

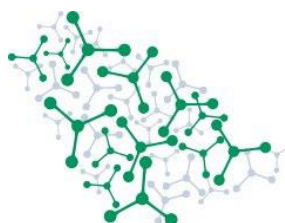
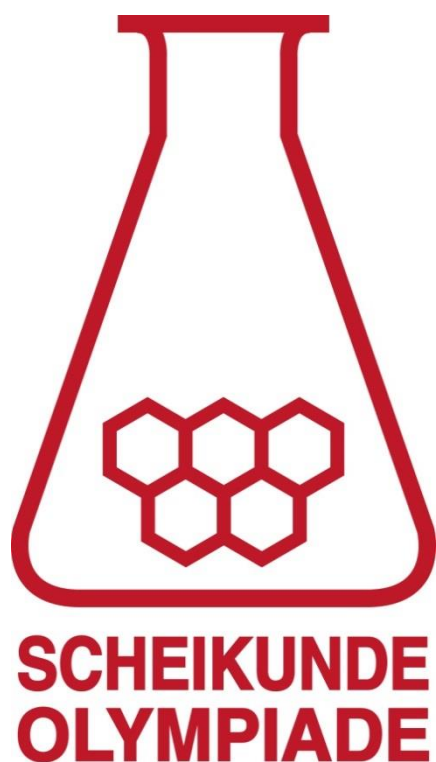
45th National Chemistry Olympiad

Maastricht University

THEORY TEST

Question booklet

Wednesday June 5, 2024



56th IChO International
Chemistry Olympiad
Saudi Arabia 2024



Maastricht University

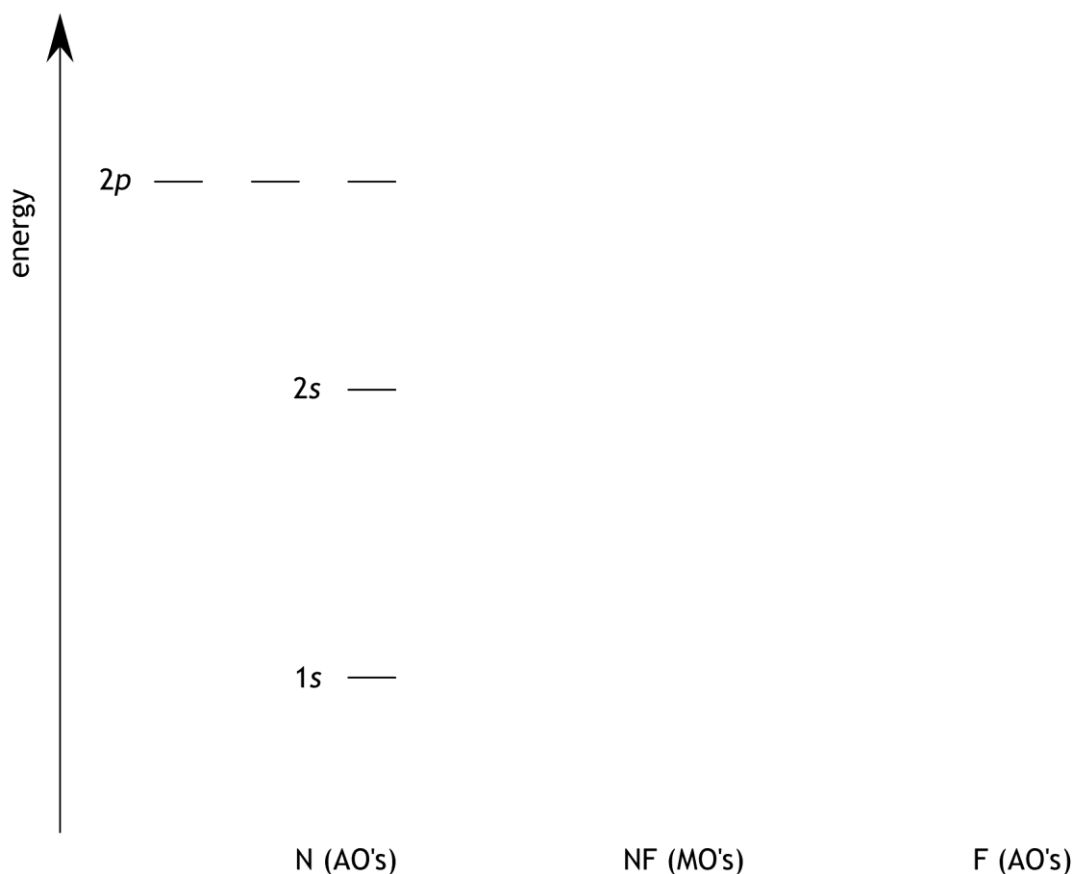
- This test consists of 7 problems with 32 open questions, an information sheet and an answer sheet.
- Use a separate answer sheet for each problem, making sure to write your name on each sheet. Maintain a 2 cm margin on all sides of the page.
- The maximum score for this test is 120 points.
- The test will last a maximum of 4 clock hours.
- Required resources: (graphic) calculator and Binas 6th or 7th edition or ScienceData 1st print.
- Each question includes the number of points that a correct answer to that question will earn.
- Unless otherwise stated, standard conditions apply: $T = 298\text{ K}$ and $p = p_0$.

Problem 1 NF

12 points

Nitrogen monofluoride, NF, is a metastable compound that has been observed during laser research.

Below and on the answer sheet, the initial setup for an MO diagram of nitrogen monofluoride is shown. The 1s, 2s, and 2p levels of the nitrogen atom have already been drawn in this diagram.



- 1 Draw in the diagram on the answer sheet:
- the 1s, 2s, and 2p levels of the fluorine atom;
 - the molecular orbitals of the nitrogen monofluoride molecule with the usual designations for 'bonding' and 'anti-bonding';
 - the filling of electrons in the atomic and molecular orbitals according to the Aufbau principle.
- 2 Calculate the bond order (BO) of the nitrogen monofluoride molecule.
- 3 Provide the Lewis structure of the nitrogen monofluoride molecule.

7

2

3

Problem 2 Dinitrogen pentoxide

19 points

From the elements nitrogen and oxygen, various compounds exist. One of these is dinitrogen pentoxide, $\text{N}_2\text{O}_5(\text{g})$.

- 4 Represent the N_2O_5 molecule in a Lewis structure. Place any formal charges in the correct positions.

Hint: each N atom is bonded to three O atoms, and there is no cyclic structure involved.

- 5 Explain whether it is possible for all seven atoms of the N_2O_5 molecule to lie in one plane.

Below are three reactions involving nitrogen oxides, along with their corresponding standard reaction enthalpies.



- 6 Calculate the standard enthalpy of formation $\Delta_f H^\circ$ of N_2O_5 in kJ mol^{-1} . Use only the standard reaction enthalpies provided above.

Dinitrogen pentoxide can be part of the following equilibrium:



The reaction enthalpy of this equilibrium is $+94.83 \text{ kJ mol}^{-1}$ at $T = 600 \text{ K}$ and $p = p_0$. In the table below, the entropies are given:

	$S \text{ (J mol}^{-1} \text{ K}^{-1}) \text{ at } T = 600 \text{ K and } p = p_0$
$\text{N}_2\text{O}_5(\text{g})$	426
$\text{NO}_2(\text{g})$	269
$\text{NO}_3(\text{g})$	293

- 7 Calculate the equilibrium constant K_p at $T = 600 \text{ K}$ and $p = p_0$ for the above equilibrium.

An equilibrium mixture of $\text{N}_2\text{O}_5(\text{g})$, $\text{NO}_2(\text{g})$, and $\text{NO}_3(\text{g})$, which is formed from $\text{N}_2\text{O}_5(\text{g})$, has a total pressure of 0.10 bar at 600 K .

- 8 Calculate how many moles of N_2O_5 per original mole of N_2O_5 have been converted to NO_2 and NO_3 .

If you couldn't calculate K_p in question 7, use the value 0.060 for K_p . This is not the correct value.

■ Problem 3 Chromium

21 points

The metal chromium can be obtained by means of the electrolysis of a solution called chromic acid. This solution is obtained from the chromium ore chromite. The formula of chromite can be represented as $\text{Cr}_2\text{O}_3 \cdot \text{FeO}$.

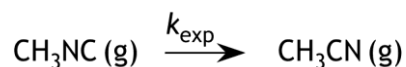
To obtain chromic acid from chromite, the chromite is first heated with sodium carbonate in the presence of air. This results in the formation of sodium chromate (Na_2CrO_4), iron(III) oxide, and carbon dioxide.

- 9 Provide the reaction equation for this conversion. 4
- Subsequently, solid sodium chromate is isolated from the resulting solid mixture of sodium chromate and iron(III) oxide.
- 10 Describe how you can obtain solid sodium chromate from the resulting solid mixture of sodium chromate and iron(III) oxide. 3
- Chromic acid is formed by adding a solution of sulfuric acid to sodium chromate. In the resulting solution, all chromate is converted to dichromate ($\text{Cr}_2\text{O}_7^{2-}$).
- 11 Provide the reaction equation for the conversion of chromate to dichromate. 3
- During the electrolysis of chromic acid, chromium is formed at the negative electrode. It appears that not all dichromate is converted to metallic chromium in such an electrolysis. A small percentage is converted to Cr^{3+} . During the execution of such an electrolysis, 95.0% of the $\text{Cr}_2\text{O}_7^{2-}$ is converted to Cr and 5.0% to Cr^{3+} .
- 12 Calculate the percentage of the electron current absorbed at the negative electrode by $\text{Cr}_2\text{O}_7^{2-}$ that was utilized to directly convert $\text{Cr}_2\text{O}_7^{2-}$ to Cr. 4
- The unit cell of the crystal lattice of metallic chromium is a body-centered cubic (bcc) structure.
- 13 Prove this by means of a calculation using data from the information book. 7

Problem 4 Methyl isocyanide

15 points

The substance methyl isocyanide can be converted to acetonitrile via an isomerization reaction according to:

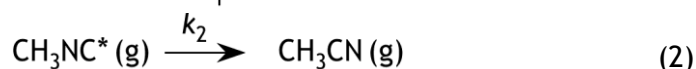
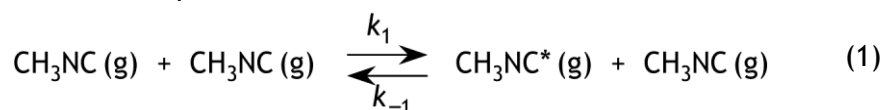


From experiments, it is evident that this reaction is a first-order reaction at high pressure and a second-order reaction at low pressure.

The mechanism of this isomerization reaction consists of two steps.

In a first step, a molecule of methyl isocyanide is activated to CH_3NC^* by collision with another molecule of methyl isocyanide. With this activated molecule, the following can occur:

1. it is converted back to the original molecule of methyl isocyanide by collision with an unactivated molecule of methyl isocyanide;
2. it reacts in a second step to form a molecule of the isomer acetonitrile.



Using the 'steady-state' approximation, it can be derived that the rate equation for the formation of acetonitrile according to this mechanism is equal to:

$$\frac{d[\text{CH}_3\text{CN}]}{dt} = \frac{k_1 k_2 [\text{CH}_3\text{NC}]^2}{k_{-1} [\text{CH}_3\text{NC}] + k_2}$$

□14 Provide this derivation. 7

□15 Derive the expression for k_{exp} using the rate equation given above question 14. 2

With the help of the above rate equation, it can be derived that the conversion of methyl isocyanide to acetonitrile is a first-order reaction at high pressure and a second-order reaction at low pressure. This is because at high pressure $s_{-1} \gg s_2$, and at low pressure $s_{-1} \ll s_2$. Here, s_{-1} represents the rate of the reaction to the left in equilibrium (1), and s_2 represents the rate of reaction (2).

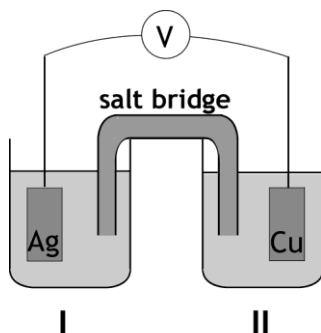
□16 Explain that at high pressure $s_{-1} \gg s_2$ and at low pressure $s_{-1} \ll s_2$. 2

□17 Explain, based on the above data, that the conversion of methyl isocyanide to acetonitrile is a first-order reaction at high pressure and a second-order reaction at low pressure. 4

Problem 5 Electrochemical cell

15 points

We construct the following electrochemical cell at 298 K:



This cell consists of:

- half-cell I: a silver plate of 15.00 g in 1.00 L of 0.150 M AgNO_3 solution;
- half-cell II: a copper plate of 30.00 g in 1.00 L of 0.300 M CuSO_4 solution.

- 18 Calculate the electromotive force (EMF) of this cell. 3

The cell is allowed to deliver a current of 0.200 A until the mass of the silver electrode is equal to the mass of the copper electrode.

- 19 Calculate the number of seconds the cell supplies this current until that point is reached. 6

With the original electrochemical cell, the following actions are performed:

1. Adding a sodium carbonate solution to half-cell I.
2. Adding a sodium carbonate solution to half-cell II.
3. Adding a sodium chloride solution to half-cell II.

- 20 Explain for each of these actions whether it lowers or raises, or whether that action has no effect on the electromotive force. 6

Problem 6 Barbituric acid

13 points

Barbituric acid is a monoprotic weak acid, denoted as HZ in this problem. The value of K_z of HZ at 298 K has been determined spectrophotometrically. In doing so, it was utilized that both HZ and Z^- absorb ultraviolet light.

To determine the value of K_z of HZ, three buffer solutions were prepared with pH values of 2.00, 3.60, and 7.20, respectively. Equal amounts of these three buffer solutions were added to equal amounts of a very dilute solution of HZ.

It can be assumed that:

- in the solution with pH = 7.20, all HZ is converted to Z^- ;
- in the solution with pH = 3.60, a part of the HZ is converted to Z^- ;
- in the solution with pH = 2.00, none of the HZ has dissociated into ions.

The obtained solutions were measured (at 298 K) for their absorbance (extinction) A with ultraviolet light of different wavelengths between 200 and 280 nm.

The same cuvette was used for all measurements.

In the diagram on the information sheet, the results of the measurements on the three solutions are shown. Using the Lambert-Beer law, the measured absorbances were converted to the absorbances that would apply if the (total) concentration of HZ and/or Z^- were 1.00 mol L^{-1} in each of the three solutions.

The absorbances in the diagram thus apply in the following cases:

- $[Z^-]$ in the solution with pH = 7.20 would be equal to 1.00 mol L^{-1} ;
- $[HZ] + [Z^-]$ in the solution with pH = 3.60 (together) would be equal to 1.00 mol L^{-1} ;
- $[HZ]$ in the solution with pH = 2.00 would be equal to 1.00 mol L^{-1} .

An absorbance measured from a solution with pH = 3.60 is the sum of the absorbances caused by Z^- and HZ separately. The graphs corresponding to pH = 7.20 and pH = 2.00 intersect at point A (at wavelength 221 nm). The graph corresponding to pH = 3.60 is not fully displayed: the part of the graph at wavelengths less than 235 nm has been omitted.

- 21 Explain whether the fully displayed graph corresponding to pH = 3.60 also passes through point A. 3

With the help of the three absorbances (from the diagram) at a certain wavelength, one can calculate the ratio between $[Z^-]$ and $[HZ]$ in the solution with pH = 3.60.

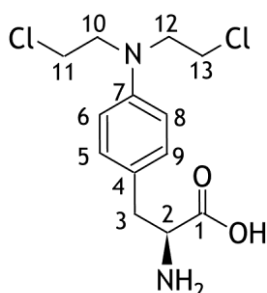
- 22 Provide the values of the three absorbances in the diagram at 257 nm (at pH values of 2.00, 3.60, and 7.20, respectively). 2
- 23 Calculate, based on the values of the three absorbances, the ratio $[Z^-] : [HZ]$ in the solution with pH = 3.60. 5
- 24 Calculate the value of K_z (298 K) of barbituric acid (HZ). 3

Als If you couldn't calculate the requested ratio in question 23, take the answer to question 23 as $[Z^-] : [HZ] = 0.55 : 1.0$. This is not the correct answer to question 23.

Problem 7 Melphalan

25 points

Melphalan (as shown below) is a medication used in the treatment of various types of cancer.



In the above structural formula of Melphalan, the carbon atoms are numbered. Melphalan exists as two enantiomers, that are both used. The enantiomer depicted above exhibits the highest activity.

- 25 Give the number of the stereocenter of the depicted enantiomer and explain its absolute configuration (*R/S*).

4

In the ^1H – NMR-spectrum of Melphalan, the following signals of protons bound to carbon atoms are observed:

chemical shift (ppm)	multiplicity	integral	number(s) of C atom(s)
2.8	doublet	2 H	
3.5	triplet	4 H	
3.6	triplet	1 H	
3.9	triplet	4 H	
6.7	doublet	2 H	
6.8	doublet	2 H	

The same table is provided on the answer sheet.

- 26 Fill in, on the answer sheet, the numbers of the carbon atoms corresponding to the listed signals. Use NMR data from the information book. .

4

On the information sheet the synthesis route of Melphalan, starting from phenylalanine is given.

- 27 Provide the structural formulas of **A** and **B**.

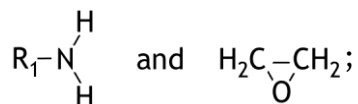
2


In step 1, the aromatic part of phenylalanine molecules is primarily nitrated at the *para*-position. During this nitration, the *ortho*-positions are also nitrated, but to a much lesser extent than would be expected based on statistical and electronic factors that control the regioselectivity of this nitration. The *meta*-positions are hardly nitrated.

- | | | |
|-----|--|---|
| □28 | Why are the <i>meta</i> -positions hardly nitrated? | 2 |
| □29 | Why are the <i>ortho</i> -positions nitrated to a much lesser extent than would be expected based on statistical and electronic factors that control the regioselectivity of this nitration? | 2 |

The reaction in step 5, where **D** is converted to **E**, can be understood as an acid-catalyzed nucleophilic substitution. The mechanism of the reaction of a molecule of **D** with one molecule epoxyethane starts with the protonation of a molecule of epoxyethane.

- 30 Present the mechanism of the reaction of a molecule of **D** with one molecule of epoxyethane by:
- using the structural formulas, shown below, for **D** and epoxyethane, respectively;



- depicting non-bonding electron pairs;
- using curved arrows () to indicate how electron pairs shift during formation and breaking of bonds;
- placing formal charges at the correct positions;
- drawing the structural formula of the product formed by the reaction of a molecule **D** with one molecule of epoxyethane.

The conversion that occurs in step 4 can be termed selective.

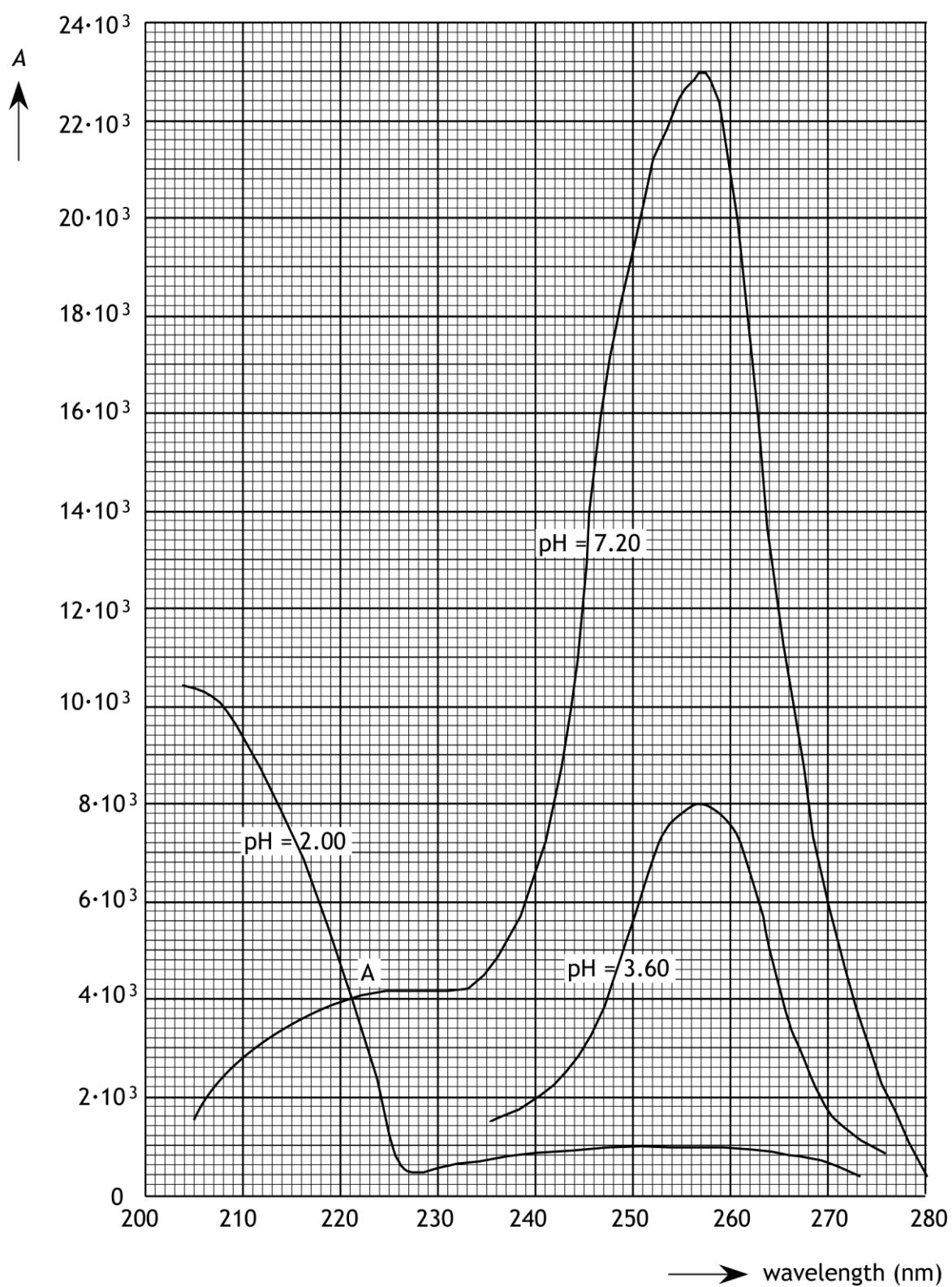
- 31 Explain this. 2

In the synthesis route, there are two instances of introducing and afterwards removing a protecting group.

- 32 For each protection, indicate:
- in which step the protection is introduced and in which step it is removed;
 - the reason why the protection in question is necessary.
- 4

Information sheet

Barbituric acid



Melphalan

synthesis route

