NATIONAL CHEMISTRY OLYMPIAD 2022
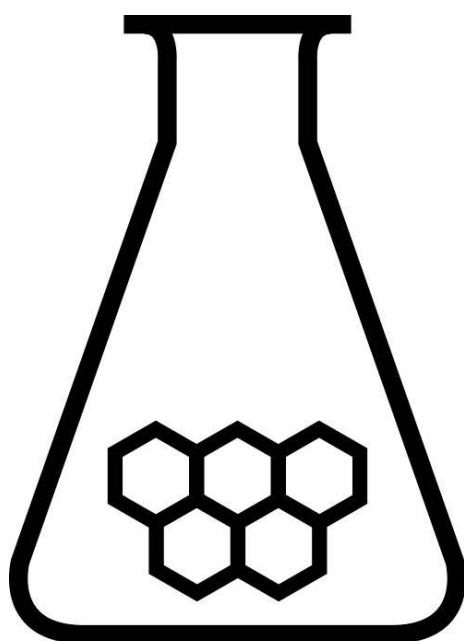
ASSIGNMENTS PRELIMINARY ROUND 1

To be conducted in the period from 12 until 28 January 2022

- This preliminary round consists of 20 multiple choice (MC) questions on 9 different topics and 2 exercises with 10 open questions in total, as well as an answer sheet for the multiple choice questions.
- Use the answer sheet to answer the multiple choice questions.
- Use a separate answer sheet for each open question, provided with your name.
- The maximum score for this work is 76 points.
- The preliminary round takes 2 clock hours.
- Necessary tools: (graphical) calculator and BINAS 6th edition or ScienceData 1st edition.
- The amount of points for each question is mentioned in the question.
- Conditions are standard temperature and pressure (T = 298 K and p = p_0) unless mentioned otherwise.

Task 1 Multiple Choice   (total 40 points)

Write your answer for every question on the answer sheet. The answer sheet is attached at the end of this test.
Standard: 2 points per correct answer.

Carbon chemistry and biochemistry

1   One method to make the ester ethyl acetate (ethyl ethanoate) is by reacting ethene with acetic acid.
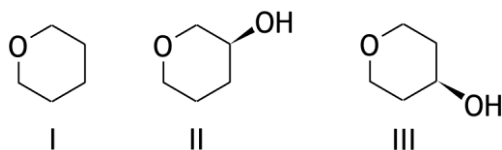
   What type of reaction is this?

   A   addition
   B   condensation
   C   elimination
   D   substitution

2   How many different compounds with molecular formula C_6H_{14} are possible?

   A   3
   B   4
   C   5
   D   6
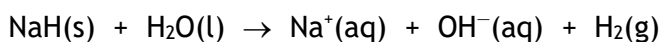

3   The structure of three compounds is provided below.

   Which of these compounds is/are optically active?

   A   only I
   B   only II
   C   only III
   D   only I and II
   E   only I and III
   F   only II and III
   G   all three

Reactions

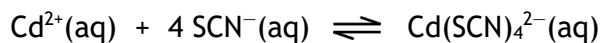**4** The salt sodium hydride reacts with water according to the following reaction equation:

$NaH(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + H_2(g)$

Which of the following statements about the reaction is/are correct?

I   It is a redox reaction.
II   It is an acid-base reaction.

A none
B only I
C only II
D both

Reaction rate and equilibrium

5 For the following equilibrium reaction,

$Cd^{2+}(aq) + 4\,SCN^-(aq) \rightleftharpoons Cd(SCN)_4^{2-}(aq)$

is at a certain temperature $K = 1.0 \cdot 10^3$.
At this temperature, the solution contains 0.50 mol $Cd^{2+}(aq)$, 0.50 mol $SCN^-(aq)$ and 0.50 mol $Cd(SCN)_4^{2-}(aq)$.

What is the volume of this solution?

A 2.0 L
B 2.2 L
C 2.8 L
D 11 L
E $2.0 \cdot 10^3$ L

6 The rate at which F_2 disappears in the reaction $Cl_2(g) + 3\,F_2(g) \rightarrow 2\,ClF_3(g)$ is equal to 1.0 mol L^{-1} s^{-1}.

What is the rate at which ClF_3 is formed?

A 0.33 mol L^{-1} s^{-1}
B 0.67 mol L^{-1} s^{-1}
C 1.0 mol L^{-1} s^{-1}
D 1.5 mol L^{-1} s^{-1}

Structures and formulas

7 In the fulminate ion (CNO^-) the N atom is in the middle.
Which of the following statements about the N atom in the Lewis structure of the fulminate ion is/are correct?

    I   The N atom has a formal positive charge.
    II   The N atom has a nonbonding electron pair.

  A none
  B only I
  C only II
  D both

8 The squarate ion can be represented by the following Lewis structure.
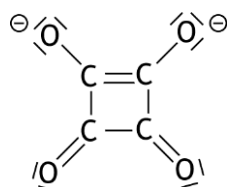

Which statement best describes the bond distances in the squarate ion?

  A All carbon-carbon bond distances are equal to each other and all carbon-oxygen bond distances are equal to each other.
  B There are two different carbon-carbon bond distances but all carbon-oxygen bond distances are equal to each other.
  C There are two different carbon-carbon bond distances and two different carbon-oxygen bond distances.
  D There are three different carbon-carbon bond distances and two different carbon-oxygen bond distances.

9 There are two stereo-isomers of the molecule diazene (N_2H_2), *cis*-diazene and *trans*-diazene.
Which of the following statements is/are true?

    I   The molecule *cis*-diazene is a dipole molecule.
    II   The molecule *trans*-diazene has a flat structure.

  A none
  B only I
  C only II
  D both

pH / acid-base

10   The pH of a NaCN solution is 9.60.

What is the molarity of this solution?

A $2.0 \cdot 10^{-5}$ mol L^{-1}
B $4.0 \cdot 10^{-5}$ mol L^{-1}
C $9.9 \cdot 10^{-5}$ mol L^{-1}
**D** $1.4 \cdot 10^{-4}$ mol L^{-1}

Redox and electrolysis

11   Bromate ions and bromide ions react to form bromine molecules in an acidic solution. The unbalanced reaction equation, in which all coefficients are omitted, follows hereafter.

$$H^+(aq) \; + \; BrO_3^-(aq) \; + \; Br^-(aq) \; \rightarrow \; Br_2(aq) \; + \; H_2O(l)$$
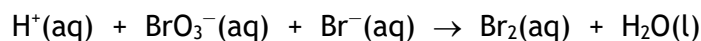
What is the ratio between the coefficients for BrO_3^- and Br^- in the balanced reaction equation?

A $BrO_3^- : Br^- = 1 : 1$
B $BrO_3^- : Br^- = 1 : 2$
C $BrO_3^- : Br^- = 1 : 3$
D $BrO_3^- : Br^- = 1 : 4$
E $BrO_3^- : Br^- = 1 : 5$
F $BrO_3^- : Br^- = 1 : 6$

12   A copper(II) sulfate solution is being electrolysed; both electrodes are made of copper.

What is the result when the solution is electrolysed for 1300 seconds with a current of 0.35 A?

A   The positive electrode is decreased in mass by 0.15 g.
B   The positive electrode is decreased in mass by 0.30 g.
C   The positive electrode is decreased in mass by 0.60 g.
D   The positive electrode is increased in mass by 0.15 g.
E   The positive electrode is increased in mass by 0.30 g.

13 Below is the figure of an electrochemical cell.
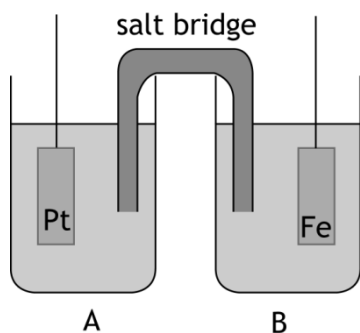
There is a 1.0 M $FeCl_3$ solution in compartment A, and a 1.0 M NaCl solution in compartment B.

Which half reaction takes place at which electrode when the cell is generating current?
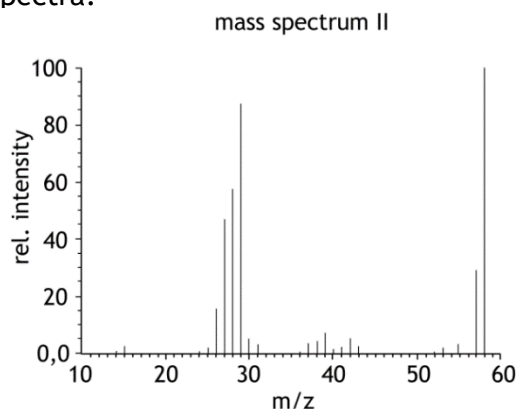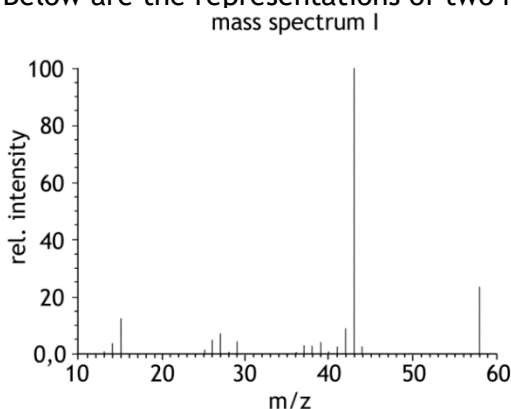
	at the positive electrode	at the negative electrode
A	$2\,Cl^- \rightarrow Cl_2 + 2\,e^-$	$Fe^{3+} + e^- \rightarrow Fe^{2+}$
B	$2\,Cl^- \rightarrow Cl_2 + 2\,e^-$	$Na^+ + e^- \rightarrow Na$
C	$Fe \rightarrow Fe^{2+} + 2\,e^-$	$Fe^{3+} + e^- \rightarrow Fe^{2+}$
D	$Fe \rightarrow Fe^{2+} + 2\,e^-$	$Na^+ + e^- \rightarrow Na$
E	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$2\,Cl^- \rightarrow Cl_2 + 2\,e^-$
F	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$Fe \rightarrow Fe^{2+} + 2\,e^-$
G	$Na^+ + e^- \rightarrow Na$	$2\,Cl^- \rightarrow Cl_2 + 2\,e^-$
H	$Na^+ + e^- \rightarrow Na$	$Fe \rightarrow Fe^{2+} + 2\,e^-$

Analysis

14 Below are the representations of two mass spectra.

Which substances do these mass spectra represent?

	mass spectrum I	mass spectrum II
A	propane-1-ol	propanal
B	propane-1-ol	propanone
C	propanal	propane-1-ol
D	propanal	propanone
E	propanone	propane-1-ol
F	propanone	propanal

15 What is a correct method to investigate whether a sample of sodium carbonate is contaminated with sodium sulphate?

   Method I: Dissolve some of the sample, add excess hydrochloric acid solution heat the solution and finally add a solution of barium nitrate.

   Method II: Dissolve some of the sample, add excess sulphuric acid solution heat the solution and finally add a solution of barium nitrate.

   A   none of the methods is correct
   B   only method I is correct
   C   only method II is correct
   D   both methods are correct

Calculations

16 A sulphuric acid solution is added to 100 g of a solution of sodium hydroxide (with mass percentage NaOH = 50.0%) in such a way that a neutral solution forms. The solution is cooled. During cooling, the solution is completely transformed into a solid with formula $Na_2SO_4.10H_2O$. No evaporation takes place.

   How many grams of the sulphuric acid solution were used?

   A   61.3 g
   B   101 g
   C   124 g
   D   151 g
   E   174 g

17 Syrup of the maple tree consists for 3.0 mass percent of sucrose. Sucrose is the disaccharide of glucose and fructose. The density of maple syrup is 1.01 g mL^{-1}.

   What is the molarity of sucrose in maple syrup?

   A $8.4 \cdot 10^{-5}$ mol L^{-1}
   B $8.9 \cdot 10^{-5}$ mol L^{-1}
   C $8.4 \cdot 10^{-2}$ mol L^{-1}
   D $8.9 \cdot 10^{-2}$ mol L^{-1}

18 A blue mineral called azurite has the formula $Cu_3(CO_3)_2(OH)_2$ (M = 345 g mol^{-1}). Upon heating, the mineral dissociates into copper(II) oxide, water and carbon dioxide.

   How many grams copper(II) oxide are formed when 50.0 g azurite is dissociated completely?

   A   11.5 g
   B   20.7 g
   C   31.1 g
   D   34.6 g

Thermochemistry and Green chemistry

Use the information below to answer questions 19 and 20.

Dow Chemical (Terneuzen, NL), the company that hosts this year's final round of the National Chemistry Olympiad, is one of the largest producers of cumene (systematic name: (1-methylethyl) benzene). Cumene is the raw material for plastics and phenol. Industrially, cumene is produced from the reaction between benzene and propene:
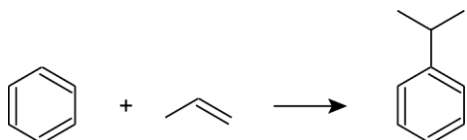
19   The reaction heat of this synthesis is $-107\ kJ\ mol^{-1}$.

Given: the heat of formation of benzene is $+49\ kJ\ mol^{-1}$ and de heat of formation of propene is $+20\ kJ\ mol^{-1}$.

What is the heat of formation of cumene?

A $-178\ kJ\ mol^{-1}$
B $-107\ kJ\ mol^{-1}$
C $-38\ kJ\ mol^{-1}$
D $+38\ kJ\ mol^{-1}$
E $+178\ kJ\ mol^{-1}$

20   During the production of cumene, an excess of benzene is used in order to avoid the formation of by-products such as di-(1-methylethyl) benzene. The unreacted benzene is being recycled.

Which statement about the atom economy and *E*-factor is correct for using excess benzene compared to equimolar ratio benzene : propene? Equimolar means that the mole ratio benzene : propene = 1 : 1.

	atom economy	*E*-factor
A	decreases	decreases
B	decreases	remains constant
C	decreases	increases
D	remains constant	decreases
E	remains constant	remains constant
F	remains constant	increases
G	increases	decreases
H	increases	remains constant
I	increases	increases

Open questions (total 36 points)

Task 2 Nitrate in groundwater (16 points)

Nitrates are substances that are found in animal excretions. When over-fertilization occurs, the nitrates can end up in groundwater. This will eventually have a negative impact on the quality of the drinking water that is prepared from groundwater. In a number of places the acceptable concentration of 50 mg nitrates per liter of groundwater is already exceeded.

In order to determine how much nitrate is present in groundwater, all of the nitrate must first be converted to ammonia. This is done with aluminium in an alkaline environment, where the aluminium is converted into aluminate, AlO_2^-.

▢1 Provide the equations of both half reactions involved in this conversion and then deduce the final equation of the reaction. OH^- and H_2O are present in both half reactions.   5

The reaction between aluminium and nitrate is carried out in a distillation flask. By boiling the liquid, all of the ammonia that is produced, is collected in a flask containing a hydrochloric acid solution.
The above-mentioned investigation is conducted using 3.00 liter of groundwater. All of the ammonia is collected in a flask that contains 35.0 ml of 0.202 M hydrochloric acid solution. The contents of the flask is then titrated with caustic soda. This titration is conducted in such a manner that the excess hydrochloric acid is neutralized, but only a very small amount of the ammonium has reacted.

To achieve this, methyl red is used as indicator and the titration is completed when the pH = 6.2.

▢2 Indicate, using a calculation that, at pH = 6.2, only a very small amount of the ammonium has reacted.   3

The titration required 26.5 mL of 0.195 M caustic soda.

▢3 Use a calculation to determine whether the groundwater meets the above-mentioned quality standard   4

If the above-mentioned method is applied to groundwater that contains not only nitrates, but also ammonium, an inaccurate nitrate content will be found.
In this case, the above-mentioned method can be adapted in order to determine the nitrate and ammonium content separately.

▢4 Give a general description of how the above-mentioned method can be adapted and indicate how both the nitrate and ammonium content can be determined. Note: no calculations are necessary.   4

## Task 3 Bisphenol A   (20 points)

Bisphenol is the collective name for a large number of compounds, of which the molecules contain two phenol groups. The most well-known bisphenol is bisphenol A, usually abbreviated with BPA:

BPA
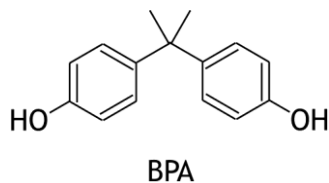
BPA is prepared by allowing phenol (benzenol) and acetone (propanone) to react with each other. Besides BPA, one other substance is produced during the reaction

☐5   Provide the reaction equation for the formation of BPA. Use structural formulas for the organic compounds.   4

Another bisphenol is bisphenol Z, BPZ:

BPZ
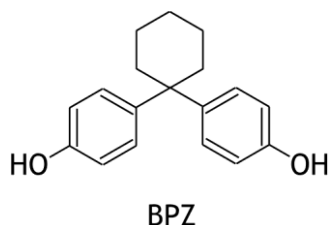
☐6   Provide the structural formula of the compound that is needed to react with phenol to produce BPZ.   2

BPA is used as the starting material for the production of certain polymers. Below is the structural formula of a section from the middle of a molecule of one of these polymers.
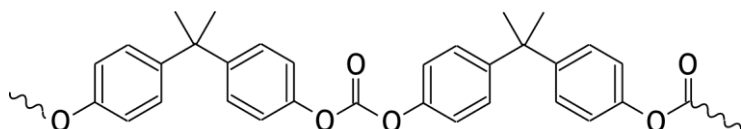
Polymers can be identified in different ways. We distinguish copolymers and non-copolymers, and also thermoplastics and thermosets.

☐7   To which of the abovementioned type(s) of polymers does the abovementioned polymer belong? Provide an explanation for your answers.   4

Polymers of BPA are often used in packaging of food. When this sort of packaging is heated, for example the sterilizing of baby bottles or heating of ready-to-eat meals in the microwave, BPA can be released through the hydrolysis of the ester bonds in the polymer. It can also happen during contact with alkaline food products or cleaning agents.

☐8   Provide the formula of the particles, other than BPA molecules, that are also produced by the complete hydrolysis of the above-mentioned polymer in an alkaline environment.   2

Due to the large scale on which BPA is used, almost everyone in the Western world has BPA in their bodies. BPA is classified as an irritant and is toxic, which is why it can have negative consequences on one's health.

BPA is also present in surface water as well as in drinking water. BPA is able to dissolve in dichloromethane better than it does in water, which is a characteristic used when the BPA content of drinking water needs to be determined. Also BPA-d16 is used as a reference substance. In molecules of BPA-d16 all sixteen hydrogen atoms have mass number 2. Such hydrogen atoms are called deuterium atoms. The following method can be used in such a determination.

1. An extra amount of 5.0 µL (microliter) of a solution containing 1.0 µg BPA per mL, is added to 500 mL drinking water, that contains BPA.
2. 15 g NaCl is then dissolved in the above solution, after which the pH is adjusted to 4.0 by adding phosphoric acid.
3. The acidic solution is then extracted with 30 mL of dichloromethane, after which the dichloromethane layer is separated from the water layer.
4. This extraction is repeated twice.
5. Subsequently the three dichloromethane fractions are combined and then evaporated to a volume of roughly 5 mL.
6. 7.0 µL of a reference substance, containing 1.0 µg BPA-d16 per mL, is added to the remaining solution.
7. A small sample of the solution which then is formed, is injected into a gas chromatograph. After obtaining the chromatogram (chromatogram 1), the peak areas of BPA and BPA-d16 are determined.
8. Steps 1 to 7 is also conducted with pure water. Another chromatogram (chromatogram 2) is obtained, where the peak areas of BPA and BPA-d16 are determined.

During an investigation of drinking water, the following values were obtained (the areas are given in arbitrary units):

	peak area of BPA	peak area of BPA-d16
chromatogram 1 (drinking water)	235	5987
chromatogram 2 (pure water)	25	1873

▢9 Calculate the BPA content in the sample of drinking water in $ng\,L^{-1}$. Assume that all BPA present in the original sample is present in the dichloromethane.

Some students discuss this determination of BPA. Joris finds that steps 5 and 7 are inaccurate. He thinks that the results will be more accurate if the volume of dichloromethane in step 5 is brought to precisely 5.00 mL and that in step 7 the 'small sample' of the solution that is injected into the chromatograph should be more precisely specified, for example 20 µL. Jorinde says that no BPA-d16 is necessary when the determination is carried out according to Joris's suggestions.

▢10 Does it have an effect on the accuracy of the final result when the experiment is carried out according to Joris's suggestions? And is it also true that in that case no BPA-d16 needs to be used? Copy the following sentences and make the correct choices for the italic printed words therein.
- The result of the determination *becomes more accurate / is equally accurate / becomes more inaccurate*.
- BPA-d16 *is / is not* needed when the determination is carried out according to Joris's suggestions.

2

43rd National Chemistry olympiad 2022 Preliminary round 1
Answer sheet multiple choice questions

name:

nr.	choice letter	(score)
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