## NATIONAL CHEMISTRY OLYMPIAD 2025

MARKING SCHEME PRELIMINARY ROUND 1

To be held between 13<sup>th</sup> and 31<sup>st</sup> January 2025



- This preliminary round consists of 25 multiple choice questions divided over 9 topics and 2 problems, with a total of 8 open questions, in addition to an answer sheet for the multiple choice questions.
- Use the answer sheet to answer the multiple choice questions.
- For the open questions, use a separate answer sheet for each of the two problems. Remember to include your name on each sheet.
- The maximum score for this paper is 76 points.
- The preliminary round lasts two hours in total.
- Required materials: (graphic) calculator and BINAS 6<sup>th</sup> or 7<sup>th</sup> edition, ScienceData 1<sup>st</sup> edition or BINAS 5<sup>th</sup> edition, English version. "Green chemistry" table is included.
- The total number of points available for each question is stated.
- 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 Short overview

nr.	answer
1	В
2	D
3	F
4	С
5	Н
6	D
7	F
8	С
9	С
10	В
11	С
12	С
13	D
14	В
15	С
16	В
17	С
18	А
19	F
20	D
21	В
22	E
23	D
24	D
25	D

		Carbon Chemistry
1	В	Compound I is a mirror image isomer of substance X, compound II is the same substance as substance X (rotated 180°).
2	D	Polymer I is formed from the 1,4-addition of buta-1,3-diene: $CH_2$ $CH_2$ $CH_2$ Polymer II is formed from the condensation of 5-hydroxypentanoic acid. $HO_2$ $CH_2$ $CH_2$ $CH_2$ $CH_2$ $CH_2$ $OH$
3	F	Below are all the structures. The asymmetric carbon atoms are indicated with *. Therefore, these structures have two stereoisomers. $H_1 = H_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3 - CH_3 - CH_2 - CH_2 - CH_3 - CH_2 - CH_2 - CH_3 - C$
		Thermochemistry
4	С	reaction enthalpy = $-E_{initial} + E_{final}$ = $-\Delta H_{formation NaClO_4(s)} - \Delta H_{melting NaClO_4(s)} + \Delta H_{formation NaCl(s)}$ = $-382.75 \text{ kJ mol}^{-1} - 14.7 \text{ kJ mol}^{-1} + -411 \text{ kJ mol}^{-1} = -43 \text{ kJ mol}^{-1}$
5	н	Electrolysis is an endothermic reaction and a catalyst lowers the activation energy, so diagram V is without a catalyst and diagram III is with a catalyst."

		Rate of reaction and equilibrium
6	D	10 mL of a 0.50 M K <sub>2</sub> SO <sub>4</sub> solution and 10 mL of a 0.50 M AgNO <sub>3</sub> solution contain, respectively, 10 mmol K <sup>+</sup> and 5.0 mmol SO <sub>4</sub> <sup>2-</sup> , and 5.0 mmol Ag <sup>+</sup> and 5.0 mmol NO <sub>3</sub> <sup>-</sup> .
		The following heterogeneous equilibrium is established:
		$2 \operatorname{Ag}^{+}(\operatorname{aq}) + \operatorname{SO}_{4}^{2-}(\operatorname{aq}) \Longrightarrow \operatorname{Ag}_{2}\operatorname{SO}_{4}(s)$
		The number of mmoles of $K^+$ and $NO_3^-$ in the solution does not change. The numbers of mmoles of $Ag^+$ and $SO_4{}^{2-}$ in the solution decrease, where the decrease in the number of mmoles of $Ag^+$ is twice as large as the decrease in the number of mmoles of $SO_4{}^{2-}$ .
		Thus: $[K^+] > [NO_3^-] > [SO_4^{2-}] > [Ag^+]$
7	F	The value of $K$ changes only with a change in temperature. The reaction rate in both directions increases at the new equilibrium due to the higher concentrations of all particles.
8	С	2.50 - 1.70 = 0.80 g CaCO <sub>3</sub> has reacted.
		This is equal to $\frac{0.80}{100.00} = 0.0080 \text{ mol CaCO}_3$ .
		Thus, 0.0080 mol CO <sub>2</sub> has been formed in 0.250 L.
		$K_c = [CO_2] = \frac{0.0080}{0.250} = 0.032$
9	С	On the left, there are more gas particles, so the reaction to the right is temporarily favoured at higher pressure.
		The reaction to the right is exothermic and is temporarily favoured at lower temperatures.
		Structures and formulas
10	В	The electronegativity of H is 2.1, of O is 3.5 and of S is 2.6. This means that every H – O bond, S – O bond and S = O bond is polar with the $\delta^+$ on H and S and the $\delta^-$ on O.
11	С	232 - 208 = 24 nuclear particles are emitted.
		A helium nucleus consists of 4 nuclear particles, so $\frac{24}{4} = 6$ alpha particles are
		emitted.
		The atomic number of Th (Thorium) is 90, and that of Pb (Lead) is 82.
		82 + 12 - 90 = 4 protons are added. Thus 4 neutrons are converted.
12	С	7 (one Cl atom) + $3 \times 6$ (three O atoms) + 1(charge 1–) = 26 valence electrons.

13	D	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
		$\begin{array}{c} c \\ c$
		$: \overset{\bullet}{\circ} : \overset{\circ}{\circ} \overset{\circ}{\circ} : \overset{\bullet}{\circ} : \overset{\circ}{\circ} : \overset{\circ}$
		pH and acid-base
14	В	$K_{a} = \frac{[H^{+}][A^{-}]}{[HA]} = \frac{(0.102 \times 0.320)^{2}}{0.898 \times 0.320} = 3.71 \cdot 10^{-3}$
15	С	In the calculation, the increase in volume due to the addition of the HCl solution can
		The initial pOH is $14.00 - 9.20 = 4.80$ so $\left[ OH^{-} \right] = 10^{-4.80} = 1.58 \cdot 10^{-5}$ mol L <sup>-1</sup>
		The pOH after the reaction is $14.00 - 8.20 = 5.80$ so $[OH^-] = 10^{-5.80} = 1.58 \cdot 10^{-6}$ mol L <sup>-1</sup>
		Then $(1.58 \cdot 10^{-5} - 1.58 \cdot 10^{-6}) \times 100 = 1.43 \cdot 10^{-3}$ mmol OH <sup>-</sup> must react.
		This reacts with an equal amount of $H_3O^+$ originating from the same amount of HCl.
		Then $\frac{1.43 \cdot 10^{-3}}{0.10} = 0.014$ mL 0.10 M HCl solution must be added.
16	В	From 0.1 mol $K_2O$ , 0.2 mol $OH^-$ is produced when the reaction proceeds to completion:
		$K_2O + H_2O \rightarrow 2 K^+ + 2 OH^-$
		From 0.1 mol KOH, 0.1 mol dissolved $OH^-$ is produced. $K_2CO_3$ and $Na_2SO_4$ both contain a weak base, so less than 0.1 mol $OH^-$ per litre is produced.
		The higher the $[OH^-]$ , the higher the pH.
		Redox and electrochemistry
17	С	The reaction equation is:
		$2 \text{ NH}_4\text{ClO}_4 \ + \ 2 \text{ Al} \ \rightarrow \ \text{Al}_2\text{O}_3 \ + \ 2 \text{ NO} \ + \ 2 \text{ HCl} \ + \ 3 \text{ H}_2\text{O}$

18	A	Zn can react with $Pb^{2+}$ in a redox reaction because Zn is a stronger reducing agent than Pb. Cu will not react.
		During discharging, the electrode where the oxidizing agent reacts is always the positive electrode, and $Pb^{2+}$ acts as the oxidizing agent here.
		Analysis
19	F	Mass spectrum 1 has the highest peak at an $m/z$ value of 59. This corresponds to the fragment $C_3H_7O^+$ , originating from hexan-3-ol. Mass spectrum 2 has the highest peak at an $m/z$ value of 45. This corresponds to the fragment $C_2H_5O^+$ , originating from hexan-2-ol.
20	D	Magnesium chloride is highly soluble in water. When a solution of the strong acid HI is added, lead(II) oxide and magnesium oxide will react in an acid-base reaction, releasing lead(II)ions and magnesium ions. Lead(II) ions form a precipitate with iodide ions, while magnesium ions do not.
		Lead(II) chloride does not react with the HI solution in an acid-base reaction. Lead(II) chloride is moderately soluble, and the lead(II) ions form a precipitate of lead(II)iodide with the $I^-$ ions.
21	В	In gas chromatography, the substance whose molecules form the strongest interactions with the column will remain in the column the longest.
		All three substances are non-polar, so London dispersion forces are the determining factor.
		Molecules of <b>substance III</b> form the strongest London dispersion forces with the stationary phase of the column, meaning <b>substance III</b> has the longest retention time.
		<b>Substance I</b> consists of the smallest molecules, which form the weakest London dispersion forces, resulting in the <b>shortest retention time</b> .
		Chemical calculations
22	E	$n_{\rm Au} = \frac{11.8}{197} = 0.0599 \text{ mol}$
		$n_{\rm NaCN} = n_{\rm CN^-} = 0.0599 \times \frac{8}{4} = 0.120  {\rm mol}$
		$V_{\rm NaCN} = \frac{0.120}{0.0100} = 12.0 \ {\rm L}$
23	D	When the amount of $Cr^{3+}$ increases, the amount of $CH_3CHO$ also increases, in the molar ratio of $Cr^{3+}$ : $CH_3CHO = 2 : 3$ .
		$0.18 \times \frac{3}{2} = 0.27 \text{ mol } L^{-1} \text{ s}^{-1}$

24	D	Silver is formed according to the half-reaction: Ag <sup>+</sup> (aq) + $e^- \rightarrow Ag(s)$
		$n_{e^{-}} = n_{Ag} = \frac{0.10}{107.9} = 9.3 \cdot 10^{-4} \text{ mol}$ charge = $9.3 \cdot 10^{-4} \times 9.65 \cdot 10^{4} = 89 \text{ C}$ $t = \frac{89}{0.10} = 890 \text{ s}$ $\frac{890}{60} = 15 \text{ min}$
		Green chemistry
25	U	$E\text{-factor} = \frac{\text{total mass of all reactants} - \text{mass of desired product}}{\text{mass of desired product}}$ The molar masses of the acid, alcohol, ester and water are respectively: 60.05 g mol <sup>-1</sup> , 88.15 g mol <sup>-1</sup> , 130.18 g mol <sup>-1</sup> , and 18.02 g mol <sup>-1</sup> . When starting with one mole of acid and one mole of alcohol: $m_{\text{reactants}} = 60.05 + 88.15 = 148.20 \text{ g}$ $m_{\text{theoretical yield}} = 130.18 \text{ g}$
		If x is the actual yield, the following applies:
		$0.34 = \frac{148.20 - x}{x}$ and $0.34x = 148.20 - x$ and $1.34x = 148.20$ , thus
		$x = \frac{148.20}{1.34} = 110.60 \text{ g}$
		percentage yield = $\frac{m_{\text{experimental yield}}}{m_{\text{theoretical yield}}} \times 100\% = \frac{110.60}{130.18} \times 100\% = 85\%$

## **Open questions**

# (total 26 points)

### Problem 2 Apple cider vinegar

(12 points)

1

1

1

1

1

#### □1 maximum score 2

A correct answer can be given as follows:



carbon skeleton with four carbon atoms and two carboxyl groups correctly drawn
 rest of the structural formula correctly drawn
 1

#### **D2** maximum score 2

 $C_2H_6O \ + \ O_2 \ \rightarrow \ C_2H_4O_2 \ + \ H_2O$ 

 $\cdot C_2H_4O_2$  after the arrow

 $\cdot$  H<sub>2</sub>O after the arrow and elements balanced with correct molecular formulas before and after the arrow 1

Notes

- When the answer  $C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O$  is given, award full marks.
- When a correct reaction equation is given in structural formulas, award full marks.

#### n3 maximum score 4

An example of a correct calculation is:

7.382 g malic acid per L is 7.382 mg malic acid per mL is  $\frac{7.382}{134.09}$  = 0.05505 mmol per mL.

In 10.00 mL malic acid there is  $\frac{7.382}{134.09} \times 10.00 = 0.5505$  mmol malic acid.

This reacts with  $2 \times \frac{7.382}{134.09} \times 10.00 = 1.101 \text{ mmol OH}^-$ 

and that is in 
$$\frac{2 \times \frac{7.382}{134.09} \times 10.00}{0.1000} = 11.01 \text{ mL } 0.1000 \text{ M sodium hydroxide.}$$

- $\cdot$  calculation of the number of mmoles of malic acid per mL
- $\cdot$  calculation of the number of mmoles of malic acid in 10.00 mL
- $\cdot$  calculation of the number of mmoles of OH- that reacted
- · conversion to the number of mL of 0.1000 M sodium hydroxide

#### n4 maximum score 4

An example of a correct calculation is:

Per litre of apple juice applies:

From  $\frac{7.382}{134.09}$  = 0.05510 mol malic acid, 0.05505 mol ethanol are formed and finally also

0.05505 mol ethanoic acid.

From glucose, therefore  $1.086 - \frac{7.382}{134.09} = 1.031$  mol ethanoic acid are formed and that is 1.086 - 7.382

ultimately formed from  $\frac{1.086 - \frac{7.382}{134.09}}{2} = 0.5155$  mol glucose and that is

 $\frac{1.086 - \frac{7.382}{134.09}}{2} \times 180.16 = 92.87 \text{ g glucose per litre apple juice.}$ 

$\cdot$ calculation of the number of moles of ethanoic acid that is produced per L of malic acid	1
$\cdot$ conversion to the number of moles of ethanoic acid that is formed per L from the glucose	1
$\cdot$ conversion to the number of moles of glucose that is converted per L	1
$\cdot$ conversion to the number of grams of glucose per L	1

Note

When an incorrect answer to question 4 is the consequent result of an incorrect reaction equation in question 2, this answer to question 4 should be considered correct.

## Problem 3 Ozonolysis

□6

- **¤**5 maximum score 2 A correct answer can be given as follows: , and  $CH_3 - CH_2 - CH_2 - C$ · correct structural formula of propanone · correct structural formula of butanal Note When the structural formula of butanal is given as  $C_{3}H_{7}-C_{1}^{//2}$ , mark this as correct. maximum score 4 Examples of a correct answer are: and · correct Lewis structure of A · correct formal charges in A · lone pairs in molozonide correct curly arrows consistently drawn with the structural formula of A If the following answer is given: ٥7 maximum score 3  $C_2H_4O_3 \ + \ 2 \ H^+ \ + \ 2 \ e^- \ \rightarrow \ 2 \ CH_2O \ + \ H_2O$ The ozonide acts as an oxidizing agent, so dimethyl sulfide acts as a reducing agent.  $\cdot$  C<sub>2</sub>H<sub>4</sub>O<sub>3</sub>, H<sup>+</sup> and e<sup>-</sup> before the arrow and CH<sub>2</sub>O and H<sub>2</sub>O after the arrow · correct coefficients
  - · consistent explanation and conclusion regarding the function of dimethyl sulfide

(14 points)

1

1

1

1

1 1

3

1 1

1

#### **B** maximum score 5

An example of a correct answer is:

$$n_{\text{formaldehyde}} = \frac{4.8 \cdot 10^{-3}}{30.0} = 1.6 \cdot 10^{-4} \text{ mol}$$
$$n_{\text{glyoxal}} = \frac{14 \cdot 10^{-3}}{58.0} = 2.4 \cdot 10^{-4} \text{ mol}$$
$$\frac{n_{\text{formaldehyde}}}{n_{\text{glyoxal}}} = \frac{1.6 \cdot 10^{-4}}{2.4 \cdot 10^{-4}} = \frac{2}{3}$$

This corresponds to the structure  $H_2C = CH - CH = CH - CH = CH - CH = CH_2$ 

- $\cdot$  calculation of the molar masses of formaldehyde and glyoxal
- · calculation of the number of moles of formaldehyde and glyoxal
- · conversion to the molar ratio of formaldehyde and glyoxal
- · correct structural formula of X

If an otherwise correct answer contains an incorrect structural formula, from which only formaldehyde and glyoxal can be formed, for example, hexane-1,3,5-triene.

1

1

1

2

4