with two unknowns 1

and

Suppose there are p oxide ions on the edges, then there are 20 – p oxide ions on exterior faces. It follows that

$$\frac{1}{4}p + \frac{1}{2}(20-p) = 7 .$$

This results in p = 12. Therefore, there are 12 oxide ions on the edges and 8 on exterior faces.

· notion that oxide ions on the edges count for one fourth each
· notion that oxide ions on the exterior faces count for one half each 1
· thus $\frac{1}{4}p + \frac{1}{2}(20-p) = 7$ 1
· rest of the calculation 1

If, without calculation or explanation, the answer „There are 12 oxide ions on the edges and 8 oxide ions on exterior faces." is given 0

□10 Maximum score 4

An example of a correct answer is:
The mass of the unit cell is 666.2 u; the volume of the unit cell is
$0.382 \times 0.389 \times 1.168\ \text{nm}^3$.
Therefore the density is:

$$\frac{666.2\ \text{u}}{0.382 \times 0.389 \times 1.168\ \text{nm}^3} = \frac{666.2\ \text{u} \times 1.66 \cdot 10^{-24}\ \text{g u}^{-1}}{0.382 \times 0.389 \times 1.168\ \text{nm}^3 \times 10^{-21}\ \text{cm}^3\ \text{nm}^{-3}} = 6.37\ \text{g cm}^{-3} .$$

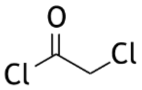
· calculation of the mass of the unit cell in u 1
· calculation of the volume of the unit cell in nm^3 1
· calculation of the density in u nm^{-3} 1
· conversion of the density in u nm^{-3} into g cm^{-3} 1

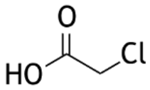
Note:
When the same mistake is made in the calculation of the unit cell mass as in the calculation of the molar mass of $YBa_2Cu_3O_{(7-x)}$ in question 8, do not penalize this again.

Problem 4 Penicillin 16 points

□11 Maximum score 2

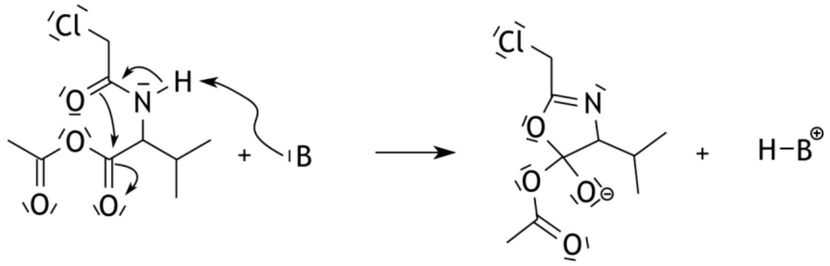
A correct answer may look as follows:



If the answer  is given 1

□12 Maximum score 4

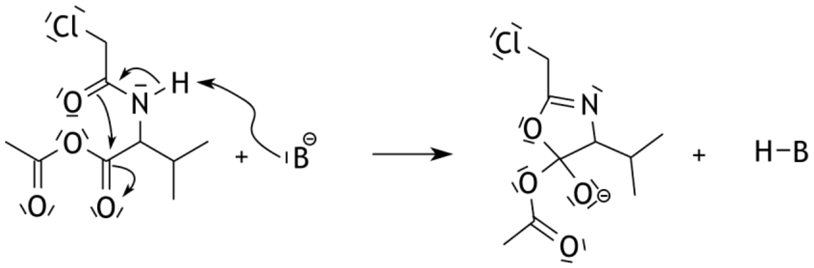
A correct answer may look as follows:



- $H-B^+$ after the arrow 1
- the shift of electron pairs before the arrow is correctly shown 1
- non-bonding electron pairs before and after the arrow correctly shown 1
- correct structural formula including formal charges of the product after the arrow 1

Note

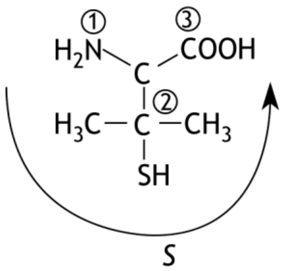
If the following answer is given:



mark this as being correct.

□13 Maximum score 3

A correct answer may look as follows:

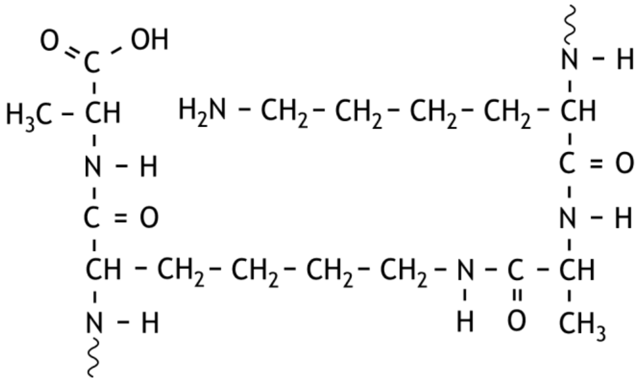


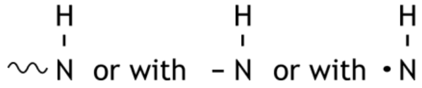
(H has priority ④)

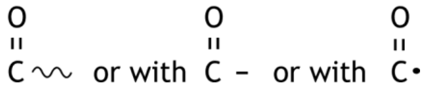
- a correct drawing 1
- correct prioritization 1
- correct indication of the configuration 1

□14 Maximum score 4

A correct answer may look as follows:

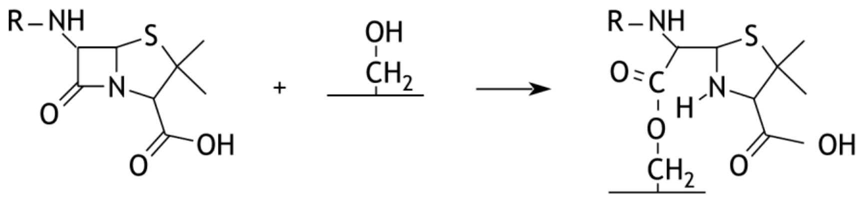


- beginning and end of the structural formula shown with  1
- the terminal alanine group correctly shown 1
- the peptide bonds correctly shown 1
- the rest groups correctly shown 1

If in an otherwise correct answer the beginning and/or end of the structural formula is shown with  3

□15 Maximum score 3

A correct answer may look as follows:



- the peptide bond in the four-membered ring is broken 1
- the formed ester bond correctly shown 1
- the formed NH group correctly shown 1