NATIONAL CHEMISTRY OLYMPIAD 2024

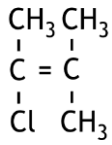
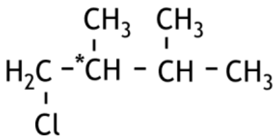
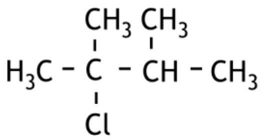
MARKING SCHEME PRELIMINARY ROUND 1

To be conducted from 15 until 31 January 2024

- This preliminary round consists of 25 multiple choice questions divided over 9 topics and 2 problems with a total of 8 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 put your name on it.
- The maximum score for this work is 77 points.
- The preliminary round lasts up to two full hours.
- Required materials: (graphic) calculator and BINAS 6th or 7th edition, 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 50 points

For every correct answer: 2 points

		Carbon chemistry
1	D	In step 1, an addition of HBr takes place to the double bond. In step 2, Br is substituted by OH.
2	B	The polymer was created by addition polymerization of 
3	B	At B, the chlorine atom can replace an H atom on C atom 1 or on C atom 2. The following monochloro substitution products are formed:  and  When the chlorine atom is placed on C atom 1, C atom 2 becomes an asymmetric C atom, indicated with an asterisk. There are therefore two mirror image isomers of that structure that have the same boiling point. The other compounds produce more than three isomers.
4	B	The electron pair from the bond between the O atom and the C atom becomes a lone pair on the O atom. The arrow must therefore point in the direction of the O atom.
		Reaction rate and equilibrium
5	D	When the solution is diluted, the equilibrium shifts to the right. The number of moles of H_3O^+ increases. However, $[H_3O^+]$ becomes smaller. So the pH increases.
6	A	$\frac{0.98\times 1.0\cdot 10^{-3}}{88}$ mol $C_5H_{12}O$ is converted in 4.0×60 sec. So the reaction rate is $\dfrac{\frac{0.98\times 1.0\cdot 10^{-3}}{88}}{4.0\times 60} = 4.6\cdot 10^{-8}$ mol s^{-1}.
7	C	$K = [Ba^{2+}][IO_3^-]^2$ 0.2000 – 0.1513 g $Ba(IO_3)_2$ has been dissolved, that is $\frac{0.2000-0.1513}{487.1}$ mol $Ba(IO_3)_2$. $[Ba^{2+}] = \dfrac{\frac{0.2000-0.1513}{487.1}}{0.100} = 9.998\cdot 10^{-4}\ mol\,L^{-1}$ and $[IO_3^-] = 2\times 9.998\cdot 10^{-4}\ mol\,L^{-1}$. So $K = 9.998\cdot 10^{-4}\times\left(2\times 9.998\cdot 10^{-4}\right)^2 = 4.00\cdot 10^{-9}$.
8	C	The reaction rate depends on the degree of distribution of the zinc, the concentration of H_3O^+ and the temperature. These have all remained the same at C.

		Thermochemistry
9	**A**	For reaction 1 applies $\Delta H = -0.133\cdot10^5 + 2\times0.332\cdot10^5 = 0.531\cdot10^5$ J per mol N_2O_5. For reaction 2 applies $\Delta H = -0.332\cdot10^5 + 0.913\cdot10^5 = 0.581\cdot10^5$ J per mol NO_2. For the total conversion, $0.725\cdot10^5$ J per mol N_2O_5 was needed. The number of moles of NO_2 that still has to be converted is therefore $\frac{0.725\cdot10^5 - 0.531\cdot10^5}{0.581\cdot10^5} = 0.334$ mol. Per mole of N_2O_5, 2 moles of NO_2 are formed, so in reaction 2, $\frac{0.334}{2}\times100 = 16.7\,\%$ of the generated NO_2 is further converted.
		Structures and formulas
10	**D**	In structure A, the charges on the nitrogen atoms are incorrect. In structures B and C the structures do not have enough electrons and the charges are also incorrect.
11	**B**	In $COCl_2$, the C has a double bond to the O and a single bond to the Cl atoms. There are no lone pairs on the C atom. In the other answers, the indicated atoms have an electron domain geometry of 4.
12	**B**	Hg^+ has 79 electrons. I^- has 54. Cu^+ and Zn^{2+} have 28. Ni^{2+} has 26.
		pH / acid-base
13	**C**	$B + H_2O \rightleftharpoons HB^+ + OH^-$ pOH = 14.00 − pH = 1.50 $[OH^-] = 10^{-1.50} = 0.032$ mol L^{-1} $\begin{array}{lcccccc} & & [B] & & [HB^+] & & [OH^-] \\ \text{initial} & & 0.15 & & 0 & & 0 \\ \text{change} & - & 0.032 & + & 0.032 & + & 0.032 \\ \hline \text{equilibrium} & & 0.12 & & 0.032 & & 0.032 \end{array}$ $K_b = \frac{0.032\times0.032}{0.12} = 8.4\cdot10^{-3}$
14	**C**	The sodium hydroxide solution contains $150\times0.150 = 22.5$ mmol OH^- and the hydrochloric acid contains $250\times0.100 = 25.0$ mmol H_3O^+. Therefore there is 25.0 − 22.5 = 2.5 mmol H_3O^+ in excess. The total volume is 150 + 250 = 400 mL, so $\left[H_3O^+\right] = \frac{2.5}{400}$; $pH = -\log\frac{2.5}{400} = 2.20$.

15	**F**	$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$ pOH = 14.00 − 7.41 = 6.59; $[OH^-] = 10^{-6.59}$ $K_b = 1.6{\cdot}10^{-7} = \dfrac{[H_2PO_4^-]\times[OH^-]}{[HPO_4^{2-}]} = \dfrac{[H_2PO_4^-]\times 10^{-6.59}}{[HPO_4^{2-}]}$ $\dfrac{[H_2PO_4^-]}{[HPO_4^{2-}]} = \dfrac{1.6{\cdot}10^{-7}}{10^{-6.59}} = 0.62$ The mole ratio is therefore 0.62 mol NaH_2PO_4 (M = 120 g mol^{-1}) : 1.0 mol Na_2HPO_4 (M = 142 g mol^{-1}). The mass ratio is 74.7 g NaH_2PO_4 : 142 g Na_2HPO_4 = 1.0 g NaH_2PO_4 : 1.9 g Na_2HPO_4.
		Redox and electrolysis
16	**C**	For the production of 1.0 g Li $\dfrac{1.0}{6.941}$ mol electrons are required. For the production of 1.0 g Al $\dfrac{1.0}{26.98}\times 3$ mol electrons are required. Therefore the production of 1.0 g Al takes $\dfrac{\frac{1.0}{26.98}\times 3}{\frac{1.0}{6.941}}$ = 0.77 times longer than the production of 1.0 g Li with the same current.
17	**C**	The standard electrode potentials of the redox couples are: $Cr_2O_7^{2-}/Cr^{3+}$ + 1.36 V MnO_4^-/Mn^{2+} + 1.51 V Therefore the oxidizing agent $Cr_2O_7^{2-}$ cannot react with the reducing agent Mn^{2+}. NO_3^-/NO_2 + 0.80 V SO_4^{2-}/SO_2 + 0.17 V Therefore the oxidizing agent NO_3^- can react with the reducing agent SO_2.
		Analysis
18	**D**	8.5 mL hydrochloric acid is required for 1.0 mL of the undiluted ammonia solution. 25.00 × 8.5 = 212.5 mL hydrochloric acid is required for 25.00 mL of the undiluted ammonia solution. Between 12 mL and 25 mL hydrochloric acid should be used, therefore the dilution factor must be between $\dfrac{212.5}{25} = 8.5$ and $\dfrac{212.5}{12} = 18$. The dilution factors of A, B, C, D and E are respectively 25, 50, 4, 10 and 20.

19	D	During the titration $14.36 \times 0.00850 = 0.122$ mmol of $AgNO_3$ was used. Because $Ag^+ + Cl^- \rightarrow AgCl$, this also makes 0.122 mmol Cl^- in the 10.00 mL of the diluted sodium chloride solution. Which means that 10.00 mL of the diluted NaCl solution contained 0.122 mmol NaCl. In 10.00 mL undiluted solution $\frac{0.122 \times 250.0}{10.00} = 3.05$ mmol NaCl was present. The molarity of the undiluted NaCl solution was: $\frac{3.05}{10.00} = 3.05 \cdot 10^{-1}$ mol L^{-1}.
20	G	Fragmentation of the molecules I en III will cause $C_3H_7^+$ fragments that peak around $m/z = 43$. Fragmentation of the molecule II will cause fragments of CH_3CO^+ that peak around $m/z = 43$.
21	A	At the first equivalence point at 6 mL sodium hydroxide solution only the stronger acid has completely reacted. At the second equivalence point, which is at 10 mL (so 4 mL later), the weaker acid has also completely reacted. Therefore, to completely convert a strong acid one needs more of the base, and the molarity of the strong acid is larger. This means that statement I is incorrect. Methyl yellow has a colour change range that lies between 2.9 and 4.0. It changes colour too early, which causes the first equivalence point to be imprecisely determined. Statement II is also wrong.
		Chemical calculations
22	E	$\frac{16.0}{55.85}$ mol Fe reacts; this has a volume of $\frac{16.0}{7.87} = 2.03$ cm^3. This creates $\frac{16.0}{55.85} \times \frac{2}{4} \times 159.7$ g Fe_2O_3 with a volume of $\frac{\frac{16.0}{55.85} \times \frac{2}{4} \times 159.7}{5.25} = 4.36$ cm^3. Increase in volume = 4.36 – 2.03 = 2.33 cm^3.
23	C	The hydrocarbon with the highest mass percentage of carbon yields the largest amount of CO_2 upon combustion. This is C_6H_6.
		Green chemistry and industry
24	D	The reaction remains the same, so the atom economy stays the same. With a higher percentage yield more of the wanted product is formed. The *E*-factor will decrease.
25	F	15 g of powder contains $\frac{15 \times 0.98}{81.38}$ mol ZnO. This will create a maximum of $\frac{15 \times 0.98}{81.38}$ mol Zn. This method produces $\frac{8.0}{65.38}$ mol Zn. The percentage yield is $\frac{\frac{8.0}{65.38}}{\frac{15 \times 0.98}{81.38}} \times 10^2 \% = 68\%$.

Open questions total 27 points

Problem 2 Determining manganese levels in tea leaves 11 points

□1 Maximum score 3

$IO_4^- + 2\,H^+ + 2\,e^- \rightarrow IO_3^- + H_2O$

- IO_4^- and H^+ before the arrow and IO_3^- and H_2O after the arrow 1
- e^- before the arrow 1
- correct coefficients 1

□2 Maximum score 4

Examples of a correct answer are:

$\frac{0.1}{100}\times 3$ g Mn^{2+} in 3 g of tea, which is $\frac{\frac{0.1}{100}\times 3}{54.94}$ mol Mn^{2+}. This reacts with $\frac{\frac{0.1}{100}\times 3}{54.94}\times\frac{5}{2}$ mol IO_4^-. Therefore, a minimum of $\frac{\frac{0.1}{100}\times 3}{54.94}\times\frac{5}{2}\times 230.00 = 3\cdot 10^{-2}$ g KIO_4 is needed.

This is substantially less than the 0.5 g which is added.

- calculation of the number of g of Mn^{2+} in 3 g tea leaves: divide 0.1(%) by 100(%) and multiply by 3 (g) 1
- calculation of the number of moles of Mn^{2+}: divide the number of g Mn^{2+} in 3 g tea by 54.94 (g mol^{-1}) 1
- calculation of number of moles of IO_4^- needed: multiply the number of moles of Mn^{2+} by $\frac{5}{2}$ 1
- calculation of the minimum number of g of KIO_4 needed: multiply the number of moles of IO_4^- needed by 230.00 (g mol^{-1}) and conclusion 1

and

0.5 g potassium periodate contains $\frac{0.5}{230.00}$ mol IO_4^-. This reacts with $\frac{0.5}{230.00}\times\frac{2}{5}$ mol Mn^{2+}; which is $\frac{0.5}{230.00}\times\frac{2}{5}\times 54.94 = 0.048$ g Mn^{2+}.

3 g tea leaves contain $\frac{0.1}{100}\times 3 = 0{,}003$ g Mn^{2+}.

This is substantially less than the 0.048 g Mn^{2+} with which 0.5 g potassium periodate can react.

- calculation of the number of moles of IO_4^- in 0.5 g potassium periodate: divide 0.5 (g) by 230.00 (g mol^{-1}) 1
- calculation of the number of moles of Mn^{2+} that can react with it: multiply the number of moles of IO_4^- in 0.5 g potassium periodate by $\frac{2}{5}$ 1
- calculation of the number of g of Mn^{2+} that can react with 0.5 g potassium periodate: multiply the number of moles of Mn^{2+} that can react with it by 54.94 (g mol^{-1}) 1
- calculation of the number of g of Mn^{2+} in 3 g tea leaves: divide 0.1(%) by 100(%) and multiply with 3 (g) and conclusion 1

□3 Maximum score 4

An example of a correct answer is:

The MnO_4^- content was 0.290 mmol L^{-1}, so there was $50.00 \times 10^{-3} \times 0.290$ mmol MnO_4^- in 50.00 mL solution. Therefore, there was $50.00 \times 10^{-3} \times 0.290$ mmol Mn^{2+} in the 2.580 g tea leaves; that is $50.00 \times 10^{-3} \times 0.290 \times 54.94$ mg. Therefore the Mn^{2+} mass percentage is

$$\frac{50.00 \times 10^{-3} \times 0.290 \times 54.94}{2.580 \times 10^{3}} \times 10^{2}\,\% = 0.0309\%.$$

- reading the MnO_4^- content: 0.290 ± 0.005 (mmol L^{-1}) 1
- calculation of the number of mmoles of Mn^{2+} in the 2.580 g tea leaves (is equal to the number of mmoles of MnO_4^- in the 50.00 mL solution): multiply the read MnO_4^- content by 10^{-3} (L mL^{-1}) and by 50.00 (mL) 1
- calculation of the number of mg of Mn^{2+} in the 2.580 g tea leaves: multiply the number of mmoles of Mn^{2+} in the 2.580 g tea leaves by 54.94 (mg $mmol^{-1}$) 1
- rest of the calculation 1

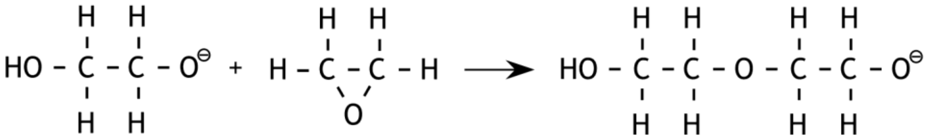
Note

When, in an otherwise correct answer, the MnO_4^- content was read as 0.29 mmol L^{-1}, award full marks.

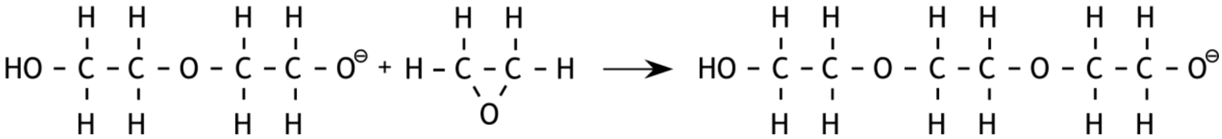
Problem 3 Vasa 16 points

4 Maximum score 3

A correct answer can be expressed as follows:

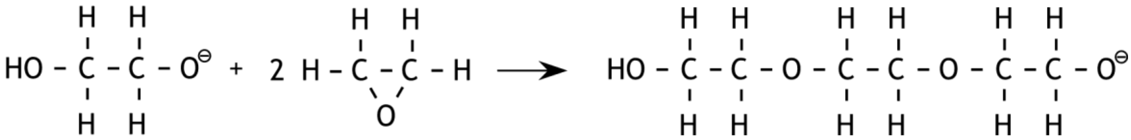


and



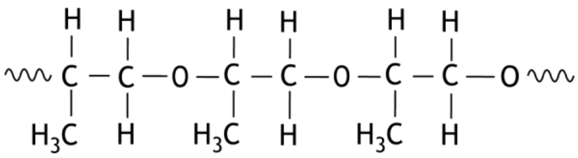
- correct structural formulas of ion A and of a molecule of epoxyethane before the arrow in the first reaction equation 1
- correct structural formula of the coupling product after the arrow in the first reaction 1
- correct coupling of the particle that is formed in the first reaction with a molecule of epoxyethane, depicted in structural formulas 1

Note:
When the following answer is given, award full marks:

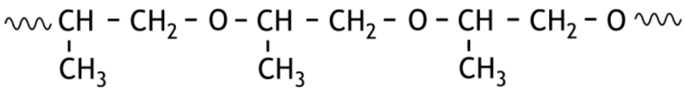


5 Maximum score 3

Examples of a correct answer are:

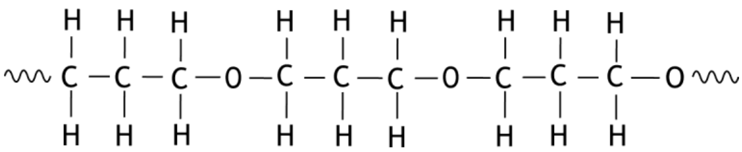


and



- main chain correctly represented 1
- methyl groups correctly represented 1
- start and end of the fragment indicated with 〰, – or • 1

If the following answer is given:



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Note
When in contradiction to the above correct structural formula a 1,2-epoxypropane unit is 'reversed' linked, do not penalize.

□6 Maximum score 3

A correct answer can be expressed as follows:

$$H\left(O-CH_2-CH_2\right)_nO^{\ominus} + H_2O \longrightarrow H\left(O-CH_2-CH_2\right)_nOH + OH^{\ominus}$$

- $H\left(O-CH_2-CH_2\right)_nO^{\ominus}$ before the arrow 1
- H_2O before the arrow 1
- correct formulas after the arrow 1

□7 Maximum score 4

An example of a correct calculation is:

$\frac{88}{44}$ mol epoxyethane reacts. And $92-88$ g H_2O reacts, that is $\frac{92-88}{18}$ mol.

Therefore $\frac{92-88}{18}$ mol polyepoxyethane forms. Thus $n = \dfrac{\frac{88}{44}}{\frac{92-88}{18}} = 9$.

- calculation of the number of moles of epoxyethane that have reacted: divide 88 (g) by the molar mass of epoxyethane 1
- calculation of the number of grams of water that has reacted: $92 - 88$ 1
- calculation of the number of moles of polyepoxyethane that has been formed (is equal to the number of moles of water that have reacted): divide the number of grams of water by the molar mass of water 1
- calculation of *n*: divide the number of moles of epoxyethane that have reacted, by the number of moles of polyepoxyethane that has been formed 1

□8 Maximum score 3

An example of a correct answer is:

Polyepoxyethane with (on average) longer molecules has a higher melting range due to stronger van der Waals forces. The less water reacts, (the fewer termination reactions occur and) the longer the chains that are formed. So, in experiment 2 (with the smallest amount of water), polyepoxyethane with the highest melting range is formed.

- polyepoxyethane with longer molecules has a higher melting range because the van der Waals forces are stronger 1
- the less water reacts, the longer the molecules that are formed 1
- so: in experiment 2, polyepoxyethane with the highest melting range is formed 1

If an answer is given as: „With more water, more OH groups are formed, causing stronger molecular attachment through hydrogen bonds. Therefore, in experiment 1, polyepoxyethane with the highest melting range is formed.” 0