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## Address from the President of the IChO-2007

Dear friends!

The $39^{\text {th }}$ International Chemistry Olympiad is in the past. What will you remember from July 2007? I really hope your memory recalls bright moments of the Opening and Closing Ceremonies, nice sites of Moscow, unforget-
 table time spent with many old and new friends. And of course, mentors will remember intriguing discussions of examination tasks, whereas students - huge efforts to solve them. I am really sure everybody agrees that the $39^{\text {th }}$ IChO became an important step in the development of International Chemistry Olympiads and science education as a whole.

Many organizations and individuals significantly contributed to the $39^{\text {th }}$ IChO success. I have a pleasure to thank the Ministry of Education and Research of Russian Federation and personally the Minister A. Fursenko for serious attention to the Olympiad, which we felt at every stage of preparation.

I address warmest words of gratitude to the Rector of Moscow State University, Full Member of Russian Academy of Sciences, Professor V. Sadovnichy. Organization of IChO required coordinated efforts of various divisions and services of the Moscow University, and we always got positive and benevolent response and readiness to help.

MSU Chemistry Department was the host organization of the $39^{\text {th }} \mathrm{IChO}$, and thus delegated the maximal number of members to the Science Committee, as well as to the working groups which assisted during examinations and other Olympiad events. I thank everyone who contributed to the IChO. Without your enormous efforts, dedicative work and high professionalism, this Olympiad would never have come true.

We are extremely grateful to all the sponsors. Their donations allowed conducting the Olympiad at a high technical level. I am absolutely sure that it was a very useful
investment in the growth of talented young people from all over the world, and the companies will gain numerous benefits in future.

It is my pleasure to thank all the students for excellent participation in IChO and following the standards of fair competition. My congratulations on excellent results achieved at quite complicated sets of practical and theoretical problems. And of course I am very grateful to all mentors, scientific observers, guests and guides. Your positive attitude, creativity and enthusiasm produced warm and friendly atmosphere which we all experienced throughout the Olympiad.

I really hope that all of you enjoyed the time spent in Moscow, and at MSU Chemistry Department, in particular. As the Dean of Chemistry Department and President of the $39^{\text {th }}$ IChO I have a pleasure to say to all the participants: You are very much welcome back!

With best wishes

Valeriy V. Lunin
Professor
Dean of MSU Chemistry Department
Full Member of Russian Academy of Science
President of the $39^{\text {th }} \mathrm{IChO}$

## OVERVIEW of the ICHO-2007

| Period | July 15-24, 2007 |
| :---: | :---: |
| Venue | Chemistry Department, <br> M.V. Lomonosov Moscow State University |
| Official Airports | Sheremetievo International <br> Domodedovo International |
| Students Location | Hotel 'Olympiets', 5 km away from Moscow |
| Mentors, Scientific Observers and Guests Location | Hotel "Holiday Inn Sokolniki" |
| Host Organization | Chemistry Department, M.V. Lomonosov Moscow State University |
| Supported by | Government of Russian Federation Ministry of Education and Science, RF M.V. Lomonosov Moscow Sate University |
| Main Sponsors | "Basic Element" Company, <br> "Lukoil"-neftekhim <br> Vladimir Potanin Foundation |
| Sponsors | Norilsk Nickel; DuPont; BASF; <br> Schlumberger; ESN Group of Companies; <br> Procter and Gamble; JSC "Sibur"; <br> Eurocement Group; Tokyo Boeki Ltd., <br> Renova Group of Companies; <br> Helios IT-Operator; Analytik Jena; <br> Institute for New Carbon Materials; <br> Russian Chemist Union; Bruker Companies; <br> Oil Transporting JSC "Transneft"; <br> Publishing House "Drofa"; <br> Bayer MaterialScience; BP Traiding Ltd.; <br> Dr. Barbara Mez-Starck Foundation; <br> Lhoist Group; ACD/Labs; <br> BioChemMac Group of Companies |

Information Sponsors
Participation
Countries 67 participating, 1 observing (Nigeria), new participant - Moldova
Students ..... 256
Mentors ..... 132
Scientific Observers ..... 44
Guests ..... 15
Results
Gold Medals ..... 31
Silver Medals ..... 56
Bronze Medals ..... 71
Honorable Mentions ..... 10
Operational Stuff ..... 230
Organizing Committee ..... 20
Science Committee ..... 34
Secretariat ..... 8
Technical Committee ..... 19
Lab Instructors ..... 24
Lab Assistants ..... 21
Spectrophotometer
Operators ..... 26
"Catalyzer" team ..... 15
Guides ..... 72

## PARTICIPATING COUNTRIES

| Country | Code | Country | Code |
| :---: | :---: | :---: | :---: |
| Argentina | ARG | Kyrgyzstan | KGZ |
| Armenia | ARM | Latvia | LVA |
| Australia | AUS | Lithuania | LTU |
| Austria | AUT | Malaysia | MYS |
| Azerbaijan | AZE | Mexico | MEX |
| Belarus | BLR | Moldova | MDA |
| Belgium | BEL | Mongolia | MNG |
| Brazil | BRA | Netherlands | NLD |
| Bulgaria | BGR | New Zealand | NZL |
| Canada | CAN | Norway | NOR |
| China | CHN | Pakistan | PAK |
| Chinese Taipei | TPE | Peru | PER |
| Croatia | HRV | Poland | POL |
| Cuba | CUB | Portugal | PRT |
| Cyprus | CYP | Romania | ROU |
| Czech Republic | CZE | Russian Federation | RUS |
| Denmark | DNK | Saudi Arabia | SAU |
| Estonia | EST | Singapore | SGP |
| Finland | FIN | Slovakia | SVK |
| France | FRA | Slovenia | SVN |
| Germany | DEU | Spain | ESP |
| Greece | GRC | Sweden | SWE |
| Hungary | HUN | Switzerland | CHE |
| Iceland | ISL | Tajikistan | TJK |
| India | IND | Thailand | THA |
| Indonesia | IDN | Turkey | TUR |
| Iran | IRN | Turkmenistan | TKM |
| Ireland | IRL | Ukraine | UKR |
| Israel | ISR | United Kingdom | GBR |
| Italy | ITA | United States | USA |
| Japan | JPN | Uruguay | URY |
| Kazakhstan | KAZ | Venezuela | VEN |
| Korea Republic | KOR | Vietnam | VNM |
| Kuwait | KWT |  |  |

Nigeria - observing country (first year)

## PROGRAMS

Students and guides

| July 15 <br> Sunday | Whole day 18.00-19.00 | Arrivals, Registration at Chemistry Department, MSU Transfer to Olympiets Hotel Welcome Dinner, Olympiets |
| :---: | :---: | :---: |
| July 16 <br> Monday | 9.00 $11.00-13.00$ $13.00-15.00$ $15.00-18.00$ 18.00 $20.00-24.00$ | Buses depart to the Opening Ceremony, MSU <br> Opening Ceremony, MSU Intellectual Centre - Fundamental Library <br> Welcome Reception, MSU Main Building <br> Moscow City tour <br> Transfer to Olympiets <br> Disco |
| July 17 <br> Tuesday | $\begin{gathered} 9.00 \\ 10.00-17.00 \\ 17.00 \\ 19.00-21.00 \end{gathered}$ | Buses depart to the North Shipping Terminal <br> Boat trip along Moscow-river, lunch included <br> Transfer to Olympiets <br> Lab safety instructions in groups |
| July 18 Wednesday | $\begin{gathered} \hline 8.00 \\ 10.00-15.00 \\ 17.00-18.30 \\ 19.00-22.00 \end{gathered}$ | Buses depart to the Practical Exam, MSU Practical Exam, MSU Chemistry Department Walk-around MSU Campus \& Lenin Hills Circus show |
| July 19 Thursday | 8.30-19.30 | Whole-day excursion to Sergiev Posad |
| July 20 Friday | $\begin{gathered} \hline 8.00 \\ 10.00-15.00 \\ 17.00-18.00 \\ 18.00-22.00 \\ 22.00 \end{gathered}$ | Buses depart to the Theoretical Exam, MSU <br> Theoretical Exam, MSU Chemistry Department <br> Walk to "Vorobjovi Gori" berth <br> Re-union Party on a boat, dinner included <br> Transfer to Olympiets |
| July 21 <br> Saturday | $\begin{gathered} \hline 8.40 \\ 10.00-14.00 \\ 15.00-18.00 \\ 18.00 \end{gathered}$ | Buses depart to excursions <br> Excursion to Kremlin <br> Excursion to Moscow Zoo <br> Transfer to Olympiets |
| July 22 <br> Sunday | $\begin{gathered} \hline 9.00-13.00 \\ 14.00-18.00 \\ 19.00-23.00 \end{gathered}$ | Paintball \& "Adventurer" game Free time, sports activities Disco |
| July 23 <br> Monday | $\begin{gathered} 9.00-12.00 \\ 12.40 \\ 15.00-18.00 \\ 18.00-18.30 \\ 18.30 \\ 19.00-23.00 \\ 23.00 \end{gathered}$ | Free time <br> Buses depart to the Closing Ceremony, MSU <br> Closing Ceremony, MSU Assembly Hall <br> Walk-around MSU Campus <br> Buses depart to the Farewell Banquet <br> Farewell Banquet, Russian Academy of Sciences <br> Transfer to Olympiets |
| July 24 <br> Tuesday | $\begin{gathered} 9.00-12.00 \\ \text { Whole day } \\ 12.00 \end{gathered}$ | Check-out <br> Departures <br> Late departures - staying in Olimpiets |

Mentors and observers

| July 15 <br> Sunday | Whole day $22.00-24.00$ | Arrivals, Registration at Chemistry Department, MSU Transfer to Holiday Inn <br> Get-together party, Holiday Inn, Vorobjevy Gory Hall |
| :---: | :---: | :---: |
| July 16 <br> Monday | 9.00 $11.00-13.00$ $13.00-15.00$ $15.00-16.00$ 16.30 $18.00-19.00$ $20.00-24.00$ | Buses depart to the Opening Ceremony, MSU <br> Opening Ceremony, MSU Intellectual Centre - Fundamental Library <br> Welcome Reception, MSU Main Building <br> Lab inspection <br> Buses depart to Holiday Inn, distribution of Practical Exam <br> Consultation with tasks authors, Polyanka Hall <br> The $1^{\text {st }}$ Jury Meeting, Sokolniki 2 Hall |
| July 17 <br> Tuesday | Whole day $22.00-24.00$ | Translation of Practical Exam, Holiday Inn, Sokolniki Hall Informal party, Holiday Inn, Vorobjevy Gory Hall |
| July 18 Wednesday | $\begin{gathered} 9.30-14.00 \\ 17.30-19.00 \\ 20.00-24.00 \end{gathered}$ | Excursions in groups: Kremlin/City tour <br> Consultation with tasks authors, Arbat Hall <br> The 2 ${ }^{\text {nd }}$ Jury Meeting, Okhotnyi Ryad \& Vorobjevy Gory Halls |
| July 19 <br> Thursday | Whole day $22.00-24.00$ | Translation of Theoretical Exam, Holiday Inn, Sokolniki Hall Informal party, Holiday Inn, Vorobjevy Gory Hall |
| July 20 Friday | $\begin{gathered} 8.00-18.00 \\ 18.00-22.00 \\ 22.00 \end{gathered}$ | Whole-day excursion to Sergiev Posad, lunch included Re-union Party on a boat, dinner included Transfer to Holiday Inn |
| July 21 <br> Saturday | $\begin{gathered} 9.30-14.00 \\ 15.00-19.00 \\ 20.00-22.00 \\ 22.00-24.00 \end{gathered}$ | Excursions in groups: City tour/Kremlin <br> Grading of students' works <br> The $3^{\text {rd }}$ (Business) Jury Meeting, Sokolniki 1 Hall Informal party, Holiday Inn, Vorobjevy Gory Hall |
| July 22 <br> Sunday | $\begin{gathered} 8.00-19.00 \\ 20.00-21.00 \\ 21.00-22.00 \\ 22.00-24.00 \end{gathered}$ | Arbitration in groups, Arbat Hall <br> Meeting with Minister of Education, RF and sponsors, Sokolniki 1 Hall The $4^{\text {th }}$ Jury Meeting, Allocation of medals, Sokolniki 1 Hall Informal party, Holiday Inn, Vorobjevy Gory Hall |
| July 23 <br> Monday | $\begin{gathered} 10.00-12.30 \\ 13.30 \\ 15.00-18.00 \\ 18.00-18.30 \\ 18.30 \\ 19.00-23.00 \\ 23.00 \\ 24.00-02.00 \end{gathered}$ | Free time, souvenir hunting <br> Buses depart to the Closing Ceremony, MSU <br> Closing Ceremony, MSU Assembly Hall <br> Walk-around MSU Campus <br> Buses depart to the Farewell Banquet <br> Farewell Banquet, Russian Academy of Sciences <br> Buses depart to Holiday Inn <br> Informal Farewell Party, Holiday Inn, Vorobjevy Gory Hall |
| July 24 <br> Tuesday | $\begin{gathered} 9.00-12.00 \\ \text { Whole day } \\ 12.00 \end{gathered}$ | Check-out <br> Departures <br> Late departures - transfer to Olimpiets hotel |

## Guests

| July 15 <br> Sunday | Whole day $22.00-24.00$ | Arrivals, Registration at Chemistry Department, MSU Transfer to Holiday Inn <br> Get-together party, Holiday Inn, Vorobjevy Gory Hall |
| :---: | :---: | :---: |
| July 16 <br> Monday | $\begin{gathered} \hline 9.00 \\ 11.00-13.00 \\ 13.00-15.00 \\ 15.00-18.00 \end{gathered}$ | Bus departs to the Opening Ceremony, MSU <br> Opening Ceremony, MSU Intellectual Centre - Fundamental Library <br> Welcome Reception, MSU Main Building <br> Moscow City tour |
| July 17 <br> Tuesday | $\begin{aligned} & \hline 10.00-14.00 \\ & 15.00-19.00 \\ & 22.00-24.00 \end{aligned}$ | Excursion to Kremlin, the Diamond Hall <br> Free time, souvenir hunting <br> Informal party, Holiday Inn, Vorobjevy Gory Hall |
| July 18 Wednesday | $\begin{gathered} \hline 10.00-13.00 \\ 13.00-15.00 \\ 15.00 \end{gathered}$ | Excursions to the Tret'yakov gallery <br> Lunch, "Godunov" restaurant, center of Moscow <br> Transfer back to the Holiday Inn. |
| July 19 <br> Thursday | $\begin{gathered} 9.00-14.00 \\ 17.30 \\ 19.00-22.00 \\ 23.00-24.00 \end{gathered}$ | Excursion to the Kolomenskoe park <br> Bus departs to the Moscow Circus, Tsvetnoi blvd. <br> Circus show <br> Informal party, Holiday Inn, Vorobjevy Gory Hall |
| July 20 Friday | $\begin{gathered} \hline 8.00-18.00 \\ 18.00-22.00 \\ 22.00 \\ \hline \end{gathered}$ | Whole-day excursion to Sergiev Posad Re-union Party on a boat Transfer to Holiday Inn |
| July 21 <br> Saturday | $\begin{aligned} & 10.00-14.00 \\ & 15.00-19.00 \\ & 22.00-24.00 \end{aligned}$ | Walk in the center of Moscow, Arbat <br> Free time <br> Informal party, Holiday Inn, Vorobjevy Gory Hall |
| July 22 <br> Sunday | $\begin{gathered} \hline 9.00-13.00 \\ 15.00-19.00 \\ 20.00-21.00 \\ \hline \end{gathered}$ | Excursion to the Cathedral of Christ the Savior <br> Excursion to the Izmailovo exhibition <br> Meeting with the Minister of Education, RF and sponsors, Sokolniki 1 Hall |
| July 23 <br> Monday | $9.00-12.30$ 13.30 $15.00-18.00$ $18.00-18.30$ 18.30 $19.00-23.00$ 23.00 $24.00-02.00$ | Free time, souvenir hunting <br> Buses depart to the Closing Ceremony, MSU <br> Closing Ceremony, MSU Assembly Hall <br> Walk-around MSU Campus <br> Buses depart to the Farewell Banquet <br> Farewell Banquet, Russian Academy of Sciences <br> Buses depart to Holiday Inn <br> Informal Farewell Party, Holiday Inn, Vorobjevy Gory Hall |
| July 24 <br> Tuesday | 9.00-12.00 <br> Whole day $12.00$ | Check-out <br> Departures <br> Late departures - transfer to Olimpiets hotel |

# Minutes of the Business Sessions of the $39^{\text {th }}$ IChO in Moscow 

MINUTES of the BUSINESS PART of the<br>$1^{\text {st }}$ JURY SESSION at the $39^{\text {th }}$ ICHO/MOSCOW<br>July $16^{\text {th }}, 2007$ (20.30-21.50)<br>Chair of the BUSINESS PART: Manfred Kerschbaumer

1. Presentation of the agenda for the meeting.
2. Number of delegations present at 20.30: 60
3. Short report of the ISC Meeting in December 2006:

Detailed minutes of the ISC-meeting may be found in the appendix of the Preparatory Problems for Moscow 2007;

ISC is aware of the situation with level 3 tasks - work on that has already begun.
In the business session of IChO (Jury session \#3) Andras Kotschy (Hungary) will distribute a proposal by Gabor Magyarfalvi (Hungary) for a new syllabus.
4. Change of regulations: possibility of a $2^{\text {nd }}$ Scientific Observer Regulations § 3, 1:
Each participating country's delegation may consist of four competitors and two accompanying persons (also known as mentors). Countries may include one scientific observer in their delegation.
Proposal:
Each participating country's delegation may consist of four competitors and two accompanying persons (also known as mentors). Countries may include two scientific observer in their delegation.
Comments: Anton Sirota (Slovakia): strongly against it, regulations should not be changed within such a short period, problems with financing, no necessity for a $2^{\text {nd }}$ scientific observer if task are shorter; I-Jy Chang (Taiwan): $2^{\text {nd }}$ scientific observer extremely important for Asian countries due to time consuming translation work; Carlos Castro-Acuna (Mexico): $2^{\text {nd }}$ scientific observer decreases injustice in connection with language groups; Marek Orlik (Poland): against it, because too many people in the Jury sessions;

Azerbaijan: supports proposal, because in case of changing the mentors ("generation change") $2^{\text {nd }}$ scientific observer may learn a lot;

Voting: A qualified majority would be 45 votes out from possible 66 (countries)

Result: $\quad 50$ votes supporting the proposal $\Rightarrow$ CHANGE ACCEPTED
5. Change of regulations: another definition of Honorable Mentions Regulations § 15, 5:

An honorable mention is awarded to competitors who do not receive a medal, but gain full marks for at least one problem.
Proposal:
An honorable mention is awarded to competitors who are among the best 10\% of non medalists.

Comments: Carlos Castro-Acuna (Mexico): his proposal, more justice for students who miss the bronze medals very tightly

## Several other comments in favour of the change.

Voting: A qualified majority would be 45 votes out from possible 66 (countries)

Result: $\quad 47$ votes supporting the proposal $\Rightarrow$ CHANGE ACCEPTED
6. Agenda for the Business Session of the IChO (draft)
$>$ Information by the Minister of Education and Science of Russia
> Election of new SC-members: one from Europe, two from Pacific Rim (proposals!)
> Distribution of "Gabor's" proposal concerning new syllabus and comments on it
> IUPAC-support
> Future Olympiads (presentation from Hungary)
> Any other business

# MINUTES of the BUSINESS SESSION of the $39^{\text {th }}$ ICHO/MOSCOW 

July $21^{\text {st }}, 2007$ (20.15-22.15)
Chair of the BUSINESS SESSION: Manfred Kerschbaumer

63 delegations are present.

Dr. Kerschbaumer presents the agenda of the meeting:

- Election of new SC-members: one from Europe, one from Asia, one from Pacific Rim
- Level and length of competition - new syllabus: Information about "Gabor's" proposal
- Level and length of competition - proposal to cut down the number of characters
- IUPAC-support
- Future Olympiads
- Information about arbitration


## - Election of new SC-members:

The following proposals are presented to the International Jury:
EUROPE: Wesley Brown (Ireland)
Kurt Nielsen (Denmark)
ASIA: Duckwhan Lee (Korea)
PACIFIC RIM: Mark Ellison (Australia)
As Duckwhan Lee and Mark Ellison are the only candidates from their respective regions, no election is necessary, they will be members of the SC for the next two years.
After short self presentations from the two European candidates, the jury elects Wesley Browne with 36 votes (Kurt Nielsen: 19 votes) as the third member of the SC from Europe.
Dr. Kerschbaumer thanks the parting member of SC, I-Yi Chang from Taiwan, Geoff Salem from Australia, and Paraic James from Ireland.

The members of the current SC are listed in appendix A.

## - Level and length of competition - new syllabus:

Manfred Kerschbaumer reports from the SC-meeting in December 2006 where the SC stated that in all the years before the regulation concerning the allowed number of level 3 topics was violated. So it was the duty of the SC to try and change this abuse.

Andras Kotschy from Hungary presents the proposal by Gabor Magyarfalvi which changes the old syllabus in its basics. Instead of topics belonging to three different levels, the new syllabus contains a section "concepts and skills" and a section "factual knowledge".

In both sections there is a list of concepts and skills or factual knowledge respectively which can be expected from the participants to be familiar with, and a list which must be covered in the preparatory problems.
A hard copy with the details of this proposal is distributed. The members of the International Jury are requested to give comments.

## - Level and length of competition - proposal to cut down the number of characters

Manfred Kerschbaumer proposes to cut down the number of characters allowed in the theoretical and practical competition ( 25.000 each, § 13, 4 of the regulations) to 22.000. He also points out that a lower number of characters does not imply an easier set of tasks because a guiding explanation needing more words may be simpler for a student than a short task with even shorter questions.

The head mentor from Belgium (Sebastien Delfosse) proposes to decrease this number to 20.000 characters.

The jury decides to vote about both proposals with 38 votes in favour.
As a change of the allowed number of characters means a change in the regulations, a qualified majority (45 votes) is necessary. After some discussion voting was carried out:

In favour to cut down to 20.000 characters: 27 votes
In favour to cut down to 22.000 characters: 35 votes
As this is not a qualified majority the current regulation (25.000) will not be changed.

## - IUPAC-support

Manfred Kerschbaumer reports about an offer from the president of IUPAC (Bryan O. Henry) in Korea to support the ICHO in some way. From December 2006 till June

2007, Dr. Kerschbaumer managed to negotiate an annual donation of US \$ 10.000 to help countries with financial troubles. A "Memorandum of Understanding" was established (appendix B) which shows the details of a possible support for the countries mentioned above.

## - Future Olympiads (presentation from Hungary)

Andras Kotschy shows a detailed presentation about the $40^{\text {th }} \mathrm{ICHO}$ in Budapest. It will be held at the Eötvös Loránd University from July $12^{\text {th }}$ to July $21^{\text {st }}$. Andras distributes the issue No. 1 of the Catalyzer.

Yoshiyuki Sugahara presents some details about the $42^{\text {nd }}$ ICHO in Tokio in 2010.
The then following host will be Turkey (2011) and USA (2012). John Kotz (USA) informs about the possible venue of the $44^{\text {th }}$ ICHO: Boston or Chicago.

## - Information about arbitration

Sasha Gladilin refers about the procedure of arbitration the next day. This time the sequence is not alphabetically but is decided by drawing lots.

## APPENDIX A:

## STEERING COMMITTEE OF THE ICHO

as constituted on July 22, 2007

## Elected members:

Representatives of Europe:
Manfred Kerschbaumer (Austria), chairman; e-mail: mkersch@gmx.net
Alexander K. Gladilin (Russia); e-mail: gladilin@direct.ru
Wesley Browne(Ireland); e-mail: w.r.browne@rug.nl

Representative of the Americas
Carlos Castro-Acuna (Mexico); e-mail: castroacuna02@yahoo.com

Representatives of Asia and the Pacific Rim:
Marc Ellison (Australia); e-mail: u3903111@anu.edu.au
Duckwhan Lee (Korea); e-mail: duckhwan@sogang.ac.kr

## Non-elected members:

Representatives of the organizers:
Valerie Lunin (Russia); e-mail: vvlunin@kge.msu.ru
Andras Kotschy (Hungary); e-mail: kotschy@chem.elte.hu
Peter Wothers (United Kingdom); e-mail: pdw12@cam.ac.uk
Representative from Japan

## Experts:

Wolfgang Hampe (Germany); e-mail: hampe@t-online.de Gabor Magyarfalvi (Hungary); e-mail: gmagyarf@chem.elte.hu

Kurt Nielsen (Denmark); e-mail: Kurt_B_Nielsen@post.tele.dk
Anton Sirota (Slovakia); e-mail: anton.sirota@stuba.sk

## APPENDIX B:

## Memorandum of Understanding

(IUPAC-support for the IChO)
> IUPAC will support the International Chemistry Olympiad by an annual donation of US\$ 10000 . This grant can be terminated by IUPAC after giving notice 12 months in advance of the next IChO.
$>$ The president of IUPAC (or nominee) will be invited to the closing
$>$ ceremony of the IChO to give a short ( 5 to 10 minutes) address and to take part in the gold medal presentations.
$>$ The first financial support will be for the 40th IChO in Budapest (Hungary) 2008.
> The money will be transferred to an account of the annual host (2008: Hungary).
> Countries who wish to apply for support will make a written application (nonformal) to the chair of the Steering Committee (SC) of the IChO. The application must contain the amount of money needed, and a (detailed) description of the problems of raising money for the IChO in that particular country. Deadline for the application is November 30th.
> The chair of the Steering Committee will present all applications to the SC in its annual meeting at the beginning of December the year preceding the IChO in question.
$>$ The SC will make decisions regarding the distribution of the money considering the following items: The money will be distributed to

- countries which cannot afford the participation fee and therefore cannot participate in the IChO
- countries which can not travel with a team of four students,
- countries which can not travel with two mentors.
> If the US\$ 10000 support is not fully allocated for a particular IChO, the unused part of the donation will be transferred to the next host.
> The IChO will provide IUPAC with a summary report of the distributions made from the IUPAC grant.

Bryan R. Henry (Date)
President IUPAC

Manfred Kerschbaumer (Date)
Chairman of the Steering Committee of the International Chemistry Olympiad

## PRACTICAL EXAMINATION PROBLEMS

## General Directions

- safety rules: follow them as in the Preparatory problems described, no eating or drinking is allowed in the lab.
- violating safety rules: you get one warning, offend again: you are out.
- problem booklet: 12 pages (incl. cover sheet and Periodic table of elements) with 2 problems. Start with problem 1.
- time: 5 hours; 30 minutes warning before the end.
- answer sheets: 5 pages (incl. cover sheet).
- your name and student code: write it on every answer sheet.
- answers: only in the appropriate places of the answer sheets, nothing else will be marked. Relevant calculations have to be shown.
- use only the pen and calculator provided.
- results: the number of significant figures in numerical answers must conform to the rules of evaluation of experimental error. Mistakes will result in penalty points even if your experimental technique is flawless.
- burette: read it as accurately as possible.
- more chemicals needed? Ask your lab assistant. No penalty for this.
- Extra sample to be analyzed or broken column: a penalty of 10 marks.
- questions concerning safety, apparatus, chemicals, organization, toilet break: ask your lab assistant.
- chemical waste: put it only in the designated containers.
- official English-language version available on request for clarification only. Ask your lab assistant.
- after the stop signal put your answer sheets and spectra in the envelope (don't seal), deliver them to your lab assistant. Keep the problem booklet together with the pen and calculator.
- You must stop your work immediately after the stop signal has been given. A delay of 5 minutes will result in zero points for the current task.
- During the Practical examination some of your glassware and plastics may have to be used more than once. Clean it carefully.


## List of Chemicals

| Reagent | Quantity | Placed in | Labeled |
| :---: | :---: | :---: | :---: |
| Task 1 |  |  |  |
| Eluent 1 | 100 mL | Amber glass bottle* | Eluent 1 |
| Eluent 1 | 1 mL | Plastic microtube | Eluent 1 |
| Eluent 2 | 50 mL | Amber glass bottle* | Eluent 2 |
| Eluent 2 | 1 mL | Plastic microtube | Eluent 2 |
| Eluent 3 | 50 mL | Amber glass bottle* | Eluent 3 |
| Eluent 3 | 1 mL | Plastic microtube | Eluent 3 |
| 0.5 M Carbonate buffer solution, pH 9.5 | 10 mL | Glass vial | $\mathrm{NaHCO}_{3}$ |
| 0.5 M Tris-HCl buffer solution, pH 8.5 | 10 mL | Glass vial | Tris- HCl |
| Mixture of amino acids to be analyzed** | 1.2 mL | Plastic microtube | A number between 301 and 600 |
| Ellmann reagent: 0.2 M Phosphate buffer solution containing 10 mM EDTA and $3 \mathrm{mM} 5,5^{\prime}$ -Dithiobis(2-nitrobenzoic acid), pH 7.0 | 10 mL | Glass vial | DTNB |
| Pauli's reagent: solution of sodium 4-diazoniumbenzenesulfonate in 0.1 M aqueous HCl | 1 ml | Plastic microtube | Pauli |
| Sodium hydroxide, 10\% aqueous solution | 10 mL | Glass vial | $\mathrm{NaOH} 10 \%$ |
| 8-Hydroxyquinoline, 5.2 mM solution in etha-nol/n-butanol (9:1) mixture | 5 ml | Glass vial | 8-HQ |
| Sodium hypobromite, 0.24 M solution in $10 \%$ aqueous NaOH | 1.2 ml | Plastic microtube | NaBrO |
| 2,4,6-Trinitrobenzenesulfonic acid, 3.4 mM aqueous solution | 1 mL | Plastic microtube | TNBS |
| 8 M Aqueous urea solution | 1 mL | Plastic microtube | Urea |
| Task 2 |  |  |  |
| HCl , standard solution, $\sim 1 \mathrm{M}$ (see exact value on the label) | 40 mL | Amber glass vial | $\begin{aligned} & \mathrm{HCl} \\ & \text { <and exact con- } \\ & \text { centration> } \end{aligned}$ |
| NaOH (to be standardized) | 200 mL | Amber glass vial | NaOH |
| Powdery sample to be analyzed** | $0.5-1 \mathrm{~g}$ | 150 mL beaker covered with watch glass | <number of workplace> |
| $\mathrm{H}_{2} \mathrm{O}$ distilled | 400 mL | Plastic wash bottle | $\mathrm{H}_{2} \mathrm{O}$ |
| $\mathrm{H}_{2} \mathrm{O}$ distilled (shared between 2 students) | 30 mL | Glass drop bottle | $\mathrm{H}_{2} \mathrm{O}$ |
| $\mathrm{H}_{2} \mathrm{O}$ distilled (for common use) | 5 L | Bottle with tubing and clamp on top of the bench | $\mathrm{H}_{2} \mathrm{O}$ |
| $\mathrm{NaH}_{2} \mathrm{PO}_{4}, 15 \%$ solution (shared between 2 students) | 20 mL | Glass drop bottle | $\mathrm{NaH}_{2} \mathrm{PO}_{4} 15 \%$ |
| Bromocresol Green, 0.5\% solution in 20\% ethanol (shared among 3-4 students in a raw) | 30 mL | Glass drop bottle | Bromcresol green |
| Thymolphthalein, $0.5 \%$ solution in ethanol (shared among 3-4 students in a raw) | 30 mL | Glass drop bottle | Thymolphtalein |
| $\mathrm{K}_{2} \mathrm{C}_{2} \mathrm{O}_{4}, 15 \%$ solution (shared between 2 students) | 50 mL | Amber glass vial | $\mathrm{K}_{2} \mathrm{C}_{2} \mathrm{O}_{4} 15 \%$ |

*Fixed on the top shelf (do not try to remove), with connected tubing and clamp
**10 marks penalty for an extra portion of the sample

## Components of Eluents 1 to 3

Eluent 1: 0.1 M aqueous sodium citrate, 50 mM sodium chloride, 40 mM thiodiglycol, 1 mM caprylic acid, 0.1\% Brij-35; pH 4.9.
Eluent 2: 0.2 M aqueous sodium phosphate, $0.1 \%$ Brij-35; pH 7.0.
Eluent 3: 0.2 M aqueous sodium hydroxide.

## Apparatus and Suppliers

| Item | Quantity |
| :---: | :---: |
| Test tube rack | 1 |
| Laboratory stand | 1 |
| Chromatography column with ion-exchange resin | 1 |
| Laboratory stand with white covering | 1 |
| Double clamp for burette | 1 |
| Ring for funnel | 1 |
| 25 mL Burette | 1 |
| 100 mL flask labeled "Waste" | 1 |
| 100 mL Volumetric flask | 2 |
| 100 mL Erlenmeyer flask | 2 |
| Syringe with needle | 1 |
| Graduated test tubes for collecting fractions and preparing mixtures | 50 |
| 96-well plate | 1 |
| Pipettor (micropipette) with fixed volume of 0.1 mL | 1 |
| Disposable tips (in blue plastic cup) | 20 |
| Spectrophotometric cuvettes labeled "A1", "B1", "A2", "B2", "A3", "B3" in cuvette holder | 6 |
| 10 mL Graduated plastic pipettes | 3 |
| 10 mL Glass pipette | 1 |
| Pipette filler | 1 |
| 3-Way Bulb | 1 |
| Glass rod | 1 |
| Filter funnel | 1 |
| Small funnel | 1 |
| 60 mL Amber glass vials for combined fractions (peaks) | 3 |
| 10 mL Measuring cylinder labeled " $\mathrm{K}_{2} \mathrm{C}_{2} \mathrm{O}_{4} 15 \%$ " (shared between 2 students) | 1 |
| 10 mL Measuring cylinder (shared between 2 students) | 1 |
| 50 mL Measuring cylinder | 1 |
| 100 mL Measuring cylinder labeled " $\mathrm{H}_{2} \mathrm{O}$ " (shared among 3-4 students in a row) | 1 |
| Plastic plate with filters ${ }^{* * *}$ (shared among 3-4 students in a row) | 3 filters per student |
| Heating plate (for common use in a fume hood) | 6 plates per hood |
| Rubber protection tips (for common use a fume hood) | 6 pairs per hood |
| Spectrophotometer (shared by a group of students; see the number of the spectrophotometer to be used at your bench "SP $\qquad$ |  |
| Marker | 1 |
| Ruler | 1 |
| White sheet of paper | 1 |

## Safety regulations, S-phrases, R-phrases

| Disodium hydrogen phosphate | $\mathrm{R}: 36 / 37 / 38 \mathrm{~S}: 26-36$ |
| :--- | :--- |
| Ethylenediaminetetraacetic acid, disodium salt | $\mathrm{R}: 36 / 37 / 38 \mathrm{~S}: 26-36 / 37 / 39$ |
| Tris-HCl | $\mathrm{R}: 36 / 37 / 38 \mathrm{~S}: 26-36$ |
| Arginine | $\mathrm{R}: 36 \mathrm{~S}: 26$ |
| Cysteine | $\mathrm{R}: 22$ |
| Histidine | $\mathrm{S}: 22-24 / 25$ |
| Hydrochloric acid | $\mathrm{R}: 34-37 \mathrm{~S}: 26-36-45$ |
| Sodium 4-diazoniumbenzenesulfonate | $\mathrm{R}: 1-37 / 37 \mathrm{~S}: 26-36$ |
| Sodium hydroxide | $\mathrm{R}: 34-35 \mathrm{~S}: 26-36-37 / 39-45$ |
| 8-Hydroxyquinoline | $\mathrm{R}: 22-36 / 37 / 38 \mathrm{~S}: 26-36 / 37$ |
| Ethanol | $\mathrm{R}: 11 \mathrm{~S}: 7-16$ |
| Butanol-1 | $\mathrm{R}: 10-22-37 / 38-41-67 \mathrm{~S}: 7 / 9-13-26-37 / 39-46$ |
| Sodium hypobromite | $\mathrm{R} 31-34 \mathrm{~S}: 26-36-45$ |
| 5,5'-Dithiobis(2-nitrobenzoic acid) | $\mathrm{R}: 36 / 37 / 38 \mathrm{~S}: 26-36$ |
| 2,4,6-Trinitrobenzene sulfonic acid | $\mathrm{R}: 1-22-36 / 38-43 \mathrm{~S}: 26-36 / 37$ |
| Sodium chloride | $\mathrm{R}: 36 \mathrm{~S}: 26$ |
| Thiodiglycol | $\mathrm{R}: 36 \mathrm{~S}: 26$ |
| Caprylic acid | $\mathrm{R}: 34 \mathrm{~S}: 26-27-45-36 / 37 / 39$ |
| Brij-35 | $\mathrm{R}: 36 / 37 / 38 \mathrm{~S}: 26-36$ |
| Sodium dihydrogen phosphate | $\mathrm{S}: 22-24 / 25$ |
| Sodium carbonate | $\mathrm{R}: 36 \mathrm{~S}: 22-26$ |
| Calcium carbonate | $\mathrm{R}: 41-37 / 38 \mathrm{~S}: 26-39$ |
| Bromocresol Green | $\mathrm{S}: 22-24 / 25$ |
| Thymolphthalein | $\mathrm{S}: 22-24 / 25$ |
| Potassium oxalate | $\mathrm{R}: 34 \mathrm{~S}: 26-27-36 / 37 / 39$ |

## Risk Phrases <br> Indication of Particular Risks

R1: Explosive when dry
10: Flammable
22: Harmful if swallowed
31: Contact with acids liberates toxic gas
34: Causes burns

35: Causes severe burns
36: Irritating to the eyes
37: Irritating to the respiratory system
41: Risk of serious damage to eyes
43: May cause sensitization by skin contact
67: Vapors may cause drowsiness and dizziness

## Combination of Particular Risks

R24/25: Toxic in contact with skin and if swallowed 36/37/38: Irritating to eyes, respiratory system and skin $36 / 38$ : Irritating to eyes and skin
37/38: Irritating to respiratory system and skin

## Safety Phrases

## Indication of Safety Precautions

S13: Keep away from food, drink and animal feeding stuffs
22: Do not breathe dust
26: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
27: Take off immediately all contaminated clothing
36: Wear suitable protective clothing

39: Wear eye/face protection
45: In case of accident or if you feel unwell, seek medical advice immediately (show label where possible)
46: If swallowed, seek medical advice immediately and show this container or label

## Combination of Safety Precautions

7/9: Keep container tightly closed and in a wellventilated place

24/25: Avoid contact with skin and eyes
36/37/39: Wear suitable protective clothing, gloves and eye/face protection

37/39: Wear suitable gloves and eye/face protection

## Problem 1. ION-EXCHANGE CHROMATOGRAPHY OF AMINO ACIDS

20 points
lon-exchange chromatography is an important analytical and preparative method, which allows fractioning of charged substances. Interaction of ionic groups of the substances with counterions attached to the resin is behind the method. In this task you will have to carry out separation of a given mixture of three amino acids followed by quantitative assay of individual amino acids eluted from the column by using specific chromogenic reactions. Since queues of students are possible at spectrophotometers, we strongly suggest you starting the exam with Problem 1.

His

Cys

Arg

Three amino acids (see the structures above) are present in the mixture. These are histidine, cysteine, and arginine. Cross-linked sulfonated polystyrene is used as a cation-exchange resin (see the picture of the system below). At the beginning of the experiment the column is equilibrated with Eluent 1 ( pH 4.9 ).

## Procedure

## Chromatography. Step 1

Apply the given solution of a mixture of amino acids to the column. First, open the stopcock to allow the solvent in the column draining into the Erlenmeyer flask labeled "Waste" so that the solvent is level with the top of packing material, still preventing the resin surface from drying off. Close the stopcock and carefully add the analyzed solution to the top of the column by using a syringe. Open the stopcock and let the sample soak inside the gel (drain the solvent into the "Waste" flask). Close the stopcock and add about 1 mL of Eluent 1 (corresponds to $\sim 1 \mathrm{~cm}$ of liquid in the column) by carefully releasing the tubing clamp. Attach the top joint tightly, fixing the column with one hand and the adaptor with the other (be sure that the joint is fitted closely to the column). Replace the "Waste" flask at the stand with the test tubes in the rack. Release the tubing clamp and open the stopcock to let the eluent flow down through
the column. Proceed with elution. (Always open the stopcock to start elution and close the stopcock to stop it).

Collect the fractions in the test tubes up to the volume of 2.5 mL (as shown in the Picture). If needed, label them with marker. After collecting each 4 to 8 fractions stop elution and carry out qualitative analysis of the collected samples.


## Qualitative analysis of samples

Qualitative assay of amino acids is based on the reaction of their $\alpha$-amino groups with sodium 2,4,6-trinitrobenzene sulfonate (TNBS):


The assay is carried out in the wells of a polystyrene plate, each well corresponding to a definite test tube. Before starting the assay, mix 1 mL of TNBS solution with 10 mL of carbonate buffer solution and place 0.1 mL of the resulting mixture into half of the plate wells (from A1 to H 5 ). Then add 0.1 mL of the analyzed fraction into a well. Start with A1 well and continue with B1, C1, etc (move top to bottom and left to
right). If an amino acid is present in the analyzed fraction, intense yellow coloration will develop in the corresponding well within 3 min . Use the coloration in the first well as the reference. To reliably estimate the coloration, place the plate on the white sheet of paper.

Note: all aliquots of 0.1 mL should be added by using the pipettor. We expect you to use one tip for all fractions of a single peak.
1.1a Draw the profile of coloration intensity (qualitatively) on the plate sketch in the Answer Sheet. Use the following symbols: (-) - no coloration, 1 - weak coloration, 2 - moderate coloration and 3 - intense coloration. Keep drawing the profile during the whole chromatography process.

Continue collecting fractions and analyzing them until you get at least two wells with coloration as in A1 well, which will indicate that the first amino acid has left the column completely (end of the first peak).

## Chromatography. Step 2

As soon as you are finished with collecting the first peak, change to Eluent 2. To do so, close the stopcock, fix the tubing clamp (Important!), disconnect the tubing leading to the bottle with Eluent 1 and connect the tubing leading to the bottle with Eluent 2. Attach the top joint tightly.
1.1b Indicate when the eluents have been changed by drawing lines between the corresponding wells on the plate sketch.

Continue elution, collecting fractions and carrying out qualitative analysis of samples as described above.

## Chromatography. Step 3

As soon as you are finished with collecting the second peak, change to Eluent 3 as described in Step 2. Continue chromatography until the third amino acid leaves the column completely.

Stop chromatography by closing the stopcock and fixing the clamp.

Based on the results of qualitative analysis, choose the fractions which contain the amino acids.
1.1c Write down in the Answer Sheet the labels of wells corresponding to the chosen fractions.
1.2 Combine the fractions from each peak and measure the volumes of combined fractions using a measuring cylinder. Report the volumes of combined fractions excluding amounts used for the qualitative analysis. Write down the obtained results in the Answer Sheet.

Pour combined fractions in the amber glass vials labeled "Peak 1", "Peak 2", "Peak 3". Prepare samples for quantitative spectrophotometric analysis as described below.

When finished with Practical exam, close the vials and leave them on the table. The combined fractions will be subsequently analyzed by lab staff.

## Spectrophotometric analysis

For each probe, you should submit two cuvettes to the operator. Prepare the probes as follows.

Important! When storing, always put cuvettes in the cuvette holder! All cuvettes have 2 ribbed and 2 working vertical surfaces. While operating with cuvettes, do not touch working surfaces, otherwise you may get incorrect values of absorbance.

Assay 1 (peak 1). Cysteine concentration is determined by the Ellmann reaction:


Test tube A1 (Reference). Place 0.1 mL of Eluent 1 from plastic microtube into a test tube and add 2.9 mL of Ellmann reagent (DTNB).

Test tube B1 (Sample). Place 0.1 mL of the analyzed solution into a test tube and add 2.9 mL of Ellmann reagent (DTNB).

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cuvettes labeled A1 (for reference) and B1 (for sample).

Assay 2 (peak 2). Determination of histidine concentration is based on the ability of imidazole moiety to react with diazonium compounds (Pauli reaction).

Test tube A2 (Reference). Place 2.8 mL of Tris- HCl buffer solution into a test tube, add 0.1 mL of Eluent 2 from plastic microtube and 0.1 mL of Pauli reagent.
Test tube B2 (Sample). Place 2.8 mL of Tris-HCI buffer solution into a test tube, add 0.1 mL of the analyzed solution and 0.1 mL of Pauli reagent.

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cuvettes labeled A2 (for reference) and B2 (for sample).

Assay 3 (peak 3). Determination of arginine concentration is based on the ability of guanidinium moiety to react with some phenols under alkaline and oxidative conditions (Sakaguchi reaction).

Test tube A3 (Reference). Place 0.1 mL of Eluent 3 into a test tube and add 1.5 mL of $10 \% \mathrm{NaOH}$ solution, 1 mL of 8 -hydroxyquinoline solution and 0.5 mL of sodium hypobromite solution.

Test tube B3 (Sample). Place 0.1 mL of the analyzed solution into a test tube and add 1.5 mL of $10 \% \mathrm{NaOH}$ solution, 1 mL 8 -hydroxyquinoline solution and 0.5 mL of sodium hypobromite solution.

Shake the test tubes vigorously for 2 min (Important!) and observe formation of orange color. Add 0.2 mL of 8 M urea solution to each test tube, mix the contents and transfer about 3 mL of each mixture to the corresponding cuvettes labeled A3 (for reference) and B3 (for sample).

All mixtures should be analyzed by spectrophotometry not earlier than 10 min and not later than 2 h after preparation. Submit the set of 6 cuvettes to the spectrophotometer operator. In case of a queue at the spectrophotometer, ask the operator to put your student code on the list at the signboard. You will be invited by the operator in due time. Meanwhile, you can answer the theoretical question and start fulfilling Problem No 2.

In case your sample(s) have not been subjected to studies within the proper time interval (which is quite improbable), prepare the sample(s) afresh.

Get the print-offs with the spectra of your samples and check it. Sign the print-offs and get the operator's signature.
1.3 Determine absorbance at the corresponding wavelengths and calculate the content (in mg ) of each amino acid in the mixture you were given. The optical length is 1.0 cm. Complete the Answer Sheets taking into account that one mole of each amino acid gives one mole of the corresponding product.

Reference data:
The values of extinction coefficients:
Product of Ellmann reaction: $13600 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ at
410 nm
Product of Pauli reaction: $6400 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ at 470
nm
Product of Sakaguchi reaction: $7700 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ at
500 nm

Molar masses of the amino acids. Cysteine $121 \mathrm{~g} / \mathrm{mol}$ Histidine $155 \mathrm{~g} / \mathrm{mol}$ Arginine $174 \mathrm{~g} / \mathrm{mol}$
1.4. Draw three resonance structures of the species responsible for mixture coloration as a result of Ellmann reaction.

## Problem 2. DETERMINATION OF CARBONATE AND HYDROGEN PHOSPHATE IN AN ABRASIVE SAMPLE

20 points
$\mathrm{Na}_{2} \mathrm{CO}_{3}, \mathrm{CaCO}_{3}$ and $\mathrm{Na}_{2} \mathrm{HPO}_{4}$ are the main constituents of abrasive powders. In this task you will have to determine carbonate and hydrogen phosphate ions in an abrasive sample by two acid-base titrations.

First, the exactly known amount of hydrochloric acid (taken in an excess) is added to the sample. As a result, hydrogen phosphates are transformed into $\mathrm{H}_{3} \mathrm{PO}_{4}$, whereas carbonates into $\mathrm{CO}_{2}$ which is further removed by boiling. Calcium ions initially present in the sample pass into the solution. Because of possible interference in subsequent analysis, they are precipitated as $\mathrm{CaC}_{2} \mathrm{O}_{4}$ and filtered off prior to the titration.

Next, the phosphoric acid formed is subjected to two titrations with pre-standardized NaOH solution and two different indicators: Bromocresol Green (BCG) and Thymolphthalein (TP). First, $\mathrm{H}_{3} \mathrm{PO}_{4}$ (and excess of HCl ) is titrated to $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$ion, the endpoint lying in slightly acidic medium (pH of $\sim 4.5$ ). It corresponds to the color change of BCG from yellow to blue. The second titration proceeds till $\mathrm{HPO}_{4}{ }^{2-}$ is formed. The endpoint of the second titration corresponds to the color change of TP from colorless to blue (moderately alkaline medium, pH of $\sim 10$ ).

The content of $\mathrm{CO}_{3}{ }^{2-}$ ions in the sample is calculated by finding the difference between:
a) the amount of the titrant equivalent to the initial amount of HCl (taken for the sample dissolution) and
b) the amount of the titrant corresponding to the second endpoint (TP).

The content of $\mathrm{HPO}_{4}{ }^{2-}$ is calculated by finding the difference between the amounts of the titrant consumed to achieve two endpoints (TP and BCG).

## Procedure

## Step 1. Dissolution of the sample and removal of $\mathrm{CO}_{2}$

To the sample of the abrasive powder in a beaker covered with watch glass add 10.00 mL (exactly, with a pipette! Carefully, not removing the glass and avoiding losses because of splashing!) of ca. $1 \mathrm{~mol} / \mathrm{L} \mathrm{HCl}$ (see the exact concentration
of the acid on the label). After the most intensive stage of gas evolution is completed, heat carefully the solution in the beaker (covered with watch glass) on a heating plate until the gas evolution stops. Then bring the solution to boiling and boil it carefully for 2-3 min.

## Step 2. Precipitation of calcium

Remove the beaker from the plate; wash the steam condensate from the watch glass down to the beaker with distilled water. Add $1-2 \mathrm{~mL}$ of $15 \% \mathrm{~K}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$ solution with measuring cylinder. Put the beaker aside until the most part of the precipitate is formed (usually takes 10 to 20 min ). Spend this time for standardization of the titrant solution of NaOH (see the procedure hereunder).

## Step 3. Standardization of NaOH solution

Place with a pipette 10.00 mL of HCl solution into a 100 mL volumetric flask, make up to the mark with distilled water and mix. Fill the burette with NaOH solution. Transfer with a pipette 10.00 mL of the diluted HCl solution from the volumetric flask to an Erlenmeyer flask. Add 1-2 drops of Thymolphthalein solution and titrate with NaOH solution until blue coloration stable on swirling for $5-10 \mathrm{~s}$ appears.

Here and after. Repeat the titrations as necessary. It is desirable that the highest and the lowest titrant volume values differ not more than by 0.10 mL . Report all the final volume values with 0.01 mL accuracy.

## 2.1a Complete the table in the Answer Sheet.

2.1b Calculate the concentration of NaOH solution (in mol/L).

## Step 4. Filtering off calcium oxalate

After the most part of $\mathrm{CaC}_{2} \mathrm{O}_{4}$ precipitates filter the precipitate off collecting the filtrate into a 100 mL volumetric flask. Slight turbidity in the filtrate is admissible, since small amounts of calcium oxalate do not interfere in the titration. Wash the filter with distilled water; make up the solution in the flask to the mark with distilled water and mix. Put the used filter into the waste basket.

## Step 5. Sample titration against Bromocresol Green

Transfer with a pipette a 10.00 mL aliquot of the sample solution coming from the step 4 from the volumetric flask to an Erlenmeyer one, and add 3 drops of BCG solution. Prepare in another Erlenmeyer flask a reference solution by adding 3 drops of $15 \% \mathrm{NaH}_{2} \mathrm{PO}_{4}$ solution and 3 drops of BCG solution to $15-20 \mathrm{~mL}$ of distilled water. Titrate the sample solution with NaOH solution until the color coincides with that of the reference solution.

### 2.2 Complete the table in the Answer Sheet.

## Step 6. Sample titration against thymolphthalein

Transfer with a pipette a 10.00 mL aliquot of the sample solution coming from the step 4 from the volumetric flask to an Erlenmeyer one. Add 2 drops of TP solution and titrate with NaOH solution until blue coloration stable on mixing for $5-10 \mathrm{~s}$ appears.

### 2.3 Complete the table in the Answer Sheet.

## Step 7. Calculations

2.4 Calculate the mass of $\mathrm{CO}_{3}{ }^{2-}$ in the sample.
2.5 Calculate the mass of $\mathrm{HPO}_{4}{ }^{2-}$ in the sample.

## Step 8. Additional questions to the problem

Answer the additional questions in the Answer Sheets.
2.6a Indicate one reaction (write down the equation) for a process interfering in the sample analysis you have carried out in the presence of $\mathrm{Ca}^{2+}$.
2.6b A list of mistakes possible at different steps is given in the table in the answer sheet. Indicate which of the mistakes can lead to errors in $\mathrm{CO}_{3}{ }^{2-}$ and/or $\mathrm{HPO}_{4}{ }^{2-}$ content determination. Use the following symbols: " 0 " if no error is expected, "+"or "-" if the result is higher (positive error) or lower (negative error) than the true one.

## THEORETICAL EXAMINATION PROBLEMS

## General Directions

- Write your name and code number on each page of the answer sheet.
- You have 5 hours to fulfil the task. Failure to stop after the STOP command may result in zero points for the task.
- Write answers and calculations within the designated box.
- Use only the pen and the calculator provided.
- There are 18 pages of Problems (incl. Cover Sheet and Periodic Table) and 22 pages of Answer Sheet.
- An English-language version is available.
- You may go to the restroom with permission.
- After finishing the examination, place all sheets including Problems and Answer Sheet in the envelope and seal.
- Remain seated until instructed to leave the room.


## Constants and useful formulas

| Gas constant | $R=8.314 \mathrm{~J} \cdot \mathrm{~K}^{-1} \cdot \mathrm{~mol}^{-1}$ |
| :--- | :--- |
| Avogadro constant | $N_{\mathrm{A}}=6.022 \cdot 10^{23} \mathrm{~mol}^{-1}$ |
| Planck constants | $h=6.626 \cdot 10^{-34} \mathrm{~J} \cdot \mathrm{~s}$ |
|  | $\hbar=1.055 \cdot 10^{-34} \mathrm{~J} \cdot \mathrm{~s}$ |
| Speed of light | $c=3.00 \cdot 10^{8} \mathrm{~m} \cdot \mathrm{~s}^{-1}$ |


| Uncertainty relation | $\Delta x \cdot \Delta p \geq \frac{\hbar}{2}$ |
| :--- | :--- |
| Gibbs energy of a condensed phase at <br> pressure $p$ | $G=p V+$ const |
| Excess pressure caused by surface <br> tension | $\Delta P_{\text {in }}=2 \sigma / r$ |
| Relation between equilibrium constant <br> and Gibbs energy | $R T \ln K=-\Delta_{\mathrm{r}} G^{\circ}$ |
| Isotherm of a chemical reaction | $\Delta G=\Delta G^{\circ}+R T \cdot \ln Q$ |
| with $Q=\frac{\text { product of } c \text { (products) }}{\text { product of } c(\text { reactants })}$ |  |
| Arrenius equation | $k=A \exp \left(-\frac{E_{\mathrm{A}}}{R T}\right)$ |

$\mathrm{V}($ cylinder $)=\pi r^{2} h$
$S($ sphere $)=4 \pi r^{2}$
$V($ sphere $)=\frac{4}{3} \pi r^{3}$

## Problem 1. PROTON TUNNELING

Proton tunneling through energy barriers is an important effect, which can be observed in many complex species containing hydrogen bonds (DNA, proteins, etc.). Propanedial (malonaldehyde) is one of the simplest molecules for which intramolecular proton transfer can occur.
1.1.1 Draw the condensed formula of propanedial and the structures of two of its isomers, which can exist in equilibrium with propanedial.
1.1.2 In a water solution propanedial is a weak acid, its strength being comparable with that of acetic acid. Specify the acidic hydrogen atom. Explain its acidity (choose one version in the Answer Sheet).

On the plot below an energy profile of the intramolecular proton transfer is given (the dependence of energy on the distance of proton motion (in nm)). Energy curve has a symmetric double-well form.

1.2.1 Draw the structures corresponding to two minima on this curve.

A proton is delocalized between two atoms and oscillates between two minima $L$ and $R$ with an angular frequency $\omega=6.48 \cdot 10^{11} \mathrm{~s}^{-1}$. Probability density for a proton depends on time as follows:

$$
\Psi^{2}(x, t)=\frac{1}{2}\left[\Psi_{\mathrm{L}}^{2}(x)+\Psi_{\mathrm{R}}^{2}(x)+\left(\Psi_{\mathrm{L}}^{2}(x)-\Psi_{\mathrm{R}}^{2}(x)\right) \cos (\omega t)\right],
$$

wavefunctions $\Psi_{\mathrm{L}}(x)$ and $\Psi_{\mathrm{R}}(x)$ describe a proton localized in the left and right wells, respectively:

1.3.1 Write down the expressions for the probability density at three moments: (a) $t=$ 0 , (b) $t=\pi /(2 \omega)$, (c) $t=\pi / \omega$. Sketch the graphs of these three functions.
1.3.2 Without calculations, determine the probability of finding the proton in the left well at $t=\pi /(2 \omega)$.
1.3.3 How much time is required for a proton to move from one well to another? What is the proton mean speed during the transfer?
1.3.4 From the energy curve, estimate the uncertainty of the position of proton forming hydrogen bonds. Estimate the minimal uncertainty of the proton speed. Compare this value with that obtained in 1.3.3 and draw a conclusion about the proton tunneling (choose one of the versions in the Answer Sheet).

## Problem 2. NANOCHEMISTRY

8 points
Metals of the iron subgroup are effective catalysts of hydrogenation of CO (FischerTropsch reaction)

$$
\mathrm{CO}+3 \mathrm{H}_{2} \xrightarrow{\mathrm{Fe}, \mathrm{Co}} \mathrm{CH}_{4}+\mathrm{H}_{2} \mathrm{O}
$$

Catalyst (e.g. cobalt) is often used in the form of solid nanoparticles that have a spherical structure (fig.1). The reduction in size of the catalyst increases catalytic activity significantly. The unwanted side-reaction however involves the oxidation of the catalyst:

$$
\begin{equation*}
\mathrm{Co}(\mathrm{~s})+\mathrm{H}_{2} \mathrm{O} \text { (gas) } \rightleftharpoons \mathrm{CoO} \text { (s) }+\mathrm{H}_{2} \text { (gas) } \tag{1}
\end{equation*}
$$

Solid cobalt oxide (bulk) is formed in the reaction vessel. This causes an irreversible loss of the catalyst's mass. Solid cobalt oxide can also be deposited on the surface of $\mathrm{Co}(\mathrm{s})$. In this case the new spherical layer is formed around the surface of the catalyst (see figure 2 ) and the catalytic activity drops.


Fig. 1


Fig. 2

Let us see how formation of nanoparticles affects the equilibrium of reaction (1). Useful equation:

$$
G^{0}(r)=G^{0}(\text { bulk })+\frac{2 \sigma}{r} V
$$

2.1.1 Calculate the standard Gibbs energy $\Delta_{\mathrm{r}} G^{0}(1)$ and the equilibrium constant for the reaction (1) at $T=500 \mathrm{~K}$.
2.1.2 Calculate the equilibrium constant for reaction (1) when the cobalt catalyst is dispersed in the form of spherical particles (Fig.1) of radius
(a) $10^{-8} \mathrm{~m}$.
(b) $10^{-9} \mathrm{~m}$.

The surface tension at the Co-gas interface is $0.16 \mathrm{~J} / \mathrm{m}^{2}$. CoO forms a bulk phase.

The mixture of gases involved in the Fischer-Tropsch reaction ( $\mathrm{CO}, \mathrm{CH}_{4}, \mathrm{H}_{2}, \mathrm{H}_{2} \mathrm{O}$ ) was put into a reaction vessel containing the cobalt catalyst. The total pressure is $p=$ 1 bar, temperature is $T=500 \mathrm{~K}$. The mole fraction of hydrogen (\%) in the mixture is 0.15\%.
2.2.1 At what minimum mole fraction of water (\%) in the gas mixture the unwanted spontaneous oxidation of the catalyst becomes possible so that solid bulk CoO may appear in the system? Assume that cobalt catalyst is in the form of
(a) a bulk phase
(b) spherical nanoparticles with $r_{a}=1 \mathrm{~nm}$ (Fig. 1).
2.2.2 What would you suggest to protect Co nanoparticles from the spontaneous oxidation with the formation of bulk CoO at a constant ratio $p\left(\mathrm{H}_{2} \mathrm{O}\right) / p\left(\mathrm{H}_{2}\right)$ and a constant temperature:
(a) to increase $r_{a}$;
(b) to decrease $r_{a}$;
(c) change of $r_{a}$ has no effect.

Assume now that solid cobalt oxide forms a spherical layer around a nanoparticle of cobalt. In this case the nanoparticle contains both a reactant (Co) and a product (CoO) (fig. 2). In the following problems denote surface tensions as $\sigma_{\mathrm{CoO}-\mathrm{gas}}, \sigma_{\mathrm{CoO}-\mathrm{Co}}$, radii as $r_{\mathrm{a}}, r_{\mathrm{b}}$, molar volumes as $V(\mathrm{Co}) ; V(\mathrm{CoO})$.
2.3.1 Write down the expression for the standard molar Gibbs function of CoO.
2.3.2 Write down the expression for the standard molar Gibbs function of Co.

Hint. If two spherical interfaces surround a nanoparticle, the excess pressure at its centre is given by the expression

$$
P_{\mathrm{in}}-P_{\mathrm{ex}}=\Delta P=\Delta P_{1}+\Delta P_{2}=2 \frac{\sigma_{1}}{r_{1}}+2 \frac{\sigma_{2}}{r_{2}}
$$

$r_{\mathrm{i}}, \sigma_{\mathrm{i}}$ are radius and surface tension at the spherical interface $i$, respectively.
2.3.3 Express the standard Gibbs energy of the reaction (1) $\Delta_{\mathrm{r}} G^{0}\left(1, r_{\mathrm{a}}, r_{\mathrm{b}}\right)$ in terms of $\sigma_{\text {coo-gas }} \sigma_{\text {coo-co }}, r_{a}, r_{b}, V(C o) ; V(C o O)$ and $\Delta_{\mathrm{r}} G^{0}(1)$.
2.3.4 When spontaneous oxidation of Co begins the radii of two layers in the nanoparticle (Fig. 2) are almost equal, $r_{a}=r_{b}=r_{0}$, and $\Delta_{\mathrm{r}} G^{0}\left(1, r_{\mathrm{a}}, r_{\mathrm{b}}\right)=\Delta_{\mathrm{r}} G^{0}\left(1, r_{0}\right)$. Assume that $\sigma_{\text {cоо-gas }}=2 \sigma_{\text {соо-со }}$. Which plot in the Answer Sheet describes correctly the dependence of $\Delta_{\mathrm{r}} G^{0}\left(1, r_{0}\right)$ on $r_{0}$ ?
2.3.5 What would you choose to protect Co nanoparticles from the spontaneous formation of the external layer of CoO at a constant ratio $p\left(\mathrm{H}_{2} \mathrm{O}\right) / p\left(\mathrm{H}_{2}\right)$ and a constant temperature:
a) increase $r_{0}$
b) decrease $r_{0}$
c) change of $r_{0}$ has no effect.

Reference data:

| Substance | $\rho, \mathrm{g} / \mathrm{cm}^{3}$ | $\Delta_{\mathrm{f}} G_{500}^{\circ}, \mathrm{kJ} / \mathrm{mol}$ |
| :---: | :---: | :---: |
| $\mathrm{Co}(\mathrm{s})$ | 8.90 |  |
| CoO (s) | 5.68 | -198.4 |
| $\mathrm{H}_{2} \mathrm{O}$ (gas) |  | -219.1 |

## Problem 3. UNSTABLE CHEMICAL REACTIONS

7 points
Many chemical reactions display unstable kinetic behavior. At different conditions (concentrations and temperature) such reactions can proceed in various modes: stable, oscillatory or chaotic. Most of these reactions include autocatalytic elementary steps.

Consider a simple reaction mechanism involving autocatalytic step:

$$
\begin{aligned}
& \mathrm{B}+2 \mathrm{X} \xrightarrow{k_{1}} 3 \mathrm{X} \\
& \mathrm{X}+\mathrm{D} \xrightarrow{k_{2}} \mathrm{P}
\end{aligned}
$$

( $B$ and $D$ are reagents, $X$ is an intermediate and $P$ is a product).
3.1.1 Write down the overall reaction equation for this two-step mechanism. Write the rate equation for $X$.
3.1.2 Deduce a rate equation using steady-state approximation. Find the orders:
(i) a partial reaction order with respect to $B$;
(ii) a partial reaction order with respect to $D$;
(iii) the overall order of a reaction.

Let the reaction occur in an open system where reagents B and D are being continuously added to the mixture so that their concentrations are maintained constant and equal: $[B]=[D]=$ const.
3.2.1 Without solving the kinetic equation draw the kinetic curve $[X](t)$ for the cases: 1) $[X]_{0}>k_{2} / k_{1}$; 2) $[X]_{0}<k_{2} / k_{1}$.
3.2.2 Without solving the kinetic equation draw the kinetic curve $[X](t)$ for the case when the reaction proceeds in a closed vessel with the initial concentrations: $[B]_{0}=$ $[D]_{0,}[X]_{0}>k_{2} / k_{1}$.

Much more complex kinetic behavior is possible for the reactions with several intermediates. Consider a simplified reaction mechanism for cold burning of ethane in oxygen:

$$
\begin{aligned}
& \mathrm{C}_{2} \mathrm{H}_{6}+\mathrm{X}+\ldots \xrightarrow{k_{1}} 2 \mathrm{X} \\
& \mathrm{X}+\mathrm{Y} \xrightarrow{k_{2}} 2 \mathrm{Y}+\ldots \\
& \mathrm{C}_{2} \mathrm{H}_{6}+\mathrm{Y}+\ldots \xrightarrow{k_{3}} 2 \mathrm{P}
\end{aligned}
$$

Under specific conditions this reaction displays oscillatory behavior.

Intermediates are peroxide $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}_{2}$ and aldehyde $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O}, \mathrm{P}$ is a stable product.
3.3.1 Identify $X, Y$, and $P$. Fill the blanks in the reaction mechanism.

Behavior of unstable reactions is often controlled by temperature which affects the rate constants. In the above oxidation mechanism oscillations of concentrations are possible only if $k_{1} \geq k_{2}$. Parameters of the Arrhenius equations were determined experimentally:

| Step | $A, \mathrm{~cm}^{3} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~s}^{-1}$ | $E_{A}, \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$ |
| :---: | :---: | :---: |
| 1 | $1.0 \cdot 10^{11}$ | 90 |
| 2 | $3.0 \cdot 10^{12}$ | 100 |

3.4.1 What is the highest temperature at which oscillatory regime is possible? Show your calculations.

## Problem 4. DETERMINATION OF WATER BY FISCHER TITRATION

8 points
Determination of water by the classical Fischer method involves titration of a sample solution (or suspension) in methanol by a methanolic iodine solution, containing also an excess of $\mathrm{SO}_{2}$ and pyridine $\left(\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N}\right.$, Py) - Fischer reagent. The following reactions occur during the titration:

$$
\begin{aligned}
& \mathrm{SO}_{2}+\mathrm{CH}_{3} \mathrm{OH}+\mathrm{H}_{2} \mathrm{O}+\mathrm{I}_{2}=2 \mathrm{HI}+\mathrm{CH}_{3} \mathrm{OSO}_{3} \mathrm{H} \\
& \mathrm{Py}+\mathrm{HI}=\mathrm{PyH}^{+} \mathrm{I}^{-} \\
& \mathrm{Py}+\mathrm{CH}_{3} \mathrm{OSO}_{3} \mathrm{H}=\mathrm{PyH}^{+} \mathrm{CH}_{3} \mathrm{OSO}_{3}^{-}
\end{aligned}
$$

lodine content is usually expressed in mg of water reacting with 1 mL of the titrant solution (hereunder $T, \mathrm{mg} / \mathrm{mL}$ ), which equals the mass of water ( mg ) reacting with 1.00 mL of the iodine solution. $T$ is determined experimentally by titration of a sample with a known water content. The sample may be, for example, a hydrated compound or a standard solution of water in methanol. In the latter case it should be taken into account that methanol itself can contain certain amount of water.

In all calculations please use the atomic masses accurate to 2 decimal points.
4.1 Sometimes titration of water is performed in pyridine medium without methanol. How would the reaction of $\mathrm{I}_{2}$ with $\mathrm{SO}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$ occur in this case? Write down balanced reaction equation.

Calculate the T values of iodine solution in each of the following cases:
4.2.1 12.20 mL of Fischer reagent solution were used for titration of 1.352 g of sodium tartrate dihydrate $\mathrm{Na}_{2} \mathrm{C}_{4} \mathrm{H}_{4} \mathrm{O}_{6} \cdot 2 \mathrm{H}_{2} \mathrm{O}$.
4.2.2 A known amount of water ( 21.537 g ) was placed into a 1.000 L volumetric flask which was filled by methanol up to the mark. For titration of 10.00 mL of the obtained solution, 22.70 mL of Fischer reagent solution were needed, whereas 2.20 mL of Fisher regent solution were used for titration of 25.00 mL of methanol.
4.2.3 5.624 g of water were diluted by methanol up to a total volume of 1.000 L (solution A); 22.45 mL of this solution were used for titration of 15.00 mL of a Fischer reagent (solution B).

Then 25.00 mL of methanol (of the same batch as used for the preparation of solution $\mathbf{A}$ ) and 10.00 mL of solution $\mathbf{B}$ were mixed, and the mixture was titrated by the solution A. 10.79 mL of the latter solution were spent.
4.3 An inexperienced analyst tried to determine water content in a sample of CaO using Fischer reagent. Write down the equation(s) of reaction(s) demonstrating possible sources of errors.

For the titration of 0.6387 g of a hydrated compound $\mathrm{Fe}_{2}\left(\mathrm{SO}_{4}\right)_{3} \cdot x \mathrm{H}_{2} \mathrm{O}, 10.59 \mathrm{~mL}$ of iodine solution ( $T=15.46 \mathrm{mg} / \mathrm{mL}$ ) were consumed.
4.4.1 What other reaction(s), beside those given in the problem, can occur during the titration? Write down the equations of two such processes.
4.4.2 Write down an equation of the overall reaction of $\mathrm{Fe}_{2}\left(\mathrm{SO}_{4}\right)_{3} \cdot \mathrm{xH}_{2} \mathrm{O}$ with the Fischer reagent.
4.4.3 Calculate the composition of the hydrate $\mathrm{Fe}_{2}\left(\mathrm{SO}_{4}\right)_{3} \cdot x \mathrm{H}_{2} \mathrm{O}$ ( $x=$ integer $)$.

## Problem 5. A MYSTERIOUS MIXTURE (ORGANIC HIDE-AND-SEEK GAME)

7.5 points

An equimolar mixture $\mathbf{X}$ of three colorless organic liquids $\mathbf{A}, \mathbf{B}, \mathbf{C}$ was treated by water with a drop of hydrochloric acid at heating to give, after separation from water, a $1: 2$ (molar ratio) mixture of acetic acid and ethanol without any other components. To the mixture after hydrolysis a catalytic amount (one-two drops) of concentrated sulfuric acid was added, and after long reflux (boiling with reflux condenser) a compound D, a volatile liquid with pleasant smell, was formed in $85 \%$ yield. Compound $\mathbf{D}$ is not identical to any of $\mathbf{A}, \mathbf{B}, \mathbf{C}$.

### 5.1.1 Draw the structure of compound $\boldsymbol{D}$.

5.1.2 Which class of organic compounds does $\boldsymbol{D}$ belong to? Choose the proper variant from those given in the Answer Sheet.
5.1.3 Even if the reflux is continued twice as long, the yield of $\boldsymbol{D}$ would not exceed 85\%. Calculate the expected yield of $\boldsymbol{D}$ if $1: 1$ (molar ratio) mixture of ethanol and acetic acid is taken. Assume that: a) volumes do not change during the reactions; b) all concomitant factors, such as solvent effects, non-additivity of volumes, variation of temperature, etc. are negligible. If you cannot make a quantitative estimate, please indicate whether the yield will be:
a) the same (85\%);
b) higher than $85 \%$;
c) lower than $85 \%$.
${ }^{1} \mathrm{H}$ NMR spectra of compounds $\mathbf{A}, \mathbf{B}, \mathbf{C}$ look very similar and each shows singlet, triplet and quartet with the ratio of integral intensities equal to 1:3:2.

The same mixture $\mathbf{X}$ was subjected to alkaline hydrolysis. A remained unchanged, and was separated. The remaining solution after acidification and short boiling gave 2:3 (molar ratio) mixture of acetic acid and ethanol with evolution of gas.

The mixture $\mathbf{X}(3.92 \mathrm{~g})$ was dissolved in diethyl ether and underwent hydrogenation in the presence of Pd on charcoal catalyst. 0.448 L (standard conditions) of hydrogen were absorbed, but after the reaction $\mathbf{A}$ and $\mathbf{C}$ were isolated unchanged ( 3.22 g
of mixture were recovered) while neither $\mathbf{B}$, nor any other organic compounds except diethyl ether could be identified after hydrogenation.
5.2.1 Determine and draw the structures of $\boldsymbol{A}, \boldsymbol{B}$, and $\boldsymbol{C}$.
5.2.2 Which intermediate compounds are formed during the acidic hydrolysis of $\mathbf{C}$, and basic hydrolysis of $\boldsymbol{B}$.

The reaction of either Bor $\mathbf{C}$ with acetone (in the presence of a base) with subsequent acidification by dilute HCl at gentle heating gives the same product, senecioic acid (SA), a compound widely occurring in Nature. Alternatively, senecioic acid can be obtained from acetone by treating it with concentrated HCl and subsequent oxidation of the intermediate product by iodine in alkaline solution. The latter reaction gives, besides sodium salt of senecioic acid, a heavy yellow precipitate $\mathbf{E}$ (see the scheme 2).

$$
\begin{align*}
& \text { B or } \mathbf{C} \xrightarrow[\text { 2. } \mathrm{HCl}, \mathrm{t}]{\xrightarrow{\text { 1. } \mathrm{Me}_{2} \mathrm{CO} / \text { base }}} \underset{\mathrm{C}_{5} \mathrm{H}_{8} \mathrm{O}_{2}}{\mathbf{S A}}  \tag{1}\\
& \rangle=\mathrm{O} \xrightarrow[\text { 2. } \mathrm{I}_{2}, \mathrm{NaOH}]{\text { 1. } \mathrm{HCl} \text { cat. }} \text { SA (sodium salt) }+\mathbf{E} \tag{2}
\end{align*}
$$

5.3.1 Determine the structure of senecioic acid and draw the reaction scheme leading to SA sodium salt from acetone.
5.3.2 Give the structure of $\boldsymbol{E}$.

## Problem 6. SILICATES AS THE BASE OF THE EARTH CRUST

7 points
Silica and compounds derived from it, silicates, constitute ca. 90 \% of the Earth crust substances. Silica gives rise to a beautiful material - glass. Nobody knows exactly how glass was discovered. There is a well-favored story related to Phoenician sailors who fused occasionally sea sand and soda ash. It is likely that they discovered the secret of "liquid glass" (LGL) - sodium metasilicate $\left(\mathrm{Na}_{2} \mathrm{SiO}_{3}\right)$ soluble in water.
6.1.1 The solution of LGL was used earlier as office glue. Write down the net ionic equation accounting for the ability of LGL to set in air.

Hydrolysis of LGL in water allows obtaining a colloidal solution of silicic acid.
6.1.2 Complete the Table in the Answer Sheet. Write down the net ionic equations matching the processes enumerated in the Table. For each process check the "Yes" box if it leads to changes of pH. Otherwise check the "No" box.

The structure of species occurring in aqueous solutions of silicates is rather complex. However, it is possible to distinguish the main building block of all species - orthosilicate tetrahedron $\left(\mathrm{SiO}_{4}{ }^{4-}, \mathbf{1}\right)$ :


For $\left[\mathrm{Si}_{3} \mathrm{O}_{9}\right]^{n-}$ ion found in aqueous solution of silicates:
6.2.1 Determine the charge (n).
6.2.2 Determine the number of oxygen atoms bridging adjacent tetrahedra.
6.2.3 Depict its structure joining together several tetrahedra (1). Take into account that any adjacent tetrahedron shares one vertex.

Charged monolayers with the composition $\left[\mathrm{Si}_{4} \mathrm{O}_{10}\right]^{m-}$ are found in kaolinite (clay).
6.2.4 Using the same strategy as in 6.2.1-6.2.3, depict a fragment of the layered structure joining 16 tetrahedra (1). Note that 10 tetrahedra have shared vertices with 2 neighbors each, and the rest 6 have shared vertices with 3 neighbors each.

Being placed into the LGL solution, salts of transition metals give rise to fancy "trees" tinted relevant to the color of the salt of the corresponding transition metal. Crystals of $\mathrm{CuSO}_{4} \cdot 5 \mathrm{H}_{2} \mathrm{O}$ produce "trees" of blue color, whereas those of $\mathrm{NiSO}_{4} \cdot 7 \mathrm{H}_{2} \mathrm{O}$ form green "trees".
6.3.1 Determine the pH of 0.1 M aqueous solution of copper sulfate at $25^{\circ} \mathrm{C}$, assuming that its hydrolysis occurs in small degree only. Use the value of the first acidity constant of $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}\right]^{2+} \mathrm{K}_{a}{ }^{1}=1 \cdot 10^{-7} \mathrm{M}$.
6.3.2 Write down equation of a reaction between aqueous solutions of $\mathrm{CuSO}_{4}$ and sodium metasilicate (LGL). Take into account the pH values of aqueous solutions of the salts.

## Problem 7. ATHEROSCLEROSIS AND INTERMEDIATES OF CHOLESTEROL BIOSYNTHESIS

7.5 points

Cholesterol is a lipid wide-spread in living nature. Disruption of its metabolism leads to atherosclerosis and related potentially fatal diseases.

Substances $\mathbf{X}$ and $\mathbf{Y}$ are two key intermediates of cholesterol biosynthesis in animals. $\mathbf{X}$ is an optically active monocarbonic acid composed of atoms of only three elements. It is formed in organisms from (S)-3-hydroxy-3-methylpentanedioylcoenzyme A (HMG-CoA). This reaction is catalyzed by enzyme E1 (which catalyses two types of reactions) and does not involve water as a substrate. $\mathbf{X}$ is further metabolized into $\mathbf{X 1}$ through a three-stage process requiring enzymes E2, E3, E4, which catalyze reactions of one and the same (and only one) type. Finally, X1 spontaneously (non-enzymatically) decomposes to give isopentenyl pyrophosphate (3-methylbut-3-enyl diphosphate, IPP) and inorganic products:

7.1.1 In the Answer Sheet, choose the reaction type(s) for E1 and E3.
7.1.2 Draw the structure of $\boldsymbol{X}$ with stereochemical details and indicate absolute configuration (R or S) of the stereocenter.
$\mathbf{Y}$ is an unsaturated acyclic hydrocarbon. Its reductive ozonolysis leads to a mixture of only three organic substances Y1, Y2 and Y3 in a molar ratio of 2:4:1. $\mathbf{Y}$ is formed as a result of a number of successive coupling reactions of two isomeric substances: IPP and dimethyl allyl pyrophosphate (3-methylbut-2-enyl diphosphate, DAP) with subsequent reduction of a double bond in the final coupling product Y5. Carbon atoms IPP and DAP involved in the formation of $\mathrm{C}-\mathrm{C}$ bonds during biosynthesis of $\mathbf{Y}$ are marked with asterisks.

7.2.1 Write down the overall reaction equation for reductive ozonolysis of DAP, if dimethyl sulfide is used as the reducing agent.

The product of the final coupling reaction (hydrocarbon $\mathbf{Y} 5$ ) is formed when two hydrocarbon residues $(\mathrm{R})$ of intermediate Y 4 are combined:


At each coupling stage but that shown in Scheme 2, pyrophosphate is released in a molar ratio of $1: 1$ to the coupling product.
7.2.2 Determine molecular formula of $\boldsymbol{Y}$, if it is known that $\boldsymbol{Y} 2$ and $\boldsymbol{Y} \mathbf{3}$ contain 5 and 4 carbon atoms, respectively.
7.2.3 Calculate the number of IPP and DAP molecules needed to give $Y 5$, if it is known that all carbon atoms of isomeric pyrophosphates are incorporated into $\boldsymbol{Y}$.
7.2.4 Draw the product of coupling reaction of one IPP molecule with one DAP molecule ( $C-C$ bond can be formed only by carbon atoms marked with asterisks), if it is known that subsequent reductive ozonolysis of the product of the coupling reaction gives Y1, Y2 and one more product, the latter containing phosphorus.

The only double bond reduced in $\mathbf{Y} 5$ during its metabolism into $\mathbf{Y}$ was formed in the reaction described in Scheme 2. All double bonds in $\mathbf{Y}$ and $\mathbf{Y 4}$ exist in trans configuration.
7.2.5 Draw the structures of $\boldsymbol{Y}$ and $\boldsymbol{Y} 4$ with stereochemical details.

## Problem 8. ATRP ALLOWS NEW POLYMERS

ATRP (Atom Transfer Radical Polymerization) is one of the most promising novel approaches towards polymer synthesis. This modification of radical polymerization is based on a redox reaction of organic halides with complexes of transition metals, Cu $(\mathrm{I})$ in particular. The process can be described by the following scheme ( M - monomer, Hal - halogen):



The reaction rate constants are: $k_{\text {act }}$ - all activation reactions, $k_{\text {deact }}-$ all reversible deactivation reactions, $k_{p}$ - chain propagation, and $k_{t}$-irreversible termination.
8.1.1 Write down the expressions for the rates of ATRP elementary stages: activation $\left(v_{\text {act }}\right)$, deactivation $\left(v_{\text {deact }}\right)$, propagation $\left(v_{p}\right)$ and termination $\left(v_{t}\right)$. Write down generalized equation assuming just one reacting species $R^{\prime} X$, where $R^{\prime}$ means any of $R$ or $R-M_{n}-$ and $X$ means Hal.

Consider that the total number of polymeric chains is equal to that of initiator molecules. Assume that at each moment throughout polymerization all chains are of the same length.

### 8.1.2 Compare the rate of deactivation to the rates of ATRP elementary stages.

Dependence of monomer concentration $([M])$ on reaction time $(t)$ for ATRP is:

$$
\ln \left(\frac{[M]}{[M]_{0}}\right)=-k_{p} \cdot\left[R^{\cdot}\right] \cdot t,
$$

[ $M]_{0}$ - the initial monomer concentration, $k_{p}$ - the rate constant of propagation, $[R]$ the concentration of active radicals.

To prepare a polymer sample by using ATRP, catalytic amounts of CuCl , organic ligand (L) and 31.0 mmol of monomer (methylmethacrylate, or MMA) were mixed. The reaction was initiated by adding 0.12 mmol of tosyl chloride (TsCl). Polymerization was conducted for $1400 \mathrm{~s} . k_{\mathrm{p}}$ is $1616 \mathrm{~L} \cdot \mathrm{~mol}^{-1} \mathrm{~s}^{-1}$, and the steady state concentration of radicals is $1.76 \cdot 10^{-7} \mathrm{~mol} \cdot \mathrm{~L}^{-1}$.


MMA


TsCl


HEMA-TMS
8.2.1 Calculate the mass $(m)$ of the polymer obtained.

In another experiment the time of MMA polymerization was changed, all the rest reaction conditions being the same. The mass of the obtained polymer was 0.73 g . Then 2-(trimethylsilyloxy)ethyl methacrylate, HEMA-TMS ( 23.7 mmol ) was added to the mixture and polymerization was continued for another 1295 s . MMA and HEMATMS reactivities are the same under reaction conditions.
8.2.2 Calculate the degree of polymerization (DP) of the obtained polymer.
8.2.3 Depict the structure of the obtained polymer (including end groups), showing MMA and HEMA-TMS units as A and B, respectively. If necessary, use the symbols in the copolymer structure representation: block (block), stat (statistical), alt (alternating), grad (gradient), graft (grafted). For example, ( $A_{65}-g r a f t-C_{100}$ )-stat- $B_{34}$ means that chains of polymer $C$ are grafted on units $A$ in the statistic copolymer of $A$ and $B$.

ATRP was applied to synthesize two block copolymers, P1 and P2. One block in both block-copolymers was the same and was synthesized from mono-(2-chloropropionyl)-polyethylene oxide used as a macroinitiator:


The other block in P1 consisted of styrene (C), and in P2 of p-chloromethylstyrene (D) units.
${ }^{1} \mathrm{H}$ NMR spectra of the macroinitiator, P1 and P2 are given below. Integral intensities of characteristic signals can be found in the table.

### 8.3.1 Assign ${ }^{1} H$ NMR signals to the substructures given in the Answer Sheet.

8.3.2 Determine the molar fractions of units $C$ and $D$ and the molecular masses of P1 and P2.
8.3.3 Write down all possible reactions of activation occurring during the synthesis of P1 and P2. You may use $R$ symbol to depict any unchanged part of the macromolecule, but you should specify what substructure you use it for.
8.3.4 Draw the structure of P1 and one of possible structures of P2 representing poly(ethylene oxide) chain by a wavy line and showing units of co-monomers as $C$ and $D$, respectively.


## ANSWER SHEETS, SOLUTIONS, AND GRADING SCHEMES

## PRACTICAL PROBLEMS

Problem 1. ION-EXCHANGE CHROMATOGRAPHY OF AMINO ACIDS

| Question | 1 a | 1 b | 1 c | $2-3$ | 4 | Total | Points |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Marks | 9 | 0 | 3 | 72 | 2 | 86 | 20 |

Number of the given mixture of amino acids $\qquad$ (A number between 301 and 600)
1.1a Draw the profile of coloration intensity on the plate sketch.
1.1b Indicate changes of eluents by drawing lines between the corresponding wells.

|  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| A | $\bigcirc$ | $\bigcirc$ | $\bigcirc$ | $\bigcirc$ | $\bigcirc$ | $\bigcirc$ | $\bigcirc$ |  | C | ) |  |  |
| B |  | $\bigcirc$ |  | $\bigcirc$ | ) | $J$ | $\bigcirc$ |  |  |  |  |  |
| c |  | ) |  | ) | $\bigcirc$ | $0$ | $\bigcirc$ |  |  |  |  |  |
| D | $0$ | $\bigcirc$ |  | ) | $\bigcirc$ | $1$ | $\bigcirc$ |  |  |  |  |  |
| E |  | $0$ | ) | ) |  |  |  |  |  |  |  |  |
| F |  | $)$ | ) |  |  |  |  |  |  |  |  |  |
| G |  | $\bigcirc$ |  | $\bigcirc$ |  |  |  |  |  |  |  |  |
| H | $0$ | $\Omega$ |  |  |  |  |  |  |  |  |  |  |

1.1c Labels of wells corresponding to the chosen fractions.

| Peak number | Labels of wells |
| :---: | :--- |
| 1 |  |
| 2 |  |
| 3 |  |

1.2-1.3 Content (in mg ) of each amino acid in the amino acid mixture you were given.
$\qquad$

Complete the table.

| Peak <br> number | Volume of <br> combined <br> fractions, $m L$ | Amino acid <br> (3-letter <br> code) | Wavelength <br> $\lambda, n m$ | Absorbance <br> $\mathrm{A}_{\lambda}$ | Amino acid mass <br> in the given mix- <br> ture, $m g$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 |  |  |  |  |  |
| 2 |  |  |  |  |  |
| 3 |  |  |  |  |  |

ATTENTION. The print-offs with the spectra of your samples should be put into the envelope and delivered at the end of examination alongside with the Answer Sheets.
1.4 Resonance structures of the substance responsible for the mixture coloration.

## Solution and grading scheme

1.1a 3 marks for each peak if at least two blank wells between peaks 9 marks maximum.
1.1b Not graded.
1.1.c 1 point for each proper choice. Combined mixtures should include all fractions identified as " 2 " and " 3 " and should be free of fractions without amino acids. Fractions identified as " 1 " may be or may be not included.

3 marks maximum.

## 1.2-1.3

Content of an amino acid $=\frac{A_{\lambda} \cdot n \cdot V \cdot M_{W}}{\varepsilon \cdot l}$,
$A_{\lambda}$ is the absorbance of the sample calculated from the spectra, I is the optical length $(1.0 \mathrm{~cm}), n$ is the dilution factor determined as a ratio of the aliquot of analyzing solution ( 0.1 mL ) and the final volume of the sample in the cuvette, $V$ is the volume of the combined fraction from the corresponding peak, and $M_{w}$ is the molar mass of the amino acid.
3 marks for correct formula,
3 marks for correct determination of optical densities (1 mark for each assay)
1 mark penalty for miscalculation.

Content of each amino acid is determined by using the following plot (values recalculated from volumes reported by students and absorbance values recorded by spectrophotometer)


Scoring:
$m<\min m_{\mathrm{acc}}$ OR $m>\max m_{\mathrm{acc}}$
$\min m_{\text {acc }}<m<\min m_{\text {exp }}$
$\min m_{\text {exp }}<m<\max m_{\text {acc }}$

0 marks
$P_{\max } \frac{\left(m-\min m_{\text {acc }}\right)}{\left(\min m_{\text {exp }}-\min m_{\text {acc }}\right)}$ marks
$P_{\text {max }}$ marks

| Amino acid | Min <br> $m_{\text {acc }} / m_{\text {exact }}$ <br> $\cdot 100 \%$ | Min <br> $m_{\text {exp }} / m_{\text {exact }}$ <br> $\cdot 100 \%$ | Max <br> $m_{\text {exp }} / m_{\text {exact }}$ <br> $\cdot 100 \%$ | Max <br> $m_{\text {acd }} / m_{\text {exact }}$ <br> $\cdot 100 \%$ | $P_{\text {max }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Cys | $70 \%$ | $85 \%$ | $110 \%$ | $115 \%$ | 22 |
| His | $60 \%$ | $85 \%$ | $110 \%$ | $115 \%$ | 22 |
| Arg | $25 \%$ | $45 \%$ | $65 \%$ | $85 \%$ | 22 |

## 72 marks maximum

1.4 As it is given in the task text, mixed disulfide and 2-thio-5-nitrobenzoic acid are formed in the reaction.


Under slightly alkaline conditions, thiol group of (II) dissociates, and thiophenolateanion is formed. Resonance structures can be realized for this compound:


The electronic structure of asymmetrical disulfide (I) does not differ considerably from that of the original Ellmann reagent. Therefore, it can be concluded that the compound responsible for coloration is thiophenolate-anion (a form containing $\mathrm{C}=\mathrm{S}$ bond).

2 marks for three correct ionized structures, one of which contains $\mathrm{C}=\mathrm{S}$ bond 1 mark for three other structures, all without $\mathrm{C}=\mathrm{S}$ bond

1 mark for less than three structures, one of which contains $\mathrm{C}=\mathrm{S}$ bond.
2 marks maximum.

## Problem 2. DETERMINATION OF CARBONATE AND HYDROGEN PHOSPHATE IN AN ABRASIVE SAMPLE

| Question | 1 a | 1 b | 2 | 3 | 4 | 5 | 6 a | 6 b | Total | Points |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Marks | 25 | 5 | 25 | 25 | 5 | 5 | 1 | 9 | 100 | $\mathbf{2 0}$ |

2.1a Standardization of NaOH solution

| Titration No | Initial burette reading, <br> mL | Final burette reading, <br> mL | Volume of NaOH solu- <br> tion consumed $\left(V_{1}\right), \mathrm{mL}$ |
| :---: | :--- | :--- | :--- |
| 1 |  |  |  |
| 2 |  |  |  |
| 3 |  |  |  |
|  |  |  |  |
| Final volume of NaOH solution $\left(V_{1, \mathrm{f}}\right), \mathrm{mL}$ |  |  |  |

## 2.1b Calculation of NaOH concentration

Your work $\quad c(\mathrm{NaOH})=\ldots \mathrm{mol} / \mathrm{L}$

### 2.2 The first titration of the sample (BCG)

| Titration No | Initial burette reading, <br> mL | Final burette reading, <br> mL | Volume of NaOH solution <br> consumed $\left(V_{2}\right), \mathrm{mL}$ |
| :---: | :--- | :--- | :--- |
| 1 |  |  |  |
| 2 |  |  |  |
| 3 |  |  |  |
|  |  |  |  |
| Final volume of NaOH solution $\left(V_{2, f}\right), \mathrm{mL}$ |  |  |  |

2.3 The second titration of the sample (TP)

| Titration No | Initial burette reading, <br> mL | Final burette reading, <br> mL | Volume of NaOH solution <br> consumed $\left(V_{3}\right), \mathrm{mL}$ |
| :---: | :--- | :--- | :--- |
| 1 |  |  |  |
| 2 |  |  |  |
| 3 |  |  |  |
|  |  |  |  |
| Final volume of NaOH solution $\left(V_{3, \mathrm{f}}\right), \mathrm{mL}$ |  |  |  |

2.4 Calculation of the mass of $\mathrm{CO}_{3}{ }^{2-}$

Your work

$$
m\left(\mathrm{CO}_{3}{ }^{2-}\right)=
$$

$\qquad$

### 2.5 Calculation of the mass of $\mathrm{HPO}_{4}{ }^{2-}$

Your work

$$
m\left(\mathrm{HPO}_{4}^{2-}\right)=
$$

$\qquad$

## Additional questions

2.6a Indicate one reaction (write down the equation) for a process interfering in the sample analysis you have carried out in the presence of $\mathrm{Ca}^{2+}$.
2.6b A list of mistakes possible at different steps is given in the table. Indicate which of the mistakes can lead to errors in $\mathrm{CO}_{3}{ }^{2-}$ and/or $\mathrm{HPO}_{4}{ }^{2-}$ content determination. Use the following symbols: " 0 " if no error is expected, "+"or "-" if the result is higher (positive error) or lower (negative error) than the true one.

| Mistake | Step | Error |  |
| :--- | :---: | :---: | :---: |
|  |  | $\mathrm{CO}_{3}{ }^{2-}$ content | $\mathrm{HPO}_{4}{ }^{2-}$ <br> content |
| Incomplete removal of $\mathrm{CO}_{2}$ | 1 |  |  |
| Too large excess of $\mathrm{K}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$ on calcium precipi- <br> tation | 2 |  |  |
| Too late indication of the endpoint (overtitration) <br> on NaOH standardization | 3 |  |  |
| Insufficient washing of the filter at $\mathrm{CaC}_{2} \mathrm{O}_{4}$ filtra- <br> tion | 4 |  |  |
| Overtitration of the sample against BCG | 5 |  |  |
| Overtitration of the sample against TP | 6 |  |  |

$\mathrm{H}_{2} \mathrm{CO}_{3}: \quad \mathrm{p} K_{\mathrm{a} 1}=6.35 ; \quad \mathrm{p} K_{\mathrm{a} 2}=10.32$
$\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}: \quad \mathrm{p} K_{\mathrm{a} 1}=1.25 ; \quad \mathrm{p} K_{\mathrm{a} 2}=4.27$

Extra samples given or column broken

| Problem No | Sample No | Column broken <br> and replaced | Student's <br> signature | Lab assistant's <br> signature |
| :--- | :--- | :--- | :--- | :---: |
|  |  |  |  |  |
|  |  |  |  |  |

## Solution and grading scheme

2.1a, 2.2, 2.3 The values of the final volumes $V_{1, \mathrm{f}}, V_{2, \mathrm{f}}$, and $V_{3, \mathrm{f}}$, (as reported in the Answer Sheet) are graded according to the following scheme:

$$
\Delta V=\left|V_{\text {reported }}-V_{\text {true }}\right|,
$$

$V_{\text {reported }}$ is either $V_{1, \mathrm{f}}, V_{2, \mathrm{f}}$, and $V_{3, \mathrm{f}}, V_{\text {true }}$ is the corresponding master value (will be given with the copies of students' works).

| Value of $\Delta V$ | Marks |
| :---: | :---: |
| $\Delta V \leq \Delta V_{\text {expected }}$ | 25 |
| $\Delta V \geq \Delta V_{\text {acceptable }}$ | 0 |
| $\Delta V_{\text {expected }} \leq \Delta V \leq \Delta V_{\text {acceptable }}$ | $25 \times\left(\frac{\Delta V_{\text {acceptable }}-\Delta V}{\Delta V_{\text {acceppable }}-\Delta V_{\text {expected }}}\right)$ |

The values of $\Delta V_{\text {expected }}$ and $\Delta V_{\text {acceptable }}$ (in mL ) are listed in the table below.

|  | $\Delta V, \mathrm{~mL}$ |  |
| :---: | :---: | :---: |
|  | expected | acceptable |
| $V_{1, \mathrm{f}}$ | $\mathbf{0 . 1 0}$ | $\mathbf{0 . 2 5}$ |
| $V_{2, f}$ | $\mathbf{0 . 1 5}$ | $\mathbf{0 . 4 0}$ |
| $V_{3, f}$ | $\mathbf{0 . 1 5}$ | $\mathbf{0 . 4 0}$ |

## 25 marks maximum for each titration

## 2.1b Calculation of NaOH concentration

$c(\mathrm{NaOH})=\frac{c(\mathrm{HCl}) \times V(\mathrm{HCl}) \times V(\text { aliquot })}{V(\text { flask }) \times V(\mathrm{NaOH})}=\frac{1.214(\mathrm{~mol} / \mathrm{L}) \times 10.00(\mathrm{~mL}) \times 10.00(\mathrm{~mL})}{100.0(\mathrm{~mL}) \times V_{1, f}(\mathrm{~mL})}=$

### 2.4 Calculation of the mass of $\mathrm{CO}_{3}{ }^{2-}$

$$
\begin{aligned}
& m\left(\mathrm{CO}_{3}{ }^{2-}\right)(g)=M\left(\mathrm{CO}_{3}{ }^{2-}\right) \times 1 / 2 \times \frac{c(\mathrm{NaOH}) \times\left(V_{1, f}-V_{3, f}\right) \times V(\text { flask })}{V(\text { aliquot })}= \\
& =60.01(\mathrm{~g} / \mathrm{mol}) \times 1 / 2 \times \frac{c(\mathrm{NaOH})(\mathrm{mol} / \mathrm{L}) \times\left(V_{1, f}-V_{3, f}\right)(\mathrm{mL}) \times 100.0(\mathrm{~mL})}{10.00(\mathrm{~mL})} \times 0.001(\mathrm{~L} / \mathrm{mL})=
\end{aligned}
$$

### 2.5 Calculation of the mass of $\mathrm{HPO}_{4}{ }^{2-}$

$$
\begin{aligned}
& m\left(\mathrm{HPO}_{4}{ }^{2-}\right)(g)=M\left(\mathrm{HPO}_{4}{ }^{2-}\right) \times \frac{c(\mathrm{NaOH}) \times\left(V_{3, f}-V_{2, f}\right) \times V(\text { flask })}{V(\text { aliquot })}= \\
& =95.98(\mathrm{~g} / \mathrm{mol}) \times \frac{c(\mathrm{NaOH})(\mathrm{mol} / \mathrm{L}) \times\left(V_{3, f}-V_{2, f}\right)(\mathrm{mL}) \times 100.0(\mathrm{~mL})}{10.00(\mathrm{~mL})} \times 0.001(\mathrm{~L} / \mathrm{mL})=
\end{aligned}
$$

## 2.1b, 2.4, 2.5

Correctness of calculations is graded by:

1) comparing the numerical result (including the number of significant figures) reported by a student with that obtained from the student's data using correct method of calculation;
2) checking out the a student's way of calculation.

## 5 marks maximum for completely correct calculation of each value

Penalty for errors in calculations or data presentation.

|  | Error type | Penalty marks (for cal- <br> culation of each value) |
| :--- | :--- | :---: |
| 1 | Incorrect method of calculation | -5 |
| 2 | Mistakes in dilution factor | -1 |
| 3 | Confusion between units of measurement | -1 |
| 4 | Mistake in stoichiometric (equivalency) relationships | -1 |
| 5 | More or less than 4 significant figures in $c(\mathrm{NaOH})$ | $-0.5^{*}$ |
| 6 | More than 4 or less than 3 significant figures in <br> $m\left(\mathrm{CO}_{3}{ }^{2-}\right)$ and $m\left(\mathrm{HPO}_{4}{ }^{2-}\right)$ | $-0.5^{*}$ |
| 7 | Rounding errors affecting the $1^{\text {st }}$ or $2^{\text {nd }}$ significant fig- <br> ures in the final result | $-0.5^{* *}$ |
| 8 | Miscalculations and slips | -0.2 per error |

*Only the number of significant figures in the final answer is taken into account.
${ }^{* *}$ Not applied if the error originates from insufficient number of significant figures in previously calculated $c(\mathrm{NaOH})$. No double penalty!

## 2.6a

$$
\mathrm{Ca}^{2+}+\mathrm{H}_{2} \mathrm{PO}_{4}^{-} \rightarrow \mathrm{CaHPO}_{4}+\mathrm{H}^{+}
$$

or

$$
3 \mathrm{Ca}^{2+}+2 \mathrm{HPO}_{4}^{2-} \rightarrow \mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right)_{2}+2 \mathrm{H}^{+}
$$

In course of these processes free protons evolve influencing the results of titration.
1 mark if the Answer Sheet contains at least one correct reaction equation. Incorrect equations are not penalized.
2.6b

| Mistake | Error |  |
| :---: | :---: | :---: |
|  | $\begin{aligned} & \mathrm{CO}_{3}{ }^{2-} \\ & \text { content } \end{aligned}$ | $\begin{aligned} & \mathrm{HPO}_{4}{ }^{2-} \\ & \text { content } \end{aligned}$ |
| Below pH 4.5 (first endpoint, $\mathrm{V}_{2}$ ) $\mathrm{H}_{2} \mathrm{CO}_{3}$ is not titrated Between pH 4.5 and 10 (second endpoint, $\mathrm{V}_{3}$ ) $\mathrm{H}_{2} \mathrm{CO}_{3}$ is titrated <br> Thus, increase of $V_{3} ; V_{1}$ and $V_{2}$ unchanged | - | + |
| No influence, $\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}$ is too weak base | 0 | 0 |
| Increase of $\boldsymbol{V}_{\mathbf{1}}$ and proportional decrease of $\boldsymbol{c}(\mathbf{N a O H})$ [as $c(\mathrm{NaOH}) V_{1}$ is equivalent to the initial amount of standard HCl and so remains constant]; $\boldsymbol{V}_{2}$ and $\boldsymbol{V}_{3}$ unchanged | - | - |
| Losses of sample leads to proportional decrease of $\boldsymbol{V}_{\mathbf{2}}$ and $V_{3}$ and therefore $V_{3}-V_{2} ; V_{1}$ unchanged | + | - |
| Increase of $V_{2}, V_{1}$ and $V_{3}$ unchanged | 0 | - |
| Increase of $V_{3}, V_{1}$ and $V_{2}$ unchanged | - | + |

## THEORETICAL PROBLEMS

## Problem 1. PROTON TUNNELING

| Question | 1.1 | 1.2 | 2.1 | 3.1 | 3.2 | 3.3 | 3.4 | Total | Points |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Marks | 3 | 3 | 2 | 4.5 | 2 | 4 | 6 | 24.5 | 7 |

1.1.1 Structures:

| Propanedial |
| :--- |
| $1^{\text {st }}$ isomer |
| $2^{\text {nd }}$ isomer |

1.1.2 Circle the acidic hydrogen atom


The acidity of propanedial is caused by
a) the stability of a carbanion due to conjugation with two carbonyl groups
b) weakness of $\mathrm{C}-\mathrm{H}$ bond in a carbonyl group
c) hydrogen bonds between two propanedial molecules

The correct answer $\qquad$
1.2.1 The structures corresponding to minima on energy curve:
$\square$
1.3.1 The probability density
(a) $t=0$
$\Psi^{2}(x, 0)=$

(b) $t=\pi /(2 \omega)$
$\Psi^{2}\left(x, \frac{\pi}{2 \omega}\right)=$

(c) $t=\pi / \omega$
$\Psi^{2}\left(x, \frac{\pi}{\omega}\right)=$


### 1.3.2

The probability of finding the proton in the left well = $\qquad$
1.3.3 The time of proton transfer

Your work:
$t=$

The proton mean speed
You
$v=$
1.3.4 The uncertainty of proton position
$\Delta x=$

The minimal uncertainty of proton velocity
Your work:
$\Delta v=$
a) Proton is a rather heavy particle, and its tunneling in malonaldehyde can be described in classical terms of position and velocity
b) Proton tunneling is a purely quantum effect; it cannot be described in classical terms
c) Uncertainty of proton velocity is so large that tunneling cannot be observed experimentally
d) Uncertainty of proton velocity is so small that tunneling cannot be observed experimentally

The correct answer is $\qquad$

## Solution and grading scheme

1.1.1 The structures of propanedial and two of its isomers
$\mathrm{O}=\mathrm{CH}-\mathrm{CH}_{2}-\mathrm{CH}=\mathrm{O}$
1 mark


1 mark


1 mark
3 marks maximum

### 1.1.2

Acidic hydrogen atom is in $\mathrm{CH}_{2}$ (in enol forms acidic hydrogen is in OH ).
1 mark
Acidity of $\mathrm{CH}_{2}$ group is caused by the stability of carbanion due to conjugation with two carbonyl groups. The first answer is correct.

## 2 marks

3 marks maximum
1.2.1 The distance between two minima on the energy curve is 0.06 nm . In a purely aldehyde form

such distance between two possible positions of proton is impossible. Tunneling takes place only in enol Z-form:



1 mark for each structure
2 marks maximum
1.3.1 Expressions and plots of probability density
(a) $\Psi^{2}(x, 0)=\frac{1}{2}\left[\Psi_{\mathrm{L}}^{2}(x)+\Psi_{\mathrm{R}}^{2}(x)+\Psi_{\mathrm{L}}^{2}(x)-\Psi_{\mathrm{R}}^{2}(x)\right]=\Psi_{\mathrm{L}}^{2}(x) \quad 1$ mark

The probability density is concentrated in the left well:

0.5 marks
(b) In the middle of the time interval

$$
\Psi^{2}\left(x, \frac{\pi}{2 \omega}\right)=\frac{1}{2}\left[\Psi_{\mathrm{L}}^{2}(x)+\Psi_{\mathrm{R}}^{2}(x)\right]
$$

1 mark

The probability density has a symmetric form, a proton is delocalized between two wells:

0.5 marks
(c) $\Psi^{2}\left(x, \frac{\pi}{\omega}\right)=\frac{1}{2}\left[\Psi_{\mathrm{L}}^{2}(x)+\Psi_{\mathrm{R}}^{2}(x)-\Psi_{\mathrm{L}}^{2}(x)+\Psi_{\mathrm{R}}^{2}(x)\right]=\Psi_{\mathrm{R}}^{2}(x) \quad 1$ mark

The probability density is concentrated in the right well:

0.5 marks
4.5 marks maximum
1.3.2 The probability of finding the proton in the left well is $1 / 2$, because probability function is symmetric, and both wells are identical.

## 2 marks

1.3.3 The time of transfer from one well to another is $t=\pi / \omega$.

$$
t=\frac{3.14}{6.48 \cdot 10^{11}}=4.85 \cdot 10^{-12} \mathrm{~s} . \quad 2 \text { marks }
$$

The proton velocity:

$$
V=\frac{0.06 \cdot 10^{-9}}{4.85 \cdot 10^{-12}}=12 \mathrm{~m} / \mathrm{s} . \quad 2 \text { marks }
$$

4 marks maximum
1.3.4 The uncertainty of proton position is approximately equal to half of the distance between minima, that is 0.03 nm ( 0.06 nm was also accepted).

1 mark
The minimal uncertainty of velocity can be obtained from the uncertainty relation:

$$
\Delta V=\frac{\hbar}{2 m \Delta x}=\frac{1.055 \cdot 10^{-34}}{2 \cdot \frac{0.001}{6.02 \cdot 10^{23}} \cdot 0.03 \cdot 10^{-9}} \approx 1000 \mathrm{~m} / \mathrm{s} . \quad 3 \text { marks }
$$

Comparing this uncertainty with the velocity $12 \mathrm{~m} / \mathrm{s}$ we see that the notion of proton velocity during transfer from one well to another is senseless. Therefore, proton tunneling is a purely quantum phenomenon and cannot be described in classical terms. The second conclusion is correct.

## Problem 2. NANOCHEMISTRY

| Question | 1.1 | 1.2 | 2.1 | 2.2 | 3.1 | 3.2 | 3.3 | 3.4 | 3.5 | Total | Points |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Marks | 1 | 2 | 4 | 2 | 1 | 5 | 2 | 3 | 2 | 22 | 8 |

2.1.1 Thermodynamic data for the reaction (1):

Your work:
$\Delta_{r} G^{0}(1)=$
$K=$
2.1.2 Equilibrium constant for the reaction (1) with cobalt nanoparticles:

Your work:
(a) $K\left(r=10^{-8} \mathrm{~m}\right)=$
(b) $K\left(r=10^{-9} \mathrm{~m}\right)=$
2.2.1 Minimum water content in the mixture:

Your work:
(a) $\mathrm{H}_{2} \mathrm{O} \%$ (bulk Co) $=$
(b) $\mathrm{H}_{2} \mathrm{O} \%\left(\right.$ nanoparticles with $\left.r=1 \cdot 10^{-9} \mathrm{~m}\right)=$
2.2.2 The correct answer is (mark the proper box):
(a) $\qquad$
(b)

(c) $\square$
2.3.1 Standard molar Gibbs function of CoO (external layer)
$G^{0}\left(\mathrm{CoO}, r_{\mathrm{b}}\right)=$
2.3.2 Standard molar Gibbs function of Co (internal layer):
$G^{0}\left(\mathrm{Co}, r_{\mathrm{a}}, r_{\mathrm{b}}\right)=$
2.3.3 Standard Gibbs energy for the reaction (1) with the double-layered nanoparticles
$\Delta_{\mathrm{r}} G^{0}\left(1, r_{\mathrm{a}}, r_{\mathrm{b}}\right)=$
2.3.4. Plot $\Delta_{r} G^{0}\left(1, r_{0}\right)$ vs. $r_{0}$





The correct plot is (mark the proper box):
(a) $\square$
(b) $\square$
(c) $\square$
(d) $\square$
2.3.5 The correct answer is (mark the proper box):
(a) $\square$
(b) $\square$
(c) $\square$

## Solution and grading scheme

2.1.1 The Gibbs energy and the equilibrium constant of reaction (1)

$$
\Delta_{r} G_{500}^{0}(1)=\Delta G_{f, 500}^{0}(\mathrm{CoO}, \mathrm{~s})-\Delta G_{f, 500}^{0}\left(\mathrm{H}_{2} \mathrm{O}, \mathrm{~g}\right)=-198.4+219.1=20.7 \mathrm{~kJ} / \mathrm{mol} \quad 0.5
$$

marks

$$
K=e^{-\frac{\Delta_{1}, G_{S 0}^{0}(1)}{R T}}=e^{-\frac{20700}{8.314 .500}}=6.88 \cdot 10^{-3}
$$

marks
1 mark maximum
2.1.2 The standard Gibbs energy of the reaction (1) with the spherical cobalt nanoparticles of radius $r_{a}$ is

$$
\begin{aligned}
& \Delta_{r} G_{500}^{0}\left(1, r_{a}\right)=G_{b u l k, 500}^{0}(\mathrm{CoO}, \mathrm{~s})+G_{500}^{0}\left(\mathrm{H}_{2}, \mathrm{~g}\right)-G_{500}^{0}\left(\mathrm{H}_{2} \mathrm{O}, \mathrm{~g}\right)-G_{s p h}^{0}(\mathrm{Co})= \\
& =G_{500}^{0}(\mathrm{CoO}, \mathrm{~s})+G_{500}^{0}\left(\mathrm{H}_{2}, \mathrm{~g}\right)-G_{500}^{0}\left(\mathrm{H}_{2} \mathrm{O}, \mathrm{gas}\right)-\left(G_{500}^{0}(\mathrm{Co}, \mathrm{~s})+\frac{2 \sigma_{\mathrm{Co-gas}} V(\mathrm{Co})}{r_{a}}\right)= \\
& =\Delta_{r} G_{500}^{0}(1)-\frac{2 \sigma_{\mathrm{Co-gas}} V(\mathrm{Co})}{r_{a}} ; \\
& \quad V(\mathrm{Co})=\frac{M_{\mathrm{C} 0}}{\rho(\mathrm{Co})}=\frac{10^{-6} \cdot 59.0}{8.90}=6.6 \cdot 10^{-6} \frac{\mathrm{~m}^{3}}{\mathrm{~mol}} ;
\end{aligned}
$$

for spherical particles with $r_{a}=10^{-8}, 10^{-9} \mathrm{~m}$ one gets, respectively

$$
\frac{2 \sigma_{\mathrm{Co-gas}} V(\mathrm{Co})}{r_{a}}=210 \text { and } 2100 \mathrm{~J} / \mathrm{mol} .
$$

$\Delta_{r} G_{500}^{\circ}\left(1, r_{a}\right)$ is equal to $20.5(\mathrm{a})$, and $18.6(\mathrm{~b}) \mathrm{kJ} / \mathrm{mol}$, respectively.
The equilibrium constant is calculated from the equation

$$
\begin{gathered}
K\left(1, r_{a}\right)=\exp \left(-\frac{\Delta_{r} G_{500}^{\circ}\left(1, r_{a}\right)}{R T}\right) ; \\
K\left(1, r_{a}\right)=7.22 \times 10^{-3} ; \quad r_{a}=10^{-8} \mathrm{~m} \quad K\left(1, r_{a}\right)=11.4 \times 10^{-3} ; \quad r_{a}=10^{-9} \mathrm{~m}
\end{gathered}
$$

2.2.1 The standard Gibbs energy for reaction (1) involving nanoparticles of cobalt is

$$
\Delta_{r} G_{500}^{\circ}\left(1, r_{a}\right)=\Delta_{r} G_{500}^{\circ}(1)-\frac{2 \sigma_{\text {cogas }}}{r_{a}} V(\mathrm{Co})
$$

$\Delta_{r} G_{500}^{\circ}(1)$ is $20.7 \mathrm{~kJ} / \mathrm{mol}$. For spherical cobalt particles with $r_{a}=1 \mathrm{~nm} \Delta_{r} G_{500}^{\circ}\left(1, r_{a}\right)$ is $18.6 \mathrm{~kJ} / \mathrm{mol}$. Solid cobalt oxide can be formed spontaneously when Gibbs energy of reaction (1) is negative. The inequality for bulk cobalt is:

$$
\Delta_{r} G(1)=\Delta_{r} G_{500}^{\circ}(1)+R T \ln \left(\frac{p\left(\mathrm{H}_{2}\right)}{p\left(\mathrm{H}_{2} \mathrm{O}\right)}\right)=\Delta_{r} G_{500}^{\circ}(1)-R T \ln \left(\frac{p\left(\mathrm{H}_{2} \mathrm{O}\right)}{p\left(\mathrm{H}_{2}\right)}\right) \leq 0
$$

and for spherical cobalt nanoparticles with $r_{a}=1 \mathrm{~nm}$ :

$$
\Delta_{r} G\left(1, r_{a}\right)=\Delta_{r} G_{500}^{\circ}\left(1, r_{a}\right)+R T \ln \left(\frac{p\left(\mathrm{H}_{2}\right)}{p\left(\mathrm{H}_{2} \mathrm{O}\right)}\right)=\Delta_{r} G_{500}^{\circ}(1)-\frac{2 \sigma_{\mathrm{Co-gas}}}{r_{a}} V(\mathrm{Co})-R T \ln \left(\frac{p\left(\mathrm{H}_{2} \mathrm{O}\right)}{p\left(\mathrm{H}_{2}\right)}\right) \leq 0
$$

The minimum ratios $\frac{p\left(\mathrm{H}_{2} \mathrm{O}\right)}{p\left(\mathrm{H}_{2}\right)}$ are $145.6(\mathrm{a})$ and $87.7(\mathrm{~b})$, respectively.
The hydrogen pressure is

$$
1 \mathrm{bar} \cdot 0.0015=1.5 \cdot 10^{-3} \mathrm{bar}
$$

The minimum pressures of water are
$1.5 \cdot 10^{-3} \cdot 145.6=0.218$ bar (a) and $1.5 \cdot 10^{-3} \cdot 87.7=0.132$ bar (b), for the bulk cobalt and for nanoparticles, respectively.

$$
\mathrm{H}_{2} \mathrm{O} \%(\text { bulk } \mathrm{Co})=21.8 \% \quad \mathrm{H}_{2} \mathrm{O} \%\left(\text { nanoparticles with } \mathrm{r}_{\mathrm{a}}=1 * 10^{-9} \mathrm{~m}\right)=
$$ $13.2 \%$.

We assume that bulk cobalt oxide is formed.
4 marks maximum
2.2.2 For the spontaneous oxidation

$$
\Delta_{r} G\left(1, r_{a}\right)=\Delta_{r} G_{500}^{\circ}(1)-\frac{2 \sigma_{\text {Co-gas }}}{r_{a}} V(\mathrm{Co})-R T \ln \left(\frac{p\left(\mathrm{H}_{2} \mathrm{O}\right)}{p\left(\mathrm{H}_{2}\right)}\right) \leq 0
$$

and

$$
\Delta_{r} G_{500}^{\circ}(1)-\frac{2 \sigma_{\mathrm{Co}-\mathrm{gas}}}{r_{a}} V(\mathrm{Co}) \leq R T \ln \left(\frac{p\left(\mathrm{H}_{2} \mathrm{O}\right)}{p\left(\mathrm{H}_{2}\right)}\right)
$$

The left hand side of the last inequality becomes more positive with the increase of $r_{a}$. At certain point the inequality will be disturbed and the spontaneous oxidation will not take place. So, to protect cobalt nanoparticles from the spontaneous oxidation in this case one has to lengthen the radius $r_{a}$. The answer (a) is correct.

2 marks maximum
2.3.1 The equation for the standard molar Gibbs function of CoO (external layer) reads:

$$
G_{s p h}^{0}\left(\mathrm{CoO}, r_{b}\right)=G_{b u l k}(\mathrm{CoO})+\frac{2 \sigma_{\mathrm{CoO}-\mathrm{gas}}}{r_{b}} V(\mathrm{CoO})=G^{\circ}(\mathrm{CoO}, \mathrm{~s})+\frac{2 \sigma_{\mathrm{CoO}-\mathrm{gas}}}{r_{b}} V(\mathrm{CoO})
$$

2.3.2 The equation for the standard molar Gibbs function of Co (internal layer) reads:

$$
\begin{aligned}
& G_{\mathrm{sph}}^{0}\left(\mathrm{Co}, r_{a}, r_{b}\right)=G_{\mathrm{bulk}}(\mathrm{Co})+V(\mathrm{Co})\left(\frac{2 \sigma_{\mathrm{CoO}-\mathrm{gas}}}{r_{b}}+\frac{2 \sigma_{\mathrm{CoO}-\mathrm{Co}}}{r_{a}}\right)= \\
& =G^{\circ}(\mathrm{Co}, \mathrm{~s})+V(\mathrm{Co})\left(\frac{2 \sigma_{\mathrm{CoO}-\mathrm{gas}}}{r_{b}}+\frac{2 \sigma_{\mathrm{CoO}-\mathrm{Co}}}{r_{a}}\right)
\end{aligned}
$$

The expression in brackets gives the additional pressure in the internal layer (see the Hint).

5 marks maximum
2.3.3 The standard Gibbs energy for reaction (1) with the double-layered nanoparticles is

$$
\begin{aligned}
& \Delta_{r} G^{0}\left(1, r_{a}, r_{b}\right)=G_{s p h}^{0}\left(\mathrm{CoO}, r_{b}\right)+G^{\circ}\left(\mathrm{H}_{2}, \text { gas }\right)-G^{\circ}\left(\mathrm{H}_{2} \mathrm{O}, \mathrm{gas}\right)-G_{s p h}^{0}\left(\text { Co, } r_{a}, r_{b}\right)= \\
& =G^{\circ}(\mathrm{CoO}, \mathrm{~s})+G^{\circ}\left(\mathrm{H}_{2}, \text { gas }\right)-G^{\circ}\left(\mathrm{H}_{2} \mathrm{O}, \mathrm{gas}\right)-G^{\circ}(\mathrm{Co}, \mathrm{~s})+ \\
& +\frac{2 \sigma_{\mathrm{CoO}-\mathrm{gas}}}{r_{b}} V(\mathrm{CoO})-2 V(\mathrm{Co})\left(\frac{\sigma_{\mathrm{CoO-gas}}}{r_{b}}+\frac{\sigma_{\mathrm{CoO-Co}}}{r_{a}}\right)= \\
& =\Delta_{r} G^{\circ}(1)+\frac{2 \sigma_{\mathrm{CoO-gas}}}{r_{b}}(V(\mathrm{CoO})-V(\mathrm{Co}))-\frac{2 \sigma_{\mathrm{CoO}-\mathrm{Co}}}{r_{a}} V(\mathrm{Co})
\end{aligned}
$$

### 2.3.4 Under the assumptions made

$$
\begin{aligned}
& \Delta_{r} G^{\circ}\left(1, r_{a}, r_{b}\right)=\Delta_{r} G^{0}\left(1, r_{0}\right)=\Delta_{r} G^{\circ}(1)+\frac{2 \sigma_{\mathrm{CoO}-\mathrm{gas}}}{r_{b}}(V(\mathrm{CoO})-V(\mathrm{Co}))-\frac{2 \sigma_{\mathrm{CoO}-\mathrm{Co}}}{r_{a}} V(\mathrm{Co})= \\
& =\Delta_{r} G^{\circ}(1)+\frac{2 \sigma_{\mathrm{CoO}-\mathrm{gas}}}{r_{0}}\left(V(\mathrm{CoO})-\frac{3}{2} V(\mathrm{Co})\right)
\end{aligned}
$$

The term in brackets in the right-hand side is positive

$$
\left(V(\mathrm{CoO})-\frac{3}{2} V(\mathrm{Co})\right)=6.56 \cdot 10^{-6} \mathrm{~m}^{3}
$$

$\Delta_{r} G^{0}\left(1, r_{0}\right)$ is directly proportional to $\left(\frac{1}{r_{0}}\right)$. The plot (a) is correct.
3 marks maximum
2.3.5. The spontaneous forward reaction (1) is possible, when $\Delta_{\mathrm{r}} G\left(1, r_{0}\right) \leq 0$, and

$$
\Delta_{r} G^{0}(1)+\frac{2 \sigma_{\mathrm{CoO}-\mathrm{gas}}}{r_{0}}\left(V(\mathrm{CoO})-\frac{3}{2} V(\mathrm{Co})\right) \leq R T \ln \frac{p_{\mathrm{H}_{2} \mathrm{O}}}{p_{\mathrm{H}_{2}}}
$$

The term in brackets in the left-hand side is positive. The left hand side of the inequality becomes more positive with the decrease of $r_{0}$. At certain point the inequality will be violated and the spontaneous oxidation will not take place.

In order to protect nanoparticles from oxidation in this case one has to shorten the radius $r_{0}$. The answer (b) is correct.

2 marks maximum

## Problem 3. UNSTABLE CHEMICAL REACTIONS

| Question | 1.1 | 1.2 | 2.1 | 2.2 | 3.1 | 4.1 | Total | Points |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Marks | 2 | 4.5 | 4 | 3 | 3 | 3 | 19.5 | 7 |

### 3.1.1 The overall reaction equation

$\square$

The kinetic equation for $X$

$$
\frac{d[\mathrm{X}]}{d t}=
$$

3.1.2 The rate equation

Your work:
$\frac{d[\mathrm{P}]}{d t}=$

Reaction orders:
with respect to $B(i)$ : $\qquad$
with respect to D (ii): $\qquad$
overall (iii): $\qquad$
3.2.1 1) An open system, $[X]_{0}>k_{2} / k_{1}$

2) An open system, $[\mathrm{X}]_{0}<k_{2} / k_{1}$

3.2.2 A closed system, $[\mathrm{B}]_{0}=[\mathrm{D}]_{0},[\mathrm{X}]_{0}>k_{2} / k_{1}$
$[\mathrm{X}]{ }^{2}$

### 3.3.1

$$
\begin{aligned}
& \mathrm{X}-\mathrm{Y}- \\
& \mathrm{Y}- \\
& \mathrm{C}_{2} \mathrm{H}_{6}+\mathrm{X}+\ldots \rightarrow 2 \mathrm{X} \\
& \mathrm{X}+\mathrm{Y} \rightarrow 2 \mathrm{Y}+\ldots \\
& \mathrm{C}_{2} \mathrm{H}_{6}+\mathrm{Y}+\ldots \rightarrow 2 \mathrm{P}
\end{aligned}
$$

3.4.1 The highest possible temperature:

Your work:
$T=$

## Solution and grading scheme

3.1.1 The overall reaction equation

$$
B+D \rightarrow P \quad 1 \text { mark }
$$

The kinetic equation for $X$

$$
\frac{d[\mathrm{X}]}{d t}=k_{1}[\mathrm{~B}][\mathrm{X}]^{2}-k_{2}[\mathrm{D}][\mathrm{X}] \quad 1 \text { mark }
$$

### 3.1.2 Under the steady-state conditions

$$
\frac{d[\mathrm{P}]}{d t}=k_{2}[\mathrm{D}][\mathrm{X}]=k_{1}[\mathrm{~B}][\mathrm{X}]^{2},
$$

whence

$$
\begin{aligned}
& {[\mathrm{X}]=\frac{k_{2}[\mathrm{D}]}{k_{1}[\mathrm{~B}]}} \\
& \frac{d[\mathrm{P}]}{d t}=\frac{k_{2}^{2}[\mathrm{D}]^{2}}{k_{1}[\mathrm{~B}]}
\end{aligned} \quad 3 \text { marks }
$$

The reaction order is 2 with respect to $D,-1$ with respect to $B$; the overall order is 1
0.5 marks for each correct order
4.5 marks maximum
3.2.1 In an open system the initial reaction rate is:

$$
\frac{d[\mathrm{X}]}{d t}=[\mathrm{B}][\mathrm{X}]\left(k_{1}[\mathrm{X}]-k_{2}\right)
$$

1) If $[\mathrm{X}]_{0}>k_{2} / k_{1}$, then $d[\mathrm{X}] / d t>0$ at any time, and the concentration of X monotonically increases:

2) If $[\mathrm{X}]_{0}<k_{2} / k_{1}$, then $d[\mathrm{X}] / d t<0$ at any time, and the concentration of X monotonically decreases. Two types of kinetic curves are possible. If $k_{2} / 2 k_{1}<[\mathrm{X}]_{0}<k_{2} / k_{1}$, the inflection point will be observed on the kinetic curve:


But if the initial concentration is too low, $[\mathrm{X}]_{0}<k_{2} / 2 k_{1}$, the concentration will monotonically decrease together with its derivative.

(any of these curves was accepted as a right answer) 2 marks

4 marks maximum
3.2.2 In a closed system the initial reaction rate is:

$$
\left.\frac{d[\mathrm{X}]}{d t}\right|_{t=0}=k_{1}[\mathrm{~B}]_{0}[\mathrm{X}]_{0}^{2}-k_{2}[\mathrm{D}]_{0}[\mathrm{X}]_{0}=[\mathrm{B}]_{0}[\mathrm{X}]_{0}\left(k_{1}[\mathrm{X}]_{0}-k_{2}\right)>0
$$

Hence, at the beginning of the reaction $[X]$ increases but it cannot increase infinitely and finally goes to its initial value, because the second reaction is irreversible:


2 marks for maximum
1 mark for the asymptotic value
3 marks maximum
3.3.1 $X-\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}_{2}, \mathrm{Y}-\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O}, \mathrm{P}-\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}$. Dots denote $\mathrm{O}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$.

$$
\begin{aligned}
& \mathrm{C}_{2} \mathrm{H}_{6}+\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}_{2} \\
& \mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}_{2}+\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O} \rightarrow 2 \mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O}+\mathrm{H}_{2} \mathrm{O} \\
& \mathrm{C}_{2} \mathrm{H}_{6}+\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O}+\mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}
\end{aligned}
$$

0.5 marks for each unknown substance ( $X, Y, P$, three blanks)

3 marks maximum
3.4.1 At the highest possible temperature the rate constants are equal:

$$
\begin{aligned}
& A_{1} \exp \left(-\frac{E_{A, 1}}{R T}\right)=A_{2} \exp \left(-\frac{E_{A, 2}}{R T}\right) \\
& T=\frac{E_{A, 2}-E_{A, 1}}{R \ln \frac{A_{2}}{A_{1}}}=354 \mathrm{~K}
\end{aligned}
$$

1 mark for the calculation
2 marks for the correct answer
3 marks maximum

## Problem 4. DETERMINATION OF WATER BY FISCHER TITRATION

| Question | 1 | 2.1 | 2.2 | 2.3 | 3 | 4.1 | 4.2 | 4.3 | Total | Points |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Marks | 1 | 1.25 | 1.75 | 2.25 | 1 | 2 | 1 | 2.25 | 12.5 | $\mathbf{8}$ |

4.1. Equation:
4.2.1. Calculation of the $T$ value:

Your work:
$T=$ $\qquad$ $m g / m L$
4.2.2. Calculation of the $T$ value:

Your work:
$T=$ $\qquad$ $m g / m L$
4.2.3. Calculation of the $T$ value:

Your work:
$T=$ $\qquad$ $m g / m L$
4.3. Equation(s):
4.4.1 Equation(s):
4.4.2. Equation:
4.4.3. The composition of the crystallohydrate is:

Your work:

Formula of the salt $\mathrm{Fe}_{2}\left(\mathrm{SO}_{4}\right)_{3} \cdot x \mathrm{H}_{2} \mathrm{O}$ :

$$
x=
$$

$\qquad$

## Solution and grading scheme

### 4.1 Equation:

$$
\mathrm{I}_{2}+\mathrm{SO}_{2}+2 \mathrm{H}_{2} \mathrm{O}+4 \mathrm{Py}=2 \mathrm{PyHI}+(\mathrm{PyH})_{2} \mathrm{SO}_{4} \quad \underline{1 \text { mark }}
$$

(0.75 marks for not accounting for the formation of Py salts)
4.2.1 $T$ is equal to:

$$
\begin{aligned}
& M\left(\mathrm{Na}_{2} \mathrm{C}_{4} \mathrm{H}_{4} \mathrm{O}_{6} \cdot 2 \mathrm{H}_{2} \mathrm{O}\right)=230.05 \quad 2 M\left(\mathrm{H}_{2} \mathrm{O}\right)=36.04 \\
& m\left(\mathrm{H}_{2} \mathrm{O}\right)=1.3520 \cdot 36.04 / 230.05=0.2118 \mathrm{~g}=211.8 \mathrm{mg} \\
& \quad 1 \text { mark for the formula }
\end{aligned}
$$

$T=211.8 / 12.20=17.36 \mathrm{mg} / \mathrm{mL}$
0.25 marks for the correct result (within 2 digits)
1.25 marks maximum
4.2.2 $T$ is equal to:

Volume of iodine spent for 10 mL of pure $\mathrm{CH}_{3} \mathrm{OH}=2.20 \cdot 10.00 / 25.00=0.88 \mathrm{~mL}$ ( 0.5 marks for the correct formula of pure methanol titration) $T=21.537 \cdot 0.01 \cdot 10^{3} /(22.70-0.88)=9.87 \mathrm{mg} / \mathrm{mL}$

## More accurately

10.00 mL of the solution contains $(1000-21.5) \times 10.00 / 1000=9.785 \mathrm{~mL}$ of methanol

Volume of iodine spent for 9.785 mL of pure $\mathrm{CH}_{3} \mathrm{OH}=2.20 \cdot 9.785 / 25.00=0.86 \mathrm{~mL}$ $T=21.537 \cdot 0.01 \cdot 10^{3} /(22.70-0.86)=9.86 \mathrm{mg} / \mathrm{mL}$
( 1 mark for the formula of water titration, only 0.5 marks without subtracting 0.88)

$$
T=9.87 \mathrm{mg} / \mathrm{mL} \quad 0.25 \text { marks for the correct result }
$$

1.75 marks maximum

### 4.2.3 $T$ is equal to:

## Approach 1.

Let 1 mL of $\mathrm{CH}_{3} \mathrm{OH}$ contain $x \mathrm{mg} \mathrm{H} \mathrm{H}_{2} \mathrm{O}$, then 1 mL of $\mathbf{A}$ contains ((1.000-0.006) $\cdot x+$ 5.624) $\mathrm{mg} \mathrm{H}_{2} \mathrm{O}$.
$15.00 \cdot T=22.45 \cdot(0.994 \cdot x+5.624)-1^{\text {st }}$ titration,
$10.00 \cdot T=25.00 \cdot x+10.79 \cdot(0.994 \cdot x+5.624)-2^{\text {nd }}$ titration.
Hence, $x=1.13 \mathrm{mg} / \mathrm{mL}, T=10.09 \mathrm{mg} / \mathrm{mL}$ ( 10.10 without taking into account 0.994 factor)

## Approach 2.

Let $y \mathrm{~mL}$ of $\mathbf{B}$ be spent for the titration of water, contained in 1 mL of $\mathrm{CH}_{3} \mathrm{OH}$. Then

$$
T=\frac{22.45 \cdot 5.624}{15.00-22.45 \cdot 0.994 \cdot y}\left(1^{\text {st }} \text { titration }\right)=\frac{10.79 \cdot 5.624}{10.00-25.00 y-10.79 y}\left(2^{\text {nd }} \text { titration }\right) .
$$

Hence, $y=0.1116$ and $T=10.10 \mathrm{mg} / \mathrm{mL}$
$T=10.09 \mathrm{mg} / \mathrm{mL}$ ( 10.10 without taking into account 0.994 factor)
(2 marks for the correct formulas (with or without taking into account 0.994 factor) and 0.25 marks for the correct result (10.10 or 10.09))

### 4.3 Equation(s):

$$
\begin{gathered}
\mathrm{CaO}+\mathrm{SO}_{2}=\mathrm{CaSO}_{3} \\
2 \mathrm{CaO}+2 \mathrm{I}_{2}=\mathrm{CaI}_{2}+\mathrm{Ca}(\mathrm{OI})_{2} \\
6 \mathrm{CaO}+6 \mathrm{I}_{2}=5 \mathrm{CaI}_{2}+\mathrm{Ca}\left(\mathrm{IO}_{3}\right)_{2} \\
\text { (Instead of } \mathrm{CaO}, \mathrm{Ca}(\mathrm{OH})_{2} \text { may be written.) }
\end{gathered}
$$

### 4.4.1 Equation(s):

$$
\mathrm{Fe}_{2}\left(\mathrm{SO}_{4}\right)_{3}+2 \mathrm{HI}=2 \mathrm{FeSO}_{4}+\mathrm{I}_{2}+\mathrm{H}_{2} \mathrm{SO}_{4} \quad 1 \text { mark }
$$

$$
\mathrm{Fe}_{2}\left(\mathrm{SO}_{4}\right)_{3}+\mathrm{H}_{2} \mathrm{O}+\mathrm{SO}_{2}+\mathrm{CH}_{3} \mathrm{OH}=2 \mathrm{FeSO}_{4}+\mathrm{CH}_{3} \mathrm{OHSO}_{3}+\mathrm{H}_{2} \mathrm{SO}_{4}
$$1

mark
(or in ionic form)
2 marks maximum

### 4.4.2 Equation:

$$
\begin{aligned}
& \mathrm{Fe}_{2}\left(\mathrm{SO}_{4}\right)_{3} \cdot x \mathrm{H}_{2} \mathrm{O}+(x-1) \mathrm{I}_{2}+x \mathrm{SO}_{2}+x \mathrm{CH}_{3} \mathrm{OH}= \\
& =2 \mathrm{FeSO}_{4}+x \mathrm{CH}_{3} \mathrm{OHSO}_{3}+\mathrm{H}_{2} \mathrm{SO}_{4}+2(x-1) \mathrm{HI}
\end{aligned}
$$

## maximum

4.4.3. The composition of the crystallohydrate is:

$$
\begin{array}{ll}
M\left(\mathrm{Fe}_{2}\left(\mathrm{SO}_{4}\right)_{3} \cdot x \mathrm{H}_{2} \mathrm{O}\right)=399.9+18.02 x & \\
m_{\mathrm{H} 2 \mathrm{O}}(\mathrm{~g})=\frac{0.6387 \cdot 18.02 x}{(399.9+18.02 x} ; & 1 \text { mark } \\
m_{\mathrm{H} 2 \mathrm{O}}(\mathrm{~g})=10.59(\mathrm{~mL}) \times 15.46(\mathrm{mg} / \mathrm{mL}) \times 0.001(\mathrm{~g} / \mathrm{mg}) \times \frac{x}{x-1} & 1 \text { mark } \\
0.1637 \cdot(399.9+18.02 x)=11.51 x-11.51 ; & \\
x=8.994 &
\end{array}
$$

Formula: $\mathrm{Fe}_{2}\left(\mathrm{SO}_{4}\right)_{3} 9 \mathrm{H}_{2} \mathrm{O} \quad x=9 \quad 0.25$ marks (for correct answer) 2.25 marks maximum

## Problem 5. A MYSTERIOUS MIXTURE (ORGANIC HIDE-AND-SEEK GAME)

| Question | 1.1 | 1.2 | 1.3 | 2.1 | 2.2 | 3.1 | 3.2 | Total | Points |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Marks | 5 | 5 | 10 | 30 | 10 | 10 | 5 | 75 | 7.5 |

### 5.1.1 Structure of product D

$\square$
5.1.2 Which class of organic compounds does $\boldsymbol{D}$ belong to? Check the appropriate box.
Note! Only one checkmark is allowed. Several checkmarks will lead to 0 marks for this question.

| ketones | ethers | acetals | esters | alcohols | aldehydes | glycols |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\square$ | $\square$ | $\square$ | $\square$ | $\square$ | $\square$ | $\square$ |

5.1.3 The expected yield of $\boldsymbol{D}$

The yield is equal to $85 \% \square$; lower than $85 \% \square$; greater than $85 \%$

Your work:
yield $=\quad \%$
5.2.1 The structures of $\boldsymbol{A}, \boldsymbol{B}$, and $\boldsymbol{C}$.

|  |  |  |
| :---: | :---: | :---: |
|  |  |  |
| $\boldsymbol{A}$ | $\boldsymbol{B}$ | $\boldsymbol{C}$ |

5.2.2 Draw in the boxes intermediate compounds formed during the acidic hydrolysis of $\boldsymbol{C}$, and basic hydrolysis of $\boldsymbol{B}$.

5.3.1 The structure of senecioic acid and the reaction scheme leading to SA sodium salt from acetone.
5.3.2 The structure of $\boldsymbol{E}$.

## Solution and grading scheme

5.1.1 Structure of product D


Ethyl acetate, ethyl ethanoate

Any structural formula or any shorter versions $\left(\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}\right)$ including the adopted shortcuts for organic radicals (Me, Et, Ac), or systematic IUPAC name - $\underline{5 \text { marks }}$
5.1.2 Which class of organic compounds does $\boldsymbol{D}$ belong to? Check the appropriate box.

| ketones | ethers | acetals | esters | alcohols | aldehydes | glycols |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\square$ | $\square$ | $\square$ | $\square$ | $\square$ | $\square$ | $\square$ |

The only correct answer is ester - $\underline{5 \text { marks }}$

### 5.1.3 The expected yield of $\boldsymbol{D}$

Statement that the reaction is an equilibrium without any further actions - 1 mark Answer to quantitative question: lower than $85 \%-2$ marks

Qualitative estimation of yield can be done assuming that the reaction is at equilibrium, and that the equilibrium constant is supposed to not vary with temperature and composition of the reaction mixtures.

$$
K=\frac{[\mathrm{AcOEt}]\left[\mathrm{H}_{2} \mathrm{O}\right]}{[\mathrm{AcOH}][\mathrm{EtOH}]}=\frac{(0.85)^{2}}{0.15 \cdot 1.15}=4.2
$$

Calculation of yield using this constant in 1:1 mixture gives $67 \%$
yield = 67\%
maximum - 10 marks, if the yield is computed within $67 \pm 1 \%$ error limits

### 5.2.1 The structures of $\boldsymbol{A}, \boldsymbol{B}$, and $\boldsymbol{C}$.

|  | $\bar{Z} \mathrm{OEt}$ $\mathrm{HC} \equiv \mathrm{COEt}$ <br> ethoxyacetylene, ethynylethyl ether | $\mathrm{CH}_{2}(\mathrm{COOEt})_{2}$ <br> diethyl malonate |
| :---: | :---: | :---: |
| A | $B$ | $C$ |

Each structure represented by structural formula or unambiguous linear notation 10 marks. Systematic name given in place of structure - 5 marks
5.2.2 Draw in the boxes intermediate compounds formed during the acidic hydrolysis of $\boldsymbol{C}$, and basic hydrolysis of $\boldsymbol{B}$.
a) Malonic acid is formed as intermediate in the hydrolysis of diethyl malonate - 5 marks


Also accepted will be monoethyl malonate -2 marks. Maximum 5 marks
b) Hydrolysis of ethoxyacetylene starts from the addition of hydroxide to the triple bond to give unstable enolic form of ethylacetate, into which it immediately is transformed


Indication of any of keto- or enol forms of ethylacetate - 5 marks
Hydrolysis of strong ether bond to give hydroxyacetylene, or any forms coming along this path (ketene, diketene) is impossible and is not allowed - 0 marks

Maximum for $a$ ) and b) together - 10 marks

### 5.3.1 The structure of senecioic acid

From acetone alone the synthesis includes aldol condensation, dehydration, with subsequent iodoform reaction

3 marks


Senecioic acid structure alone - 4 marks, with scheme - maximum 10 marks

### 5.3.2 The structure of $\boldsymbol{E}$.

lodoform, triiodomethane, $\mathrm{CHI}_{3}-\underline{5 \text { marks }}$

## Problem 6. SILICATES AS THE BASE OF THE EARTH CRUST

| Question | 1.1 | 1.2 | 2.1 | 2.2 | 2.3 | 2.4 | 3.1 | 3.2 | Total | Points |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Marks | 3 | 9 | 2 | 2 | 3 | 10 | 5 | 3 | 37 | 7 |

6.1.1 The net ionic equation accounting for the ability of LGL to set in air
6.1.2 Write down the net ionic equations matching the processes enumerated in the Table. For each process check the "Yes" box if it leads to changes of pH . Otherwise check the "No" box.
a) protonation of ortho-silicate ions leading to the formation of $\mathrm{Si-OH}$ groups

Reaction equation:
b) formation of hydrated $\left[\mathrm{SiO}_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{4-}$ anions

Reaction equation:

Yes $\square \quad$ No $\qquad$
c) polycondensation of ortho-silicate ions leading to the formation of Si-O-Si bonds Reaction equation:

Yes $\qquad$ No $\square$
6.2 For $\left[\mathrm{Si}_{3} \mathrm{O}_{9}\right]^{n-}$ ion found in aqueous solution of silicates:
6.2.1 Determine the charge (n).

Your justification

$$
\mathrm{n}=
$$

$\qquad$
6.2.2 Determine the number of oxygen atoms bridging adjacent tetrahedra.

Your justification

Number of oxygen atoms = $\qquad$
6.2.3 Depict the ion structure joining together several tetrahedra (1).
6.2.4 The fragment of the layered structure joining 16 tetrahedra (1)

Your justification

Structure
6.3.1 pH of 0.1 M aqueous solution of copper sulfate

Your justification
$\mathrm{pH}=$ $\qquad$
6.3.2 Equation of a reaction between aqueous solutions of $\mathrm{CuSO}_{4}$ and sodium metasilicate (LGL)

## Solution and grading scheme

### 6.1.1

$$
\mathrm{SiO}_{3}{ }^{2-}+2 \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}=\text { " } \mathrm{H}_{2} \mathrm{SiO}_{3} \text { " } \downarrow \text { (Silica acid gel) }+2 \mathrm{HCO}_{3}^{-}
$$

or

$$
\mathrm{SiO}_{2}(\mathrm{OH})_{2}^{2-}+2 \mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}=" \mathrm{H}_{2} \mathrm{SiO}_{3} " \downarrow+2 \mathrm{HCO}_{3}^{-}
$$

or

$$
\mathrm{SiO}_{3}{ }^{2-}+\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}=" \mathrm{H}_{2} \mathrm{SiO}_{3} \text { " } \downarrow+\mathrm{CO}_{3}{ }^{2-}
$$

3 marks maximum
2 marks if silicic acid is written in any form
1 mark if the reaction contains carbonate (or bicarbonate) ions with silicic acid missing

### 6.1.2

a) protonation of ortho-silicate ions leading to the formation of $\mathrm{Si}-\mathrm{OH}$ groups
$\mathrm{SiO}_{4}{ }^{4-}+\mathrm{H}_{2} \mathrm{O}=\left[\mathrm{SiO}_{3}(\mathrm{OH})\right]^{3-}+\mathrm{OH}^{-}$or
$\mathrm{SiO}_{4}{ }^{4-}+\mathrm{H}^{+}=\left[\mathrm{SiO}_{3}(\mathrm{OH})\right]^{3-}$ or
$\left[\mathrm{SiO}_{2}(\mathrm{OH})_{2}\right]^{2-}+\mathrm{H}^{+}=\left[\mathrm{SiO}(\mathrm{OH})_{3}\right]^{-} \quad$ Yes $\boxtimes$ No $\square$
b) formation of hydrated $\left[\mathrm{SiO}_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{4-}$ anions
$\mathrm{SiO}_{4}{ }^{4-}+2 \mathrm{H}_{2} \mathrm{O}=\left[\mathrm{SiO}_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{4-}$
Yes $\square$ No $\boxtimes$
c) polycondensation of ortho-silicate ions leading to the formation of $\mathrm{Si}-\mathrm{O}-\mathrm{Si}$ bonds
$2 \mathrm{SiO}_{4}{ }^{4-}+\mathrm{H}_{2} \mathrm{O}=\left[\mathrm{O}_{3} \mathrm{Si}-\mathrm{O}-\mathrm{SiO}_{3}\right]^{6-}+2 \mathrm{OH}^{-}$or
$2 \mathrm{SiO}_{4}^{4-}+2 \mathrm{H}^{+}=\left[\mathrm{O}_{3} \mathrm{Si}-\mathrm{O}-\mathrm{SiO}_{3}\right]^{6-}+\mathrm{H}_{2} \mathrm{O}$ or
$2 \mathrm{SiO}_{2}(\mathrm{OH})_{2}{ }^{2-}+\mathrm{H}_{2} \mathrm{O}=\left[\mathrm{O}-\mathrm{Si}(\mathrm{OH})_{2}-\mathrm{O}-\mathrm{Si}(\mathrm{OH})_{2}-\mathrm{O}\right]^{2-}+2 \mathrm{OH}^{-}$


9 marks maximum
2 marks for each correct reaction
1 mark for each correct choice of check-boxes
6.2.1 $n=6$ (assuming oxidation numbers of silicon (+4) and oxygen ( -2 ), or taking into account its structure and the charge of orthosilicate ion ( -4 )

2 marks maximum
1 mark penalty for miscalculation

### 6.2.2

$\mathrm{Si}_{3} \mathrm{O}_{9} \equiv 3\left[\mathrm{SiO}_{4}\right]-3 \mathrm{O}$, i.e. there are 3 oxygen atoms bridging adjacent tetrahedra

2 points maximum
1 point penalty for miscalculation

### 6.2.3



3 marks maximum

### 6.2.4 Calculations:

$m=4$ (assuming oxidation numbers of silicon (+4) and oxygen ( -2 ), or taking into account its structure and the charge of orthosilicate ion ( -4 ))
$\mathrm{Si}_{4} \mathrm{O}_{10} \equiv 4\left[\mathrm{SiO}_{4}\right]-6$ O, i.e. the formula of the tetrahedron is now $\mathrm{SiO}_{2.5}$, which is possible if 1 O atom belongs to this tetrahedron and the other three are shared between 2 tetrahedra (their contribution $=3 / 2$ ). This is possible if the tetrahedra are set on a plane and joined together through all apexes of their bases.


10 marks maximum
2 marks for charge determination
3 marks for determination of the number of oxygen bridges

5 marks for the correct structure
1 mark penalty if 6 to 15 tetrahedra shown, the connection being correct
3 marks penalty if less than 6 tetrahedra shown (i.e. it is not clear that polyhedra form layer)

4 marks penalty for connection via apexes, but in 3D network
4 marks penalty for connection via apexes, but in 1D chain
0 mark of 5 for any other structure
6.3.1 $\mathrm{pH}=4$

$$
\begin{aligned}
& \mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}^{2+}+\mathrm{H}_{2} \mathrm{O}=\mathrm{Cu}(\mathrm{OH})\left(\mathrm{H}_{2} \mathrm{O}\right)_{3}{ }^{+}+\mathrm{H}_{3} \mathrm{O}^{+}, \\
& {\left[\mathrm{H}^{+}\right] \approx\left(\mathrm{c} \mathrm{~K}_{\mathrm{a}}\right)^{1 / 2}=1 \cdot 10^{-4} \mathrm{M}, \mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=4}
\end{aligned}
$$

5 marks maximum
1 mark penalty for miscalculation
2 marks penalty for wrong expression of $\left[\mathrm{H}^{+}\right]$via $\mathrm{K}_{\mathrm{a}}{ }^{1}$
2 marks penalty if there are some errors in definition of pH (e.g. using In instead of log)
3 marks penalty if the hydrolysis reaction is wrong

### 6.3.2

$$
\mathrm{CuSO}_{4}+\mathrm{Na}_{2} \mathrm{SiO}_{3}+2 \mathrm{H}_{2} \mathrm{O}=\mathrm{Cu}(\mathrm{OH})_{2} \downarrow+{ }^{2} \mathrm{H}_{2} \mathrm{SiO}_{3}{ }^{\prime} \downarrow+\mathrm{Na}_{2} \mathrm{SO}_{4}
$$

or

$$
2 \mathrm{CuSO}_{4}+\mathrm{Na}_{2} \mathrm{SiO}_{3}+2 \mathrm{H}_{2} \mathrm{O}=(\mathrm{CuOH})_{2} \mathrm{SO}_{4} \downarrow+\mathrm{H}_{2} \mathrm{SiO}_{3}{ }^{\prime} \downarrow+\mathrm{Na}_{2} \mathrm{SO}_{4}
$$

This (or those) reaction(s) (apart from formation of copper silicate) can be deduced from the fact that the reaction describes mutual (self-amplifying) hydrolysis. It comes from the previous parts of the task: pH of LGL is greater than 7 (see questions 6.2), and pH of copper sulfate solution is less than 7 (see 6.3.1).

3 marks maximum
2 marks if reaction coefficients are wrong
1 mark if only one of two principal precipitates shown $\left(\mathrm{Cu}(\mathrm{OH})_{2} \downarrow\right.$ or " $\mathrm{H}_{2} \mathrm{SiO}_{3}$ " $\downarrow$ )

## Problem 7. ATHEROSCLEROSIS AND INTERMEDIATES OF CHOLESTEROL BIOSYNTHESIS

| Question | 1.1 | 1.2 | 2.1 | 2.2 | 2.3 | 2.4 | 2.5 | Total | Points |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Marks | 12 | 12 | 5 | 12 | 7 | 8.5 | 16 | 72.5 | $\mathbf{7 . 5}$ |

7.1.1 A number of reaction types is listed in the table below. All reactions involved in metabolism of HMG-CoA to IPP are in the list. Choose those types of reactions which are catalyzed by E1 and E3 (put numbers in appropriate places).

| No | Reaction type |
| :---: | :--- |
| 1. | Dehydration |
| 2. | Decarboxylation |
| 3. | Dephosphorylation |
| 4. | 4 electron reduction |
| 5. | Release of the reduced form of coenzyme A (CoA-SH) |
| 6. | Monophosphorylation |
| 7. | Oxidation of hydroxyl group as the third stage of HMG-CoA $\beta$-oxidation <br> cycle |

## E1

$\qquad$
E3 $\qquad$
7.1.2 Draw the structure of $\boldsymbol{X}$ with stereochemical details and indicate absolute configuration ( $R$ or $S$ ) of the stereocenter.

7.2.1 Write down the overall reaction equation for reductive ozonolysis of DAP with dimethyl sulfide used as the reducing agent.
7.2.2 Determine molecular formula of $\boldsymbol{Y}$.

Your justification

Number of carbon atoms $\qquad$

Number of hydrogen atoms $\qquad$ Molecular formula: $\qquad$
7.2.3 Calculate the number of IPP and DAP molecules needed to give $\mathbf{Y} 5$.

Your justification:

Number of IPP molecules $\qquad$ Number of DAP molecules $\qquad$
7.2.4 Draw the product of coupling reaction between one IPP molecule and one DAP molecule, subsequent reductive ozonolysis of which gives Y1, Y2 and one more product, the latter containing phosphorus.
$\square$
7.2.5 Draw the structures of $\boldsymbol{Y}$ and $\mathbf{Y} 4$ with stereochemical details.
$\square$

## Solution and grading scheme

7.1.1 E2-E4 catalyze one and the same (and only one) reaction type. The only reaction which can be carried out three times in a row is monophosphorylation (all the rest reaction types are not consistent with either initial or final products). This is also supported by presence of pyrophosphate residue in IPP and liberation of inorganic products (including inorganic phosphate) upon spontaneous decomposition of X1.
$\mathbf{X}$ is a monocarboxylic acid composed of atoms of three elements: carbon, hydrogen and oxygen. It can contain neither sulfur which is found in CoA nor phosphorus which is introduced into intermediates on the pathway from HMG-CoA towards IPP or present in CoA. Thus, E1 catalyzes non-hydrolytic removal of CoA from HMGCoA and is not involved in phosphorylation. Since water is not a substrate in this reaction, liberation of CoA must be conjugated with another reaction which affects the carboxylic group esterified in HMG-CoA. The only possible variant is its 4 electron reduction towards hydroxyl group. E1 can not catalyze dehydration because of optical activity of $\mathbf{X}$ (removal of water leads to the loss of sole chiral center). Decarboxylation is excluded, since $\mathbf{X}$, being an acid, must contain a carboxylic group. Oxidation of tertiary hydroxyl group in HMG-CoA according to $\beta$-oxidation mechanism is impossible. Further evidence comes from the fact that the carboxylic group initially involved in thioester bond formation is present as the residue of hydroxyl group in IPP. So:

E1 $\qquad$
4, 5
E3
6
12 marks maximum
E1: 9 marks if 2 variants are given and both are correct.
4 marks if only one variant is given and it is correct

4 marks if two correct and one incorrect variants are given
0 mark if one correct and any number of incorrect variants are given
0 mark if more than three variants are given.
E3: 3 marks if only correct variant is given. Otherwise 0 mark
7.1.2 Based on the reaction types catalyzed by $\mathbf{E} 1$ and configuration of HMG-CoA stereocenter, the structure of $\mathbf{X}$ is:


X, mevalonic acid

Note the absolute configuration of the chiral center is changed as a result of HMGCoA metabolism into mevalonic acid due to alteration of substituents priority.


12 marks maximum
8 marks for correct structural formula
4 marks for correct stereochemistry (only in case both the structure is correct and Risomer is indicated; otherwise 0 mark).

No penalty for incorrect stereochemistry or absence of stereochemical information
7.2.1 Reaction equation for reductive ozonolysis


5 marks maximum
4.5 marks for correct products (1.5 marks each), incorrect structures not penalized 0.5 mark for correct equation coefficients
7.2.2 DAP molecule contains only one carbon atom which can be involved in the formation of $\mathbf{C - C}$ bond during $\mathbf{Y}$ biosynthesis. Irrespective of the way this molecule is incorporated in Y, ozonolysis of this fragment will lead to dimethyl ketone (acetone). (See DAP ozonolysis reaction in 7.2.1). Thus, acetone can be unambiguously attrib-
uted to Y1, since it contains 3 carbon atoms ( $\mathbf{Y} 2$ and $\mathbf{Y} 3$ contain 5 and 4 carbon atoms, respectively). Taking into account the ratio between ozonolysis products, we have:

$$
n_{\mathrm{Y}}(\mathrm{C})=2 \cdot n_{Y 1}(\mathrm{C})+4 \cdot n_{Y 2}(\mathrm{C})+n_{Y 3}(\mathrm{C})=2 \cdot 3+4 \cdot 5+4=30
$$

$\mathbf{Y}$ is an acyclic molecule, thus DAP residues can be found only at its ends. $\mathbf{Y}$ has only two ends, since IPP contains only two elongation sites (at least three such sites are needed to get a branched molecule). Since reductive ozonolysis of one $\mathbf{Y}$ molecule produces two acetone molecules, $\mathbf{Y}$ contains 30 carbon atoms.

To determine the number of hydrogen atoms double bonds in $\mathbf{Y}$ should be counted. Formation of each double bond reduces by 2 the number of hydrogen atoms in the coupling product as compared to the sum of atoms of starting substances. The ratio of $\mathbf{Y}$ to the sum of its ozonolysis products is $1: 7(2+4+1)$, which corresponds to 6 double bonds in $\mathbf{Y}$. Then, by using the general formula for alkanes we have:

$$
n(\mathrm{H})=2 \cdot n_{\mathrm{Y}}(\mathrm{C})+2-2 \cdot n_{\mathrm{c}=\mathrm{c}}=30 \cdot 2+2-6 \cdot 2=50
$$

$\mathbf{Y}$ (squalene) formula - $\mathrm{C}_{30} \mathrm{H}_{50}$.
Number of carbon atoms 30
Number of hydrogen atoms 50
Gross formula of $\mathbf{Y}-\mathrm{C}_{30} \mathrm{H}_{50}$
12 marks maximum
8 marks for correct justification of molecular formula
4 marks for correct molecular formula
7.2.3 IPP and DAP are structural isomers containing 5 carbon atoms each. Since all carbon atoms of these substances are found in $\mathbf{Y}$, one can calculate the total quantity of IPP and DAP molecules needed to synthesize $\mathbf{Y}$ :

$$
\mathrm{n}(\mathrm{IPP} \& \mathrm{DAP})=n_{Y}(\mathrm{C}) / 5=30 / 5=6
$$

The number of DAP molecules was determined earlier and is equal to 2 . Then, 4 molecules of IPP are needed.

Number of DAP molecules $\underline{2} \quad$ Number of IPP molecules 4
7 marks maximum
3.5 marks for calculation of the total number of DAP and IPP molecules
3.5 marks for correct individual numbers of DAP and IPP molecules
7.2.4 All possible combinations that do not alter hydrocarbon skeleton are given below (pyrophosphate fragments not shown). Two groups of products differing in carbon atoms involved in coupling reaction are separated by the dashed line. IPP fragments should be attached to DAP so that ozonolysis of the product leads to Y2 containing 5 carbon atoms. Only one variant is possible if stereochemistry is not taken into consideration and two variants with stereochemical details

8.5 marks maximum
8.5 marks for correct structure

No penalty for stereochemistry, any correct structure is accepted
2.5 marks if ozonolysis of the product leads to acetone, but does not lead to the compound with 5 carbon atoms
2.5 marks if ozonolysis of the product leads to the compound with 5 carbon atoms, but does not lead to acetone 0 mark for any other variant
7.2.5 It is seen from the coupling reaction (Scheme 2) that Y4 contains 15 carbon atoms or 1 DAP and 2 IPP fragments, the latter being attached to the former consecutively. It is important to note that Y3 can not be found in two hydrocarbon residues originating for $\mathbf{Y 4}$, since $\mathbf{Y} 3$ is formed as a result of ozonolysis in a molar ratio of $1: 1$ to $\mathbf{Y}$. Thus, geranyl phosphate is the intermediate on the way to $\mathbf{Y}$ (all double bonds in trans configuration). Attachment of the next IPP fragment to geranyl phosphate leads to the product giving 1 molecule of Y1 and 2 molecules of Y2 upon its ozonolysis. Thus, Y4 structure with stereochemical details:


Y4, farnesyl pyrophosphate

Combining two hydrocarbon fragments of $\mathbf{Y 4}$ and taking into account that the double bond between them is being reduced we get the following structure of $\mathbf{Y}$ :


16 marks maximum
9 marks for farnesyl pyrophosphate ( 6.5 marks for correct structural formula and 2.5 marks for correct stereochemistry)
7 marks for squalene ( 5 marks for correct structural formula and 2 marks for correct stereochemistry)
2.5 marks penalty for unreduced double bond in squalene

## Problem 8. ATRP ALLOWS NEW POLYMERS

| Question | 1.1 | 1.2 | 2.1 | 2.2 | 2.3 | 3.1 | 3.2 | 3.3 | 3.4 | Total | Points |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Marks | 8 | 9 | 5 | 11 | 14 | 16.5 | 12 | 10 | 13.5 | 99 | $\mathbf{8}$ |

8.1.1 Expressions for the rates:

| $v_{\text {act }}=$ | $v_{\mathrm{p}}=$ |
| :--- | :--- |
| $v_{\text {deact }}=$ | $v_{\mathrm{t}}=$ |

8.1.2 Compare rates using operators $\ll, \leq, \approx, \geq$, >>

|  | $v_{\text {deact }} \quad v_{\text {act }}$ | $v_{\text {deact }} \quad v_{t}$ |
| :--- | :--- | :--- |
|  | $v_{\text {deact }} \quad v_{p}$ |  |

8.2.1 Mass of the obtained polymer.

Your justification:
$m=$
8.2.2 Degree of polymerization of the obtained polymer.

Your justification:

DP =
8.2.3 Structure of the obtained polymer.
8.3.1 Fill in the right column with symbols (a-g) of ${ }^{1} \mathrm{H}$ NMR signals corresponding to substructures in the left column.
ces:
8.3.2 Composition and molecular weights of copolymers P1 and P2.

| Your justification: | Your justification: |  |
| :--- | :--- | :--- |
|  |  |  |
|  | $n(\mathrm{D})=$ | $M(\mathrm{P} 1)=$ |

8.3.3. All possible reactions of activation

P1:

P2:
8.3.4 Structure of P1 and one of possible structures of P2

| P1: | P2: |
| :--- | :--- |
|  |  |
|  |  |
|  |  |
|  |  |

## Solution and grading scheme

8.1.1 Expressions for the rates of ATRP elementary stages: activation $\left(v_{\text {act }}\right)$, deactivation ( $v_{\text {deact }}$ ), propagation $\left(v_{p}\right)$ and termination $\left(v_{t}\right)$
$v_{\text {act }}=k_{\text {act }} \cdot[\mathrm{R}-\mathrm{Hal}] \cdot\left[\mathrm{CuHal}(\text { Ligand })_{\mathrm{k}}\right] \quad 2$ marks
$v_{\text {deact }}=k_{\text {deact }} \cdot[\mathrm{R}] \cdot\left[\mathrm{CuHal}_{2}(\text { Ligand })_{\mathrm{k}}\right] \quad 2$ marks
$v_{\mathrm{p}}=k_{\mathrm{p}} \cdot[\mathrm{R}] \cdot[\mathrm{M}]$
$v_{\mathrm{t}}=2 k_{\mathrm{t}} \cdot[\mathrm{R}]^{2}$
2 marks
2 marks (no penalty for missing
2)

8 marks maximum

### 8.1.2 Comparison of rates of ATRP elementary stages

Since all the chains grow with equal rate, the process proceeds as living polymerization. Living radical polymerization is possible only if concentration of active radicals is low to prevent chain transfer and termination. So:

$$
v_{\text {deact }} \gg v_{\text {act }} \quad 3 \text { marks }
$$

The portion of active radicals must be small, so the equilibrium is shifted towards dormant species.

$$
v_{\text {deact }} \gg V_{p} \quad 3 \text { marks }
$$

Propagation rate should be much slower than that of deactivation to make chains propagate with equal rate.

Termination does not occur since the total number of polymer chains is equal to a certain constant number - number of initiator molecules.

9 marks maximum
8.2.1 Calculation of mass $(m)$ of the obtained polymer.

$$
\begin{gather*}
1^{\text {st }} \text { variant } \\
{[M]=[M]_{0} \exp \left(-k_{P}[R \cdot] t\right) \text { or } n(\mathrm{MMA})=n_{0}(\mathrm{MMA}) \exp \left(-k_{P}[R \cdot] t\right)} \tag{1}
\end{gather*}
$$

mark
Quantity of MMA monomer remaining after polymerization during 1400 s is

$$
31.0 \cdot \exp \left(-1616 \cdot 1.76 \cdot 10^{-7} \cdot 1400\right)=20.8 \mathrm{mmol} .2 \text { marks }
$$

Quantity of monomer consumed during polymerization:

$$
31-20.8=10.2 \mathrm{mmol}
$$

Mass of the obtained polymer is

$$
m=\Delta n(\mathrm{MMA}) \cdot M(\mathrm{MMA})=(10.2 / 1000) \cdot 100.1=1.03 \mathrm{~g} \quad 1 \text { mark }
$$

$$
\begin{aligned}
& 2^{\text {nd }} \text { variant } \\
{[M]=} & {[M]_{0} \exp \left(-k_{P}[R \cdot] t\right) \text { or } n(\mathrm{MMA})=n_{0}(\mathrm{MMA}) \exp \left(-k_{P}[R \cdot] t\right) \quad 1 \text { mark } }
\end{aligned}
$$

Quantity of MMA monomer consumed during 1400 seconds of polymerization is $\Delta n(\mathrm{MMA})=n_{0}(\mathrm{MMA})\left(1-\exp \left(-k_{p} \cdot\left[R^{\bullet}\right] \cdot t\right)\right)=31.0 \cdot\left(1-1616 \cdot 1.76 \cdot 10^{-7} \cdot 1400\right)=10.2 \mathrm{mmol}$ 3 marks

Mass of the obtained polymer is

$$
\begin{array}{ll}
m=\Delta n(\mathrm{MMA}) \cdot M(\mathrm{MMA})=(10.2 / 1000) \cdot 100.1=1.03 \mathrm{~g} & 1 \text { mark } \\
3^{\text {rd }} \text { variant } & \\
\ln \left(\frac{[M]}{[M]_{0}}\right)=-k_{P}[R \cdot] t=-1616 \cdot 1.76 \cdot 10^{-7} \cdot 1400=-0.398 & 1 \text { mark } \\
\frac{[M]}{[M]_{0}}=e^{-0.398}=0.672 & 1 \text { mark } \\
\frac{[M]}{[M]_{0}}=\frac{n(\mathrm{MMA})}{n_{0}(\mathrm{MMA})} & \\
n(\mathrm{MMA})=0.672 \cdot n_{0}(\mathrm{MMA})=20.8 \mathrm{mmol} & 1 \text { mark }
\end{array}
$$

Quantity of monomer consumed during polymerization is $31-20.8=10.2 \mathrm{mmol}$

Mass of the obtained polymer is

$$
\begin{array}{lc}
m=\Delta n(\mathrm{MMA}) \cdot M(\mathrm{MMA})=(10.2 / 1000) \cdot 100.1=1.03 \mathrm{~g} & 1 \text { mark } \\
\boldsymbol{m}=\mathbf{1 . 0 3} \mathbf{g} & \underline{5 \text { marks maximum }}
\end{array}
$$

### 8.2.2 Calculation of degree of polymerization (DP) of the obtained polymer.

The number of growing chains is equal to the number of TsCl molecules ( 0.12 mmol ) 2 marks

At the first stage, 7.3 mmol of MMA was consumed ( $0.73 / 100.1$ ).
The total quantity of monomers at the beginning of the $2^{\text {nd }}$ stage is

$$
23.7+23.7=47.4 \text { mmol. } 2 \text { marks }
$$

Since the monomers have the same reactivity, they will be involved in polymerization with the same rate.

Quantity of monomers consumed during the second stage is

$$
\Delta n=n_{0}\left(1-\exp \left(-k_{P}[R \cdot] t\right)\right)=47.4\left(1-\exp \left(-1616 \cdot 1.76 \cdot 10^{-7} \cdot 1295\right)\right)=14.6 \mathrm{mmol} .
$$

4 marks
Totally $7.3+14.6=21.9 \mathrm{mmol}$ of monomers was polymerized during two stages.
2 marks
$D P=21.9 / 0.12=182.5$
DP =182-183 (all answers within this range are credited) 11 marks maximum

### 8.2.3 Structure of the obtained polymer.

The product of polymerization is a block copolymer because it was obtained by sequential polymerization on living chains.

The first block is built of MMA units solely. The DP is $7.3 / 0.12=60.8 \approx 61$ monomer units.

The second block is obtained by copolymerization of two competing monomers with the same reactivity. So, it is a statistical copolymer. Fractions of $A$ and $B$ in the $2^{\text {nd }}$ block are equal because their concentrations in the reaction mixture at the beginning of the $2^{\text {nd }}$ stage were equal. The DP of the $2^{\text {nd }}$ block is $183-61=122$ monomer units ( 121 is also correct if the total DP in 8.2.2 is 182).

$$
\text { Ts-A } \left.{ }_{61} \text {-block-(A-stat-B) }\right)_{61}-\mathrm{Cl} \text { or Ts- } \mathrm{A}_{61} \text {-block- }\left(\mathrm{A}_{61}-\text { stat- } \mathrm{B}_{61}\right)-\mathrm{Cl}
$$

4 marks for block copolymer with blocks A and co-AB
4 marks for an indication of the statistic character of the $2^{\text {nd }}$ block

1 mark for equal fractions of $A$ and $B$ in the $2^{\text {nd }}$ block
2 marks for correct DPs of each block
1 mark for indication of terminal groups
8.3.1 Assignment of NMR signals to substructures given in the Answer Sheet.
(as,
16.5 marks maximum
8.3.2 Determination of molar fractions of units $C$ and $D$ and molecular weights of P1 and $P 2$.

Intensity of multiplets $b$ and $g$ is 40.2 , so intensity per 1 proton is $40.2 / 4 / 58=0.173$ for both copolymer spectra
Intensity of multiplet c is 13.0 , which is equivalent to $13.0 / 0.173=75$ protons. Taking into account that each styrene ring has 5 aromatic protons, DP of styrene block is
$75 / 5=15$.

Molar fraction of styrene units in P1 is $15 /(15+58)=\mathbf{2 0 . 5} \%$ each monomer unit of $p$-chloromethylstyrene has 4 protons, DP of PCS is $60 / 4=15$.

2 marks
Molar fraction of $D$ is $15 /(15+58)=\mathbf{2 0 . 5 \%}$
$M(P 1)=15.03+58.44 .05+72.06+15 \cdot 104.15+35.45=4240$

2 marks
1 mark

Intensity of multiplet d is 10.4 , which is equivalent to $10.4 / 0.173=60$ protons. Since

1 mark
2 marks
$M(P 2)=15.03+58.44 .05+72.06+15 \cdot 152.62+35.45=4967$
8.3.3 All possible reactions of activation occurring during the synthesis of P1 and P2.

10 marks maximum
P1:
(1.5+2) marks



Here $R$ is used for the macroinitiator fragment with one or several styrene units attached.

P2:
(1.5+2+3) marks




Here $R$ is used for the macroinitiator fragment with one or several $p$ chloromethylstyrene units attached.

### 8.3.4 The structure of P1 and one of possible structures of P2

P1 is a block copolymer of PEO and PS. The PS block contains 15 units.
P2 is a block copolymer composed of PEO block and branched styrene block. The integral intensity of multiplet $f$ is 2.75 , so $2.75 / 0.173=15.9$, that is about 16 protons or 8 chloromethyl groups.
d) If there is no branching in molecule P2, it would contain 15 chloromethyl groups. Each branching reduces the number of such groups by 1. Thus P2 has $15-$ $8=7$ branchings. Every structure with 7 branchings is correct if each monomer unit is linked with not more than 3 other monomer units

P1


P2

13.5 marks maximum

2 marks for P1
7.5 marks for completely correct structure of P2

4 marks for structure of P2 with nonzero but incorrect number of branchings
4 marks penalty if there is a unit linked with more than 3 other monomer units

STATISTICAL ANALYSIS OF THE PROBLEMS





Theoretical problem 2



Theoretical problem 4


Theoretical problem 5


Theoretical problem 6






## RESULTS PER STUDENT

| Rank | Name | Country | $\begin{aligned} & \text { Practical } \\ & \text { exam } \\ & (\max 40) \end{aligned}$ | $\begin{array}{\|l} \hline \text { Theoretical } \\ \text { exam } \\ (\max 60) \end{array}$ | $\begin{gathered} \text { Total } \\ (\max 100) \end{gathered}$ | Medal |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | Lei XU | China | 19.771 | 56.300 | 76.071 | Gold |
| 2 | Yuan FANG | China | 25.768 | 47.541 | 73.309 | Gold |
| 3 | Leonid ROMASHOV | Russian Federation | 32.556 | 39.712 | 72.267 | Gold |
| 4 | Vasiliy VOROBYEV | Russian Federation | 28.200 | 43.408 | 71.609 | Gold |
| 5 | Zi-yang ZHANG | China | 20.397 | 50.192 | 70.588 | Gold |
| 6 | Ying Yu HO | Chinese Taipei | 23.385 | 47.016 | 70.401 | Gold |
| 7 | Dimitry Ur'evic LOUTCHKO | Germany | 26.113 | 44.115 | 70.228 | Gold |
| 8 | Jae Soo KIM | Korea Republic | 35.000 | 34.721 | 69.721 | Gold |
| 9 | Simon GOURDIN-BERTIN | France | 27.457 | 40.529 | 67.986 | Gold |
| 10 | Tae Gon OH | Korea Republic | 22.718 | 45.027 | 67.745 | Gold |
| 11 | Wei-Lun HUANG | Chinese Taipei | 23.136 | 44.214 | 67.349 | Gold |
| 12 | Dawid Grzegorz LICHOSYT | Poland | 37.806 | 27.458 | 65.264 | Gold |
| 13 | Krzysztof Cezary KOSINSKI | Poland | 28.209 | 35.500 | 63.710 | Gold |
| 14 | Le YANG | China | 13.729 | 49.136 | 62.865 | Gold |
| 15 | Stanislav TEREHOV | Russian Federation | 25.214 | 37.564 | 62.778 | Gold |
| 16 | Philipp Albert STEININGER | Germany | 31.457 | 30.621 | 62.078 | Gold |
| 17 | Bavorn HONGSRICHINDA | Thailand | 32.136 | 29.501 | 61.638 | Gold |
| 18 | Eugeny NEKHOROSHEV | Russian Federation | 12.991 | 48.481 | 61.472 | Gold |
| 19 | Wojciech Dominik MAGON | Poland | 23.189 | 37.745 | 60.935 | Gold |
| 20 | Chang Ho LEE | Korea Republic | 22.308 | 37.602 | 59.911 | Gold |
| 21 | Hande BOYACI | Turkey | 26.934 | 32.959 | 59.893 | Gold |
| 22 | Sumit SOMANI | India | 16.191 | 43.569 | 59.759 | Gold |
| 23 | Soham MEHTA | India | 13.961 | 45.797 | 59.757 | Gold |
| 24 | Martin LUKACISIN | Slovakia | 26.865 | 32.135 | 59.000 | Gold |
| 25 | Gyula PALFY | Hungary | 19.153 | 39.712 | 58.866 | Gold |
| 26 | Karolis LEONAVICIUS | Lithuania | 25.819 | 32.580 | 58.399 | Gold |
| 27 | Minh Nguyen Thi NGOC | Vietnam | 11.198 | 47.043 | 58.241 | Gold |
| 28 | Aurimas VYSNIAUSKAS | Lithuania | 23.883 | 34.212 | 58.095 | Gold |
| 29 | Hyeonjin BAE | Canada | 26.640 | 31.362 | 58.003 | Gold |
| 30 | Przemyslaw Krzysztof TREDAK | Poland | 19.577 | 38.006 | 57.582 | Gold |
| 31 | Ehsan SHABANI | Iran | 28.640 | 28.783 | 57.423 | Gold |
| 32 | Kai-Jui CHANG | Chinese Taipei | 17.192 | 40.002 | 57.194 | Silver |
| 33 | Tanatorn KHOTAVIVATTANA | Thailand | 16.211 | 40.858 | 57.069 | Silver |
| 34 | Samvel BARDAKHCHYAN | Armenia | 15.005 | 41.874 | 56.878 | Silver |
| 35 | Erik ANDRIS | Slovakia | 28.207 | 28.495 | 56.701 | Silver |
| 36 | Andres LAAN | Estonia | 18.755 | 37.569 | 56.324 | Silver |
| 37 | Dzianis HRAMAZDOU | Belarus | 22.505 | 33.778 | 56.283 | Silver |
| 38 | Frank Meng LIN | Chinese Taipei | 18.174 | 37.600 | 55.774 | Silver |
| 39 | Ostap CHERVAK | Ukraine | 16.959 | 38.429 | 55.388 | Silver |
| 40 | Brian Kihoon LEE | United States | 15.090 | 40.156 | 55.246 | Silver |
| 41 | Ctirad CERVINKA | Czech Republic | 27.686 | 27.448 | 55.134 | Silver |
| 42 | Andrew TULLOCH | Australia | 18.304 | 36.723 | 55.027 | Silver |
| 43 | Justin KOH | United States | 25.441 | 29.480 | 54.921 | Silver |
| 44 | Boris FACKOVEC | Slovakia | 22.485 | 32.361 | 54.846 | Silver |
| 45 | Ha Phan Tran HONG | Vietnam | 12.005 | 42.435 | 54.439 | Silver |
| 46 | Vikas PRAJAPATI | India | 13.814 | 40.031 | 53.845 | Silver |
| 47 | Attila LOVAS | Hungary | 26.400 | 26.948 | 53.348 | Silver |


| 48 | Narek DSHKHUNYN | Armenia | 4.345 | 48.776 | 53.121 | Silver |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 49 | Alexander PUCHHAMMER | Austria | 20.593 | 32.482 | 53.075 | Silver |
| 50 | Matthew James CLIFFE | United Kingdom | 14.930 | 38.144 | 53.074 | Silver |
| 51 | Zeqi YANG | Singapore | 16.398 | 36.193 | 52.591 | Silver |
| 52 | Yerdos ORDABAYEV | Kazakhstan | 20.921 | 31.572 | 52.493 | Silver |
| 53 | Frederick Robert William Meath MANNERS | United Kingdom | 17.898 | 34.542 | 52.44 | Silver |
| 54 | Jonathan LIN | New Zealand | 26.423 | 25.257 | 51.679 | Silver |
| 55 | Petr HOSEK | Czech Republic | 21.159 | 30.501 | 51.661 | Silver |
| 56 | Pornchai KAEWSAPSAK | Thailand | 14.586 | 35.859 | 50.445 | Silver |
| 57 | Assaf Avraham SHAPIRA | Israel | 19.610 | 30.628 | 50.238 | Silver |
| 58 | Zhivko Atanasov GEORGIEV | Bulgaria | 26.508 | 23.691 | 50.199 | Silver |
| 59 | Lorinc SARKANY | Hungary | 20.169 | 29.837 | 50.005 | Silver |
| 60 | Stefan Michael PUSCH | Germany | 14.908 | 35.053 | 49.961 | Silver |
| 61 | Teuku Mahfuzh Aufar KARI | Indonesia | 19.428 | 30.374 | 49.802 | Silver |
| 62 | Vasile GRAUR | Moldova | 26.640 | 23.153 | 49.793 | Silver |
| 63 | Bernardas MORKUNAS | Lithuania | 12.547 | 37.061 | 49.608 | Silver |
| 64 | Jong Soo YOON | Korea Republic | 10.165 | 39.100 | 49.265 | Silver |
| 65 | Kenneth BREWER | United States | 14.651 | 34.210 | 48.861 | Silver |
| 66 | Muhamad FAIZ | Indonesia | 12.228 | 36.543 | 48.770 | Silver |
| 67 | Ioan Teodor TROTUS | Romania | 12.031 | 36.713 | 48.744 | Silver |
| 68 | Alena VASKOVA | Belarus | 17.046 | 31.173 | 48.219 | Silver |
| 69 | Andi KIPPER | Estonia | 22.559 | 25.525 | 48.084 | Silver |
| 70 | Stephan PRIBITZER | Austria | 25.128 | 22.485 | 47.613 | Silver |
| 71 | Kartik RAMESH | Australia | 12.765 | 34.793 | 47.558 | Silver |
| 72 | Vlad Alexandru PUSCASU | Romania | 16.199 | 31.328 | 47.527 | Silver |
| 73 | Kaveh MATINKHOO | Iran | 15.477 | 31.912 | 47.388 | Silver |
| 74 | Chuan Zheng LEE | New Zealand | 21.221 | 25.880 | 47.101 | Silver |
| 75 | Thais Macedo Bezerra Terceiro JORGE | Brazil | 6.805 | 40.260 | 47.064 | Silver |
| 76 | Balint BALAZS | Hungary | 21.647 | 25.160 | 46.807 | Silver |
| 77 | Jan KOGOJ | Slovenia | 11.955 | 34.755 | 46.71 | Silver |
| 78 | Vincenzo GRANDE | Italy | 15.437 | 31.064 | 46.501 | Silver |
| 79 | Ionut Gabriel DUMITRU | Romania | 11.135 | 35.354 | 46.489 | Silver |
| 80 | Linh Bui LE | Vietnam | 12.571 | 33.874 | 46.445 | Silver |
| 81 | Christian OBERENDER | Germany | 14.951 | 31.469 | 46.420 | Silver |
| 82 | Kainar KAMALOV | Kyrgyzstan | 13.044 | 33.033 | 46.077 | Silver |
| 83 | Jan BITENC | Slovenia | 17.450 | 28.546 | 45.996 | Silver |
| 84 | Benjamin CHEN | Singapore | 16.318 | 29.592 | 45.909 | Silver |
| 85 | Matias Daniel Gomez ELIAS | Argentina | 15.446 | 30.324 | 45.771 | Silver |
| 86 | Oscar Carl Gunnar GRANBERG | Sweden | 23.490 | 22.188 | 45.677 | Silver |
| 87 | Techin CHULADESA | Thailand | 12.103 | 33.544 | 45.647 | Silver |
| 88 | Gabriel Eduardo Sanoja LOPEZ | Venezuela | 26.834 | 18.351 | 45.185 | Bronze |
| 89 | Mihails ARHANGELSKIS | Latvia | 7.063 | 37.904 | 44.967 | Bronze |
| 90 | Christian MARBOE | Denmark | 21.828 | 23.029 | 44.857 | Bronze |
| 91 | Derek Steven Hung-Che CHAN | United Kingdom | 10.785 | 34.012 | 44.797 | Bronze |
| 92 | Takashi HIROI | Japan | 7.035 | 37.491 | 44.526 | Bronze |
| 93 | Ayana BADRAKOVA | Kazakhstan | 16.875 | 27.297 | 44.172 | Bronze |
| 94 | Volodymyr TKACHENKO | Ukraine | 13.031 | 30.852 | 43.883 | Bronze |
| 95 | Rafael de Cesaris Araujo TAVARES | Brazil | 11.694 | 32.007 | 43.701 | Bronze |
| 96 | Shabnam SHARIFZADEH | Iran | 15.455 | 28.165 | 43.620 | Bronze |
| 97 | Florian LANGMANN | Austria | 11.869 | 31.661 | 43.529 | Bronze |
| 98 | Raoul ROSENTHAL | Netherlands | 24.573 | 18.952 | 43.525 | Bronze |
| 99 | Ahmet Selim HAN | Turkey | 14.401 | 28.972 | 43.373 | Bronze |


| 100 | Naru TANAKA | Japan | 6.453 | 36.910 | 43.363 | Bronze |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 101 | Vincentius Jeremy SUHARDI | Indonesia | 17.791 | 25.311 | 43.102 | Bronze |
| 102 | Jun Yan GOH | Malaysia | 25.190 | 17.864 | 43.054 | Bronze |
| 103 | Shotaro TSUNODA | Japan | 7.017 | 35.679 | 42.696 | Bronze |
| 104 | Taavi PUNGAS | Estonia | 14.557 | 28.097 | 42.654 | Bronze |
| 105 | Arshavir GHAHRAMANYAN | Armenia | 0.900 | 41.616 | 42.516 | Bronze |
| 106 | Kirill POLISCHUK | Ukraine | 8.118 | 34.367 | 42.485 | Bronze |
| 107 | Gonzalo Jose MUNAR | Argentina | 20.343 | 22.106 | 42.449 | Bronze |
| 108 | Guang Jun Joseph LIM | Singapore | 11.426 | 30.918 | 42.344 | Bronze |
| 109 | Andrew Brian CAIRNS | Ireland | 18.006 | 24.284 | 42.290 | Bronze |
| 110 | Lucia Domenica MEIER | Switzerland | 22.642 | 19.641 | 42.283 | Bronze |
| 111 | Thorbjørn Juul MORSING | Denmark | 24.159 | 17.954 | 42.112 | Bronze |
| 112 | Dauren KALIYEV | Kazakhstan | 18.433 | 23.598 | 42.031 | Bronze |
| 113 | Tsimafei BALOTNIK | Belarus | 15.347 | 26.017 | 41.364 | Bronze |
| 114 | Zijun (Jim) GE | Australia | 7.476 | 33.874 | 41.350 | Bronze |
| 115 | Zhanbolat ZHOLGELDIYEV | Kazakhstan | 14.752 | 26.473 | 41.225 | Bronze |
| 116 | Serdar ROZYYEV | Turkmenistan | 17.227 | 23.638 | 40.865 | Bronze |
| 117 | Shaina KHAN | Pakistan | 20.955 | 19.891 | 40.847 | Bronze |
| 118 | Petr JURIK | Czech Republic | 15.377 | 25.109 | 40.486 | Bronze |
| 119 | Olha BALABON | Ukraine | 6.926 | 33.471 | 40.398 | Bronze |
| 120 | Dan PENG | Canada | 14.376 | 25.672 | 40.048 | Bronze |
| 121 | WILLIAM | Indonesia | 8.977 | 30.489 | 39.466 | Bronze |
| 122 | Romāns ČAPLINSKIS | Latvia | 12.821 | 26.535 | 39.356 | Bronze |
| 123 | Liudmila KUSHNIR | Belarus | 4.124 | 34.946 | 39.071 | Bronze |
| 124 | Elise DUBOUE-DIJON | France | 13.223 | 25.577 | 38.800 | Bronze |
| 125 | Batyr GARLYYEV | Turkmenistan | 11.647 | 27.108 | 38.755 | Bronze |
| 126 | Chin Heng GAN | Singapore | 10.653 | 28.078 | 38.731 | Bronze |
| 127 | Henrik SOENSTEBY | Norway | 19.194 | 19.266 | 38.460 | Bronze |
| 128 | Immanuel Ilavarasan THOMAS | India | 7.641 | 30.614 | 38.255 | Bronze |
| 129 | Daniel Enrique Cardenas ARMAS | Venezuela | 17.315 | 20.688 | 38.003 | Bronze |
| 130 | Simone CALVELLO | Italy | 11.900 | 25.906 | 37.806 | Bronze |
| 131 | Thomas Ashton Christopher WONG | New Zealand | 15.165 | 22.590 | 37.755 | Bronze |
| 132 | Ivan OGIBALOV | Estonia | 20.033 | 17.698 | 37.731 | Bronze |
| 133 | Khursand YOROV | Tajikistan | 6.462 | 31.250 | 37.712 | Bronze |
| 134 | Ingrid Cristiana VREJA | Romania | 8.593 | 29.015 | 37.608 | Bronze |
| 135 | Ivanka Rosenova ZHIVKOVA | Bulgaria | 12.109 | 25.325 | 37.435 | Bronze |
| 136 | Taneli Toivo Hermanni RAJALA | Finland | 15.913 | 21.495 | 37.408 | Bronze |
| 137 | Muhamad Azri Muhamad MARICAN | Malaysia | 16.076 | 21.185 | 37.261 | Bronze |
| 138 | Gah Hung LEE | Malaysia | 13.741 | 23.358 | 37.098 | Bronze |
| 139 | Jorio Almino de Alencar Arrais MOTA | Brazil | 10.298 | 26.788 | 37.086 | Bronze |
| 140 | Michael James PLUNKETT | New Zealand | 9.372 | 27.179 | 36.551 | Bronze |
| 141 | Lubica KRAUSKOVA | Slovakia | 15.294 | 21.194 | 36.488 | Bronze |
| 142 | Nicholas MOULAF | Australia | 5.543 | 30.779 | 36.322 | Bronze |
| 143 | Jaroslav ZAK | United Kingdom | 8.125 | 28.067 | 36.191 | Bronze |
| 144 | Victor Lopez FERRANDO | Spain | 16.276 | 19.873 | 36.149 | Bronze |
| 145 | Hubert KALAUS | Austria | 13.146 | 22.585 | 35.731 | Bronze |
| 146 | Dogukan DIKMEN | Turkey | 4.730 | 30.941 | 35.672 | Bronze |
| 147 | Irena MATKOVIČ | Slovenia | 6.191 | 29.430 | 35.621 | Bronze |
| 148 | Kazuki YAMAGUCHI | Japan | 12.328 | 23.116 | 35.444 | Bronze |
| 149 | Anita PABANI | Pakistan | 15.947 | 18.986 | 34.933 | Bronze |
| 150 | Manuel Garcia RICARDO | Cuba | 10.006 | 24.846 | 34.852 | Bronze |
| 151 | Max HAFLIGER | Switzerland | 5.936 | 28.640 | 34.575 | Bronze |

$\left.\begin{array}{|l|l|l|l|l|l|l|}\hline 152 & \text { Sofia IZMAILOV } & \text { United States } & 12.278 & 22.193 & 34.471 & \text { Bronze } \\ \hline 153 & \text { Mathijs de JONG } & \text { Netherlands } & 17.322 & 17.121 & 34.443 & \text { Bronze } \\ \hline 154 & \text { Luciano Hector DI STEFANO } & \text { Argentina } & 12.951 & 21.413 & 34.364 & \text { Bronze } \\ \hline 155 & \text { Itamar Avraham David SHAMAI } & \text { Israel } & 8.463 & 25.672 & 34.135 & \text { Bronze } \\ \hline 156 & \text { Cristiana FANCIULLO } & \text { Italy } & 15.728 & 17.914 & 33.643 & \text { Bronze } \\ \hline 157 & \text { Muradov NURMUHAMMET } & \text { Turkmenistan } & 7.700 & 25.691 & 33.391 & \text { Bronze } \\ \hline 158 & \text { Pablo Gustavo LEVRAND } & \text { Argentina } & 11.167 & 22.168 & 33.335 & \text { Bronze } \\ \hline 159 & \text { Sergio Fonseca CHITICA } & \text { Mexico } & 12.978 & 20.035 & 33.013 & \text { Honor. Mention } \\ \hline 160 & \text { Roberta POCEVICIUTE } & \text { Lithuania } & 8.430 & 24.572 & 33.002 & \text { Honor. Mention } \\ \hline 161 & \text { Quentin LEFEBVRE } & \text { France } & 4.698 & 28.219 & 32.917 & \text { Honor. Mention } \\ \hline 162 & \text { Andreas FRUTIGER } & \text { Switzerland } & 17.922 & 14.839 & 32.761 & \text { Honor. Mention } \\ \hline 163 & \text { Manh Le DINH } & \text { Viennam } & 4.047 & 28.585 & 32.632 & \text { Honor. Mention } \\ \hline 164 & \text { Amirhady KAMKARAMOLI } & \text { Iran } & 9.323 & 23.252 & 32.575 & \text { Honor. Mention } \\ \hline 165 & \text { Geir Haakon BECKSTROEM } & \text { Norway } & 11.213 & 21.347 & 32.560 & \text { Honor. Mention } \\ \hline 166 & \text { Javzansuren NORVANCHIG } & \text { Mongolia } & 19.940 & 12.369 & 32.309 & \text { Honor. Mention } \\ \hline 167 & \text { Umed BOLTAEV } & \text { Tajikistan } & 6.581 & 25.623 & 32.204 & \text { Honor. Mention } \\ \hline 168 & \text { Sabyrbek ZHEENTAEV } & \text { Kyrgyzstan } & 11.125 & 21.073 & 32.198 & \text { Honor. Mention } \\ \hline 169 & \text { Jose Enrique Robles SOTO } & \text { Mexico } & 9.053 & 23.109 & 32.162 & \\ \hline 170 & \text { Vincenzo SPALLUTO } & \text { Italy } & 19.643 & 12.481 & 32.124 & \\ \hline 171 & \text { Juraj AHEL } & \text { Croatia } & 10.906 & 21.088 & 31.994 & \\ \hline 172 & \text { Dan Liraz LIDJI } & \text { Croatia } & 7.094 & 18.803 & 25.897 & \\ \hline 173 & \text { Christiaan Alwin DOUMA } & \text { } & \text { Netherlands } & 1179 & 16.564 & 25.743\end{array}\right]$

| 205 | Axel Nils Ola GOTTFRIES | Sweden | 10.125 | 14.801 | 24.927 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 206 | John Christopher JANETZKO | Canada | 4.758 | 20.104 | 24.862 |  |
| 207 | Johan Yuan WANG | Norway | 2.883 | 21.874 | 24.756 |  |
| 208 | Tina KANSTRUP | Denmark | 8.823 | 15.645 | 24.468 |  |
| 209 | Jose Ernando Sousa FILHO | Brazil | 2.863 | 21.546 | 24.409 |  |
| 210 | Juan Ivan GOMEZ-PERALTA | Mexico | 9.277 | 14.958 | 24.234 |  |
| 211 | Panagiotis PALANTAS | Greece | 5.106 | 18.826 | 23.932 |  |
| 212 | Grigoris KATSIOLIDIS | Cyprus | 12.632 | 10.737 | 23.369 |  |
| 213 | Charis Antonis ANTONIOU | Cyprus | 8.125 | 15.176 | 23.301 |  |
| 214 | Ioannis BOTIS | Greece | 7.950 | 15.092 | 23.042 |  |
| 215 | Grellan Jerome Kevin TUOHY | Ireland | 10.116 | 12.747 | 22.863 |  |
| 216 | Vanessa LOODTS | Belgium | 6.211 | 16.556 | 22.767 |  |
| 217 | Frederic COTTIER | Switzerland | 7.529 | 14.979 | 22.508 |  |
| 218 | Alexandru CARTALEANU | Moldova | 5.053 | 17.351 | 22.403 |  |
| 219 | Alberto Sanchez MOLERO | Spain | 9.554 | 12.339 | 21.893 |  |
| 220 | Shahzad IQBAL | Pakistan | 4.009 | 17.060 | 21.069 |  |
| 221 | Joseph Hernan Pena ECHEVARRIA | Peru | 4.056 | 16.917 | 20.973 |  |
| 222 | Battulga BYAMBASUREN | Mongolia | 7.648 | 13.250 | 20.898 |  |
| 223 | Leonid BIBIN | Moldova | 4.891 | 15.658 | 20.549 |  |
| 224 | David Van CAUWENBERGE | Belgium | 6.442 | 14.073 | 20.515 |  |
| 225 | Saidullo SULAYMONZODA | Tajikistan | 0.200 | 20.001 | 20.201 |  |
| 226 | Hamza Khan SHAHBAZI | Pakistan | 3.236 | 16.374 | 19.61 |  |
| 227 | Vesteinn SNAEBJARNARSON | Iceland | 8.010 | 11.492 | 19.502 |  |
| 228 | Raul Joao de Sousa PEREIRA | Portugal | 1.700 | 17.775 | 19.475 |  |
| 229 | Jānis JERMAKS | Latvia | 5.723 | 12.879 | 18.602 |  |
| 230 | Carlos Leonel Ahumada MANUEL | Mexico | 4.001 | 14.163 | 18.164 |  |
| 231 | Khusrav OLIMI | Tajikistan | 7.695 | 9.478 | 17.174 |  |
| 232 | Christoffer NORN | Denmark | 6.830 | 9.317 | 16.147 |  |
| 233 | Camilla ESPEDAL | Norway | 6.282 | 8.980 | 15.262 |  |
| 234 | Stefan Dimitrov KADIYSKY | Bulgaria | 3.777 | 11.429 | 15.206 |  |
| 235 | Linus Benjamin TÖRNQVIST | Finland | 5.883 | 8.921 | 14.803 |  |
| 236 | Jorn WALSCHARTS | Belgium | 6.200 | 8.248 | 14.448 |  |
| 237 | Mari Liisa TEINILÄ | Finland | 6.281 | 8.021 | 14.302 |  |
| 238 | Gergana Sasheva VALCHEVA | Bulgaria | 0.930 | 13.367 | 14.297 |  |
| 239 | Rui Emanuel Ferreira da SILVA | Portugal | 3.864 | 9.715 | 13.579 |  |
| 240 | Joaquin GRASSI | Uruguay | 3.691 | 9.487 | 13.178 |  |
| 241 | Rui Filipe Goncalves APOSTOLO | Portugal | 4.770 | 7.717 | 12.487 |  |
| 242 | Memmed MIRZEYEV | Azerbaijan | 12.458 | 0.000 | 12.458 |  |
| 243 | Argyroula LAVI | Greece | 7.598 | 4.483 | 12.081 |  |
| 244 | Nicat MUSAYEV | Azerbaijan | 9.665 | 0.000 | 9.665 |  |
| 245 | Sebastian BARCARDAL | Uruguay | 2.326 | 7.189 | 9.515 |  |
| 246 | Rui Filipe Lebres LOPES | Portugal | 1.450 | 7.862 | 9.312 |  |
| 247 | Uyanga DAGVADORJ | Mongolia | 2.093 | 6.712 | 8.805 |  |
| 248 | Osamah Altaib SAFWAN | Saudi Arabia | 0.450 | 7.233 | 7.683 |  |
| 249 | Diego OTERO | Uruguay | 3.388 | 4.266 | 7.655 |  |
| 250 | Sebastian FIAMENE | Uruguay | 2.326 | 4.011 | 6.336 |  |
| 251 | Mohammed Abdullah ALGASIM | Saudi Arabia | 1.960 | 4.323 | 6.283 |  |
| 252 | Ibrahim Abdullah Ba JAAFR | Saudi Arabia | 1.928 | 3.844 | 5.772 |  |
| 253 | Ataallah Naif ALHARBI | Saudi Arabia | 1.150 | 4.590 | 5.740 |  |
| 254 | Abdulla AHMADOV | Azerbaijan | 5.365 | 0.000 | 5.365 |  |
| 255 | Sohbet HOJAMUHAMMEDOV | Turkmenistan | 0.000 | 4.352 | 4.352 |  |
| 256 | Orxan RZAYEV | Azerbaijan | 0.233 | 0.000 | 0.233 |  |

## DETAILED RESULTS PER COUNTRY

| Country | Name | P_1 | P_2 | T_1 | T_2 | T_3 | T_4 | T_5 | T_6 | T_7 | T_8 | Practice | Theory | Total | Rank | Medal |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Argentina | Matias Daniel Gomez ELIAS | 4.963 | 10.483 | 5.571 | 3.636 | 4.846 | 5.024 | 3.200 | 2.838 | 3.103 | 2.105 | 15.446 | 30.324 | 45.771 | 85 | Silver |
|  | Gonzalo Jose MUNAR | 2.093 | 18.250 | 2.286 | 4.000 | 3.769 | 3.840 | 3.500 | 3.216 | 0.569 | 0.926 | 20.343 | 22.106 | 42.449 | 107 | Bronze |
|  | Luciano Hector DI STEFANO | 8.951 | 4.000 | 5.000 | 0.727 | 4.128 | 3.520 | 1.700 | 5.108 | 0.724 | 0.505 | 12.951 | 21.413 | 34.364 | 154 | Bronze |
|  | Pablo Gustavo LEVRAND | 6.167 | 5.000 | 3.857 | 6.182 | 3.410 | 5.120 | 0.000 | 0.946 | 0.000 | 2.653 | 11.167 | 22.168 | 33.335 | 158 | Bronze |
| Armenia | Samvel BARDAKHCHYAN | 13.605 | 1.400 | 6.714 | 7.091 | 7.000 | 3.456 | 6.200 | 2.270 | 7.500 | 1.642 | 15.005 | 41.874 | 56.878 | 34 | Silver |
|  | Narek DSHKHUNYN | 1.395 | 2.950 | 7.000 | 8.000 | 7.000 | 5.888 | 6.700 | 4.541 | 7.500 | 2.147 | 4.345 | 48.776 | 53.121 | 48 | Silver |
|  | Arshavir GHAHRAMANYAN | 0.000 | 0.900 | 7.000 | 6.182 | 6.641 | 2.080 | 6.700 | 1.892 | 7.500 | 3.621 | 0.900 | 41.616 | 42.516 | 105 | Bronze |
| Australia | Andrew TULLOCH | 8.721 | 9.583 | 6.286 | 5.818 | 6.282 | 4.000 | 0.200 | 4.919 | 4.966 | 4.253 | 18.304 | 36.723 | 55.027 | 42 | Silver |
|  | Kartik RAMESH | 7.255 | 5.510 | 5.857 | 3.455 | 4.128 | 5.280 | 2.800 | 4.919 | 4.397 | 3.958 | 12.765 | 34.793 | 47.558 | 71 | Silver |
|  | Zijun (Jim) GE | 2.209 | 5.267 | 4.143 | 4.909 | 4.487 | 5.280 | 2.100 | 4.919 | 3.362 | 4.674 | 7.476 | 33.874 | 41.350 | 114 | Bronze |
|  | Nicholas MOULAF | 2.093 | 3.450 | 5.429 | 4.182 | 5.205 | 2.208 | 2.100 | 5.297 | 1.810 | 4.547 | 5.543 | 30.779 | 36.322 | 142 | Bronze |
| Austria | Alexander PUCHHAMMER | 8.893 | 11.700 | 4.714 | 4.000 | 5.026 | 4.000 | 4.200 | 5.676 | 1.034 | 3.832 | 20.593 | 32.482 | 53.075 | 49 | Silver |
|  | Stephan PRIBITZER | 19.111 | 6.017 | 3.571 | 3.273 | 4.128 | 3.040 | 1.700 | 4.162 | 1.810 | 0.800 | 25.128 | 22.485 | 47.613 | 70 | Silver |
|  | Florian LANGMANN | 4.419 | 7.450 | 5.286 | 2.000 | 3.410 | 2.880 | 3.600 | 4.730 | 6.766 | 2.989 | 11.869 | 31.661 | 43.529 | 97 | Bronze |
|  | Hubert KALAUS | 6.746 | 6.400 | 3.286 | 0.364 | 4.128 | 1.920 | 1.700 | 1.514 | 7.190 | 2.484 | 13.146 | 22.585 | 35.731 | 145 | Bronze |
| Azerbaijan | Memmed MIRZEYEV | 2.558 | 9.900 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 12.458 | 0.000 | 12.458 | 242 |  |
|  | Nicat MUSAYEV | 0.465 | 9.200 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 9.665 | 0.000 | 9.665 | 244 |  |
|  | Abdulla AHMADOV | 0.465 | 4.900 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 5.365 | 0.000 | 5.365 | 254 |  |
|  | Orxan RZAYEV | 0.233 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.233 | 0.000 | 0.233 | 256 |  |
| Belarus | Dzianis HRAMAZDOU | 8.605 | 13.900 | 5.857 | 5.636 | 4.308 | 6.880 | 3.700 | 4.162 | 0.414 | 2.821 | 22.505 | 33.778 | 56.283 | 37 | Silver |
|  | Alena VASKOVA | 8.296 | 8.750 | 6.429 | 4.727 | 3.949 | 5.600 | 2.800 | 3.973 | 1.759 | 1.937 | 17.046 | 31.173 | 48.219 | 68 | Silver |
|  | Tsimafei BALOTNIK | 11.447 | 3.900 | 4.000 | 3.273 | 5.205 | 4.160 | 3.500 | 3.500 | 0.569 | 1.811 | 15.347 | 26.017 | 41.364 | 113 | Bronze |
|  | Liudmila KUSHNIR | 2.674 | 1.450 | 6.714 | 5.091 | 4.846 | 4.000 | 1.200 | 5.297 | 2.534 | 5.263 | 4.124 | 34.946 | 39.071 | 123 | Bronze |


| Belgium | Quentin HISETTE | 5.642 | 9.800 | 4.143 | 0.727 | 0.359 | 1.600 | 0.700 | 1.324 | 0.155 | 0.800 | 15.442 | 9.809 | 25.251 | 201 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Vanessa LOODTS | 6.211 | 0.000 | 5.286 | 2.909 | 0.538 | 0.544 | 1.200 | 3.784 | 0.569 | 1.726 | 6.211 | 16.556 | 22.767 | 216 |  |
|  | David Van CAUWENBERGE | 3.442 | 3.000 | 3.286 | 1.091 | 1.436 | 2.112 | 1.200 | 3.405 | 0.828 | 0.716 | 6.442 | 14.073 | 20.515 | 224 |  |
|  | Jorn WALSCHARTS | 0.000 | 6.200 | 3.143 | 0.091 | 0.000 | 2.176 | 0.000 | 2.838 | 0.000 | 0.000 | 6.200 | 8.248 | 14.448 | 236 |  |
| Brazil | Thais Macedo Bezerra Terceiro JORGE | 3.605 | 3.200 | 5.000 | 5.091 | 5.205 | 4.160 | 5.000 | 5.297 | 7.138 | 3.368 | 6.805 | 40.260 | 47.064 | 75 | Silver |
|  | Rafael de Cesaris Araujo TAVARES | 1.744 | 9.950 | 5.571 | 5.091 | 5.026 | 4.800 | 1.200 | 4.351 | 4.241 | 1.726 | 11.694 | 32.007 | 43.701 | 95 | Bronze |
|  | Jorio Almino de Alencar Arrais MOTA | 7.698 | 2.600 | 5.571 | 1.091 | 5.205 | 4.160 | 1.900 | 6.054 | 0.828 | 1.979 | 10.298 | 26.788 | 37.086 | 139 | Bronze |
|  | Jose Ernando Sousa FILHO | 1.163 | 1.700 | 4.571 | 2.545 | 3.949 | 3.776 | 1.700 | 4.162 | 0.000 | 0.842 | 2.863 | 21.546 | 24.409 | 209 |  |
| Bulgaria | Zhivko Atanasov GEORGIEV | 9.158 | 17.350 | 1.429 | 2.364 | 4.487 | 4.608 | 2.700 | 4.635 | 0.310 | 3.158 | 26.508 | 23.691 | 50.199 | 58 | Silver |
|  | Ivanka Rosenova ZHIVKOVA | 2.209 | 9.900 | 4.857 | 2.000 | 6.103 | 2.720 | 2.500 | 3.878 | 2.172 | 1.095 | 12.109 | 25.325 | 37.435 | 135 | Bronze |
|  | Stefan Dimitrov KADIYSKY | 2.977 | 0.800 | 2.000 | 0.364 | 3.410 | 1.920 | 2.500 | 0.000 | 0.983 | 0.253 | 3.777 | 11.429 | 15.206 | 234 |  |
|  | Gergana Sasheva VALCHEVA | 0.930 | 0.000 | 5.286 | 1.818 | 0.718 | 2.464 | 1.000 | 2.081 | 0.000 | 0.000 | 0.930 | 13.367 | 14.297 | 238 |  |
| Canada | Hyeonjin BAE | 12.307 | 14.333 | 5.286 | 5.273 | 4.487 | 1.504 | 3.500 | 4.351 | 2.793 | 4.168 | 26.640 | 31.362 | 58.003 | 29 | Gold |
|  | Dan PENG | 10.476 | 3.900 | 5.143 | 4.545 | 5.744 | 1.574 | 1.700 | 3.595 | 0.466 | 2.905 | 14.376 | 25.672 | 40.048 | 120 | Bronze |
|  | Shervin GHAFOURITABRIZI | 4.208 | 1.110 | 6.714 | 2.182 | 5.923 | 3.200 | 1.000 | 1.703 | 1.138 | 0.674 | 5.318 | 22.533 | 27.852 | 192 |  |
|  | John Christopher JANETZKO | 3.558 | 1.200 | 4.714 | 0.182 | 4.487 | 0.320 | 2.700 | 2.459 | 3.052 | 2.189 | 4.758 | 20.104 | 24.862 | 206 |  |
| China | Lei XU | 3.721 | 16.050 | 7.000 | 8.000 | 7.000 | 7.200 | 5.900 | 6.811 | 7.190 | 7.200 | 19.771 | 56.300 | 76.071 | 1 | Gold |
|  | Yuan FANG | 9.535 | 16.233 | 6.714 | 8.000 | 6.462 | 6.400 | 7.000 | 5.108 | 2.172 | 5.684 | 25.768 | 47.541 | 73.309 | 2 | Gold |
|  | Zi-yang ZHANG | 14.047 | 6.350 | 5.571 | 5.818 | 5.923 | 6.720 | 6.200 | 6.243 | 7.190 | 6.526 | 20.397 | 50.192 | 70.588 | 5 | Gold |
|  | Le YANG | 4.279 | 9.450 | 6.714 | 8.000 | 6.641 | 5.728 | 5.100 | 7.000 | 6.921 | 3.032 | 13.729 | 49.136 | 62.865 | 14 | Gold |
| Chinese <br> Taipei | Ying Yu HO | 6.485 | 16.900 | 6.714 | 7.636 | 6.103 | 5.440 | 5.700 | 4.919 | 6.672 | 3.832 | 23.385 | 47.016 | 70.401 | 6 | Gold |
|  | Wei-Lun HUANG | 15.669 | 7.467 | 6.143 | 5.455 | 4.487 | 6.560 | 5.100 | 5.676 | 4.267 | 6.526 | 23.136 | 44.214 | 67.349 | 11 | Gold |
|  | Kai-Jui CHANG | 10.925 | 6.267 | 5.286 | 5.818 | 3.949 | 5.280 | 2.900 | 5.865 | 5.431 | 5.474 | 17.192 | 40.002 | 57.194 | 32 | Silver |
|  | Frank Meng LIN | 7.624 | 10.550 | 6.714 | 5.818 | 4.846 | 4.160 | 5.100 | 4.919 | 4.190 | 1.853 | 18.174 | 37.600 | 55.774 | 38 | Silver |


| Croatia | Juraj AHEL | 3.256 | 7.650 | 5.571 | 2.455 | 2.692 | 1.120 | 1.200 | 3.973 | 0.414 | 3.663 | 10.906 | 21.088 | 31.994 | 171 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Ivana BREKALO | 2.385 | 4.500 | 6.143 | 1.455 | 4.487 | 3.360 | 2.800 | 3.784 | 0.310 | 1.474 | 6.885 | 23.812 | 30.698 | 178 |  |
|  | Ivan PREPOLEC | 6.894 | 3.783 | 4.143 | 1.091 | 4.308 | 6.240 | 2.000 | 0.568 | 0.000 | 0.000 | 10.678 | 18.349 | 29.027 | 189 |  |
|  | Ivan BARUN | 4.311 | 0.860 | 6.143 | 4.727 | 3.590 | 4.160 | 0.000 | 0.000 | 1.190 | 0.000 | 5.171 | 19.810 | 24.980 | 204 |  |
| Cuba | Manuel Garcia RICARDO | 3.140 | 6.867 | 2.000 | 3.273 | 4.487 | 6.656 | 3.700 | 4.730 | 0.000 | 0.000 | 10.006 | 24.846 | 34.852 | 150 | Bronze |
| Cyprus | Michalis ROSSIDES | 11.939 | 2.610 | 3.286 | 2.727 | 4.487 | 1.862 | 1.000 | 1.892 | 0.310 | 0.000 | 14.549 | 15.565 | 30.114 | 182 |  |
|  | Konstantinos HADJIPETROU | 8.372 | 1.500 | 4.429 | 3.636 | 2.872 | 3.200 | 1.300 | 0.568 | 0.000 | 0.674 | 9.872 | 16.678 | 26.550 | 197 |  |
|  | Grigoris KATSIOLIDIS | 11.066 | 1.567 | 4.286 | 1.455 | 1.436 | 0.480 | 1.000 | 2.081 | 0.000 | 0.000 | 12.632 | 10.737 | 23.369 | 212 |  |
|  | Charis Antonis ANTONIOU | 2.558 | 5.567 | 4.143 | 0.818 | 2.333 | 2.528 | 2.200 | 3.027 | 0.000 | 0.126 | 8.125 | 15.176 | 23.301 | 213 |  |
| Czech Republic | Ctirad CERVINKA | 17.386 | 10.300 | 5.857 | 6.182 | 3.410 | 2.880 | 1.000 | 3.027 | 1.345 | 3.747 | 27.686 | 27.448 | 55.134 | 41 | Silver |
|  | Petr HOSEK | 5.476 | 15.683 | 6.143 | 0.000 | 4.128 | 4.736 | 2.000 | 4.730 | 5.017 | 3.747 | 21.159 | 30.501 | 51.661 | 55 | Silver |
|  | Petr JURIK | 13.177 | 2.200 | 5.143 | 2.545 | 5.385 | 5.376 | 0.200 | 3.595 | 0.466 | 2.400 | 15.377 | 25.109 | 40.486 | 118 | Bronze |
|  | Petr STADLBAUER | 3.930 | 7.500 | 1.429 | 0.000 | 2.333 | 2.560 | 2.900 | 2.838 | 0.828 | 0.716 | 11.430 | 13.603 | 25.033 | 202 |  |
| Denmark | Christian MARBOE | 9.278 | 12.550 | 5.857 | 2.091 | 2.692 | 3.840 | 1.000 | 3.973 | 0.207 | 3.368 | 21.828 | 23.029 | 44.857 | 90 | Bronze |
|  | Thorbjørn Juul MORSING | 10.659 | 13.500 | 4.286 | 0.727 | 4.846 | 2.560 | 1.000 | 3.784 | 0.414 | 0.337 | 24.159 | 17.954 | 42.112 | 111 | Bronze |
|  | Tina KANSTRUP | 3.023 | 5.800 | 4.286 | 1.164 | 1.974 | 1.600 | 2.000 | 1.135 | 1.086 | 2.400 | 8.823 | 15.645 | 24.468 | 208 |  |
|  | Christoffer NORN | 6.830 | 0.000 | 1.571 | 0.727 | 0.718 | 2.886 | 1.900 | 1.514 | 0.000 | 0.000 | 6.830 | 9.317 | 16.147 | 232 |  |
| Estonia | Andres LAAN | 9.955 | 8.800 | 6.143 | 2.364 | 5.744 | 4.800 | 5.200 | 3.973 | 6.103 | 3.242 | 18.755 | 37.569 | 56.324 | 36 | Silver |
|  | Andi KIPPER | 12.059 | 10.500 | 4.714 | 0.909 | 5.026 | 4.480 | 0.500 | 3.784 | 5.017 | 1.095 | 22.559 | 25.525 | 48.084 | 69 | Silver |
|  | Taavi PUNGAS | 3.907 | 10.650 | 5.429 | 5.455 | 5.205 | 1.760 | 2.200 | 4.730 | 0.414 | 2.905 | 14.557 | 28.097 | 42.654 | 104 | Bronze |
|  | Ivan OGIBALOV | 11.733 | 8.300 | 4.429 | 1.091 | 4.308 | 1.120 | 0.700 | 3.784 | 1.552 | 0.716 | 20.033 | 17.698 | 37.731 | 132 | Bronze |
| Finland | Taneli Toivo Hermanni RAJALA | 6.047 | 9.867 | 5.571 | 1.818 | 3.949 | 3.136 | 2.400 | 2.649 | 0.414 | 1.558 | 15.913 | 21.495 | 37.408 | 136 | Bronze |
|  | Janne Valo Verner HENRIKSSON | 8.605 | 6.200 | 3.857 | 0.364 | 1.615 | 3.040 | 1.000 | 1.324 | 0.724 | 0.000 | 14.805 | 11.925 | 26.729 | 196 |  |
|  | Linus Benjamin TÖRNQVIST | 3.083 | 2.800 | 3.286 | 0.182 | 0.000 | 0.480 | 1.000 | 3.973 | 0.000 | 0.000 | 5.883 | 8.921 | 14.803 | 235 |  |
|  | Mari Liisa TEINILÄ | 5.381 | 0.900 | 0.857 | 0.727 | 1.436 | 1.920 | 1.000 | 2.081 | 0.000 | 0.000 | 6.281 | 8.021 | 14.302 | 237 |  |
| France | Simon GOURDIN-BERTIN | 9.607 | 17.850 | 6.143 | 6.909 | 6.641 | 6.080 | 4.500 | 5.486 | 0.517 | 4.253 | 27.457 | 40.529 | 67.986 | 9 | Gold |
|  | Elise DUBOUE-DIJON | 4.613 | 8.610 | 5.571 | 2.909 | 6.282 | 5.120 | 2.000 | 1.514 | 1.086 | 1.095 | 13.223 | 25.577 | 38.800 | 124 | Bronze |
|  | Quentin LEFEBVRE | 4.698 | 0.000 | 5.571 | 4.000 | 6.641 | 3.648 | 1.200 | 4.541 | 1.397 | 1.221 | 4.698 | 28.219 | 32.917 | 161 | HM |
|  | Benjamin BOUSQUET | 8.721 | 1.350 | 3.857 | 1.818 | 4.846 | 1.702 | 2.000 | 3.595 | 1.034 | 1.516 | 10.071 | 20.369 | 30.440 | 179 |  |


| Germany | Dimitry Ur'evic LOUTCHKO | 13.796 | 12.317 | 5.000 | 7.818 | 5.564 | 4.768 | 7.000 | 4.919 | 6.983 | 2.063 | 26.113 | 44.115 | 70.228 | 7 | Gold |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Philipp Albert STEININGER | 17.707 | 13.750 | 5.857 | 4.000 | 5.564 | 5.280 | 1.000 | 3.595 | 1.241 | 4.084 | 31.457 | 30.621 | 62.078 | 16 | Gold |
|  | Stefan Michael PUSCH | 3.674 | 11.233 | 6.143 | 4.364 | 4.487 | 4.960 | 3.000 | 4.919 | 1.707 | 5.474 | 14.908 | 35.053 | 49.961 | 60 | Silver |
|  | Christian OBERENDER | 7.851 | 7.100 | 4.571 | 4.545 | 4.128 | 6.720 | 1.800 | 4.351 | 0.931 | 4.421 | 14.951 | 31.469 | 46.420 | 81 | Silver |
| Greece | Sotirios CHRISTODOULOU | 0.233 | 15.700 | 4.429 | 3.273 | 3.410 | 0.000 | 0.200 | 1.135 | 0.000 | 1.642 | 15.933 | 14.089 | 30.021 | 184 |  |
|  | Panagiotis PALANTAS | 1.163 | 3.943 | 5.286 | 2.000 | 1.974 | 0.320 | 5.500 | 1.135 | 0.000 | 2.611 | 5.106 | 18.826 | 23.932 | 211 |  |
|  | loannis BOTIS | 0.000 | 7.950 | 5.429 | 0.364 | 5.923 | 0.000 | 0.200 | 1.703 | 0.000 | 1.474 | 7.950 | 15.092 | 23.042 | 214 |  |
|  | Argyroula LAVI | 0.698 | 6.900 | 0.857 | 1.091 | 0.359 | 0.870 | 0.000 | 0.000 | 0.000 | 1.305 | 7.598 | 4.483 | 12.080 | 243 |  |
| Hungary | Gyula PALFY | 3.953 | 15.200 | 5.286 | 6.909 | 4.487 | 4.320 | 1.700 | 6.054 | 7.293 | 3.663 | 19.153 | 39.712 | 58.866 | 25 | Gold |
|  | Attila LOVAS | 12.400 | 14.000 | 5.286 | 0.000 | 4.487 | 6.560 | 3.500 | 4.730 | 0.828 | 1.558 | 26.400 | 26.948 | 53.348 | 47 | Silver |
|  | Lorinc SARKANY | 6.019 | 14.150 | 3.143 | 4.727 | 6.462 | 4.480 | 3.500 | 4.351 | 0.310 | 2.863 | 20.169 | 29.837 | 50.005 | 59 | Silver |
|  | Balint BALAZS | 8.347 | 13.300 | 5.286 | 1.091 | 4.487 | 1.216 | 2.800 | 4.730 | 0.414 | 5.137 | 21.647 | 25.160 | 46.807 | 76 | Silver |
| Iceland | Andri Vilberg ORRASON | 2.558 | 5.000 | 6.286 | 4.000 | 4.846 | 3.936 | 0.000 | 2.649 | 0.828 | 1.053 | 7.558 | 23.597 | 31.155 | 176 |  |
|  | Hordur Freyr YNGVASON | 9.179 | 0.000 | 4.143 | 0.000 | 6.282 | 2.016 | 0.700 | 1.892 | 0.310 | 1.221 | 9.179 | 16.564 | 25.743 | 199 |  |
|  | Karl NJALSSON | 6.299 | 1.600 | 4.000 | 0.000 | 4.308 | 3.424 | 0.700 | 2.270 | 0.828 | 1.600 | 7.899 | 17.130 | 25.029 | 203 |  |
|  | Vesteinn SNAEBJARNARSON | 0.000 | 8.010 | 1.714 | 1.091 | 2.872 | 2.560 | 0.500 | 1.703 | 0.000 | 1.053 | 8.010 | 11.492 | 19.502 | 227 |  |
| India | Sumit SOMANI | 2.791 | 13.400 | 6.000 | 7.636 | 4.487 | 6.400 | 3.400 | 6.054 | 4.707 | 4.884 | 16.191 | 43.569 | 59.759 | 22 | Gold |
|  | Soham MEHTA | 8.561 | 5.400 | 6.714 | 6.000 | 5.923 | 5.760 | 5.100 | 5.865 | 5.845 | 4.589 | 13.961 | 45.797 | 59.757 | 23 | Gold |
|  | Vikas PRAJAPATI | 1.814 | 12.000 | 6.429 | 8.000 | 4.846 | 6.560 | 3.200 | 6.243 | 2.690 | 2.063 | 13.814 | 40.031 | 53.845 | 46 | Silver |
|  | Immanuel Ilavarasan THOMAS | 5.891 | 1.750 | 6.429 | 7.455 | 6.282 | 1.280 | 1.900 | 4.351 | 0.517 | 2.400 | 7.641 | 30.614 | 38.255 | 128 | Bronze |
| Indonesia | Teuku Mahfuzh Aufar KARI | 2.728 | 16.700 | 5.429 | 5.818 | 5.205 | 3.200 | 1.700 | 2.932 | 3.310 | 2.779 | 19.428 | 30.374 | 49.802 | 61 | Silver |
|  | Muhamad FAIZ | 10.228 | 2.000 | 6.714 | 5.636 | 5.923 | 3.680 | 2.100 | 5.486 | 1.655 | 5.347 | 12.228 | 36.543 | 48.770 | 66 | Silver |
|  | Vincentius Jeremy SUHARDI | 3.008 | 14.783 | 4.571 | 3.455 | 4.487 | 4.000 | 2.000 | 2.838 | 0.466 | 3.495 | 17.791 | 25.311 | 43.102 | 101 | Bronze |
|  | WILLIAM | 6.927 | 2.050 | 4.857 | 6.545 | 5.923 | 4.704 | 1.300 | 3.973 | 1.966 | 1.221 | 8.977 | 30.489 | 39.466 | 121 | Bronze |
| Iran | Ehsan SHABANI | 11.640 | 17.000 | 6.143 | 2.909 | 4.128 | 3.840 | 3.900 | 4.919 | 2.017 | 0.926 | 28.640 | 28.783 | 57.423 | 31 | Gold |
|  | Kaveh MATINKHOO | 6.427 | 9.050 | 5.000 | 7.273 | 4.487 | 2.880 | 4.000 | 4.351 | 0.931 | 2.989 | 15.477 | 31.912 | 47.388 | 73 | Silver |
|  | Shabnam SHARIFZADEH | 8.605 | 6.850 | 5.286 | 4.364 | 4.128 | 3.040 | 4.500 | 4.351 | 0.517 | 1.979 | 15.455 | 28.165 | 43.620 | 96 | Bronze |
|  | Amirhady KAMKARAMOLI | 3.023 | 6.300 | 5.429 | 3.091 | 3.410 | 3.680 | 0.000 | 3.216 | 0.931 | 3.495 | 9.323 | 23.252 | 32.575 | 164 | HM |


| Ireland | Andrew Brian CAIRNS | 3.256 | 14.750 | 2.714 | 5.818 | 4.128 | 3.520 | 2.000 | 3.216 | 1.034 | 1.853 | 18.006 | 24.284 | 42.290 | 109 | Bronze |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Martina FEYZRAKHMANOVA | 3.442 | 3.150 | 4.714 | 4.909 | 4.846 | 3.136 | 1.400 | 2.838 | 1.319 | 0.337 | 6.592 | 23.499 | 30.091 | 183 |  |
|  | Patrick Michael O'SULLIVAN | 1.860 | 5.233 | 4.857 | 3.273 | 4.487 | 2.720 | 1.200 | 1.703 | 0.310 | 0.253 | 7.094 | 18.803 | 25.897 | 198 |  |
|  | Grellan Jerome Kevin TUOHY | 3.256 | 6.860 | 3.857 | 0.182 | 2.692 | 0.736 | 1.000 | 1.703 | 0.724 | 1.853 | 10.116 | 12.747 | 22.863 | 215 |  |
| Israel | Assaf Avraham SHAPIRA | 8.210 | 11.400 | 6.714 | 7.636 | 4.308 | 4.320 | 3.600 | 1.986 | 0.000 | 2.063 | 19.610 | 30.628 | 50.238 | 57 | Silver |
|  | Itamar Avraham David SHAMAI | 2.163 | 6.300 | 5.143 | 6.545 | 5.923 | 4.096 | 1.000 | 2.459 | 0.000 | 0.505 | 8.463 | 25.672 | 34.135 | 155 | Bronze |
|  | Dan Liraz LIDJI | 8.140 | 2.483 | 3.857 | 2.182 | 6.282 | 0.480 | 2.500 | 3.405 | 2.121 | 0.505 | 10.623 | 21.332 | 31.955 | 172 |  |
|  | Haleluya SAGIT | 11.433 | 2.950 | 3.857 | 1.091 | 3.949 | 2.560 | 0.900 | 2.459 | 0.000 | 1.011 | 14.383 | 15.827 | 30.209 | 181 |  |
| Italy | Vincenzo GRANDE | 8.837 | 6.600 | 5.286 | 6.727 | 4.846 | 4.896 | 3.400 | 2.838 | 1.345 | 1.726 | 15.437 | 31.064 | 46.501 | 78 | Silver |
|  | Simone CALVELLO | 4.650 | 7.250 | 3.571 | 3.636 | 4.487 | 3.200 | 2.700 | 5.297 | 1.034 | 1.979 | 11.900 | 25.906 | 37.806 | 130 | Bronze |
|  | Cristiana FANCIULLO | 11.195 | 4.533 | 6.429 | 0.000 | 3.410 | 3.840 | 0.000 | 2.838 | 0.724 | 0.674 | 15.728 | 17.914 | 33.643 | 156 | Bronze |
|  | Vincenzo SPALLUTO | 7.093 | 12.550 | 1.143 | 1.091 | 2.333 | 3.040 | 1.600 | 0.946 | 2.328 | 0.000 | 19.643 | 12.481 | 32.124 | 170 |  |
| Japan | Takashi HIROI | 5.475 | 1.560 | 6.143 | 2.545 | 4.487 | 5.440 | 1.800 | 4.541 | 6.724 | 5.811 | 7.035 | 37.491 | 44.526 | 92 | Bronze |
|  | Naru TANAKA | 4.853 | 1.600 | 6.429 | 4.182 | 6.282 | 2.720 | 4.500 | 5.486 | 2.679 | 4.632 | 6.453 | 36.910 | 43.363 | 100 | Bronze |
|  | Shotaro TSUNODA | 6.217 | 0.800 | 5.857 | 8.000 | 6.641 | 3.840 | 1.700 | 4.824 | 1.448 | 3.368 | 7.017 | 35.679 | 42.696 | 103 | Bronze |
|  | Kazuki YAMAGUCHI | 9.778 | 2.550 | 6.571 | 2.182 | 3.769 | 1.536 | 2.500 | 3.595 | 0.310 | 2.653 | 12.328 | 23.116 | 35.444 | 148 | Bronze |
| Kazakhstan | Yerdos ORDABAYEV | 13.721 | 7.200 | 6.143 | 5.818 | 7.000 | 4.256 | 2.100 | 3.973 | 0.724 | 1.558 | 20.921 | 31.572 | 52.493 | 52 | Silver |
|  | Ayana BADRAKOVA | 4.975 | 11.900 | 5.000 | 7.091 | 5.923 | 4.320 | 0.000 | 3.405 | 0.000 | 1.558 | 16.875 | 27.297 | 44.172 | 93 | Bronze |
|  | Dauren KALIYEV | 10.066 | 8.367 | 1.714 | 1.091 | 2.333 | 6.336 | 4.100 | 3.973 | 2.534 | 1.516 | 18.433 | 23.598 | 42.031 | 112 | Bronze |
|  | Zhanbolat ZHOLGELDIYEV | 14.302 | 0.450 | 4.357 | 2.182 | 4.308 | 2.880 | 0.800 | 4.257 | 5.121 | 2.568 | 14.752 | 26.473 | 41.225 | 115 | Bronze |
| Korea <br> Republic | Jae Soo KIM | 19.000 | 16.000 | 5.857 | 5.636 | 6.641 | 3.520 | 1.800 | 5.486 | 0.517 | 5.263 | 35.000 | 34.721 | 69.721 | 8 | Gold |
|  | Tae Gon OH | 6.568 | 16.150 | 6.143 | 8.000 | 4.487 | 4.800 | 6.200 | 6.432 | 5.007 | 3.958 | 22.718 | 45.027 | 67.745 | 10 | Gold |
|  | Chang Ho LEE | 3.558 | 18.750 | 6.714 | 8.000 | 4.487 | 3.200 | 1.600 | 5.865 | 4.241 | 3.495 | 22.308 | 37.602 | 59.911 | 20 | Gold |
|  | Jong Soo YOON | 3.755 | 6.410 | 6.429 | 6.364 | 5.923 | 2.400 | 5.000 | 4.351 | 5.897 | 2.737 | 10.165 | 39.100 | 49.265 | 64 | Silver |
| Kyrgyzstan | Kainar KAMALOV | 7.501 | 5.543 | 5.571 | 3.818 | 3.231 | 4.736 | 5.500 | 2.649 | 6.517 | 1.011 | 13.044 | 33.033 | 46.077 | 82 | Silver |
|  | Sabyrbek ZHEENTAEV | 3.225 | 7.900 | 2.143 | 1.818 | 5.744 | 4.096 | 3.100 | 2.459 | 0.155 | 1.558 | 11.125 | 21.073 | 32.198 | 168 | HM |
|  | Zamirbek AKIMBEKOV | 0.000 | 6.850 | 3.429 | 1.091 | 3.410 | 4.096 | 3.700 | 2.838 | 0.828 | 2.358 | 6.850 | 21.749 | 28.599 | 191 |  |


| Latvia | Mihails ARHANGELSKIS | 5.463 | 1.600 | 5.714 | 5.091 | 4.308 | 4.640 | 5.400 | 5.676 | 4.086 | 2.989 | 7.063 | 37.904 | 44.967 | 89 | Bronze |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Romāns ČAPLINSKIS | 7.971 | 4.850 | 1.429 | 0.182 | 5.564 | 5.440 | 3.600 | 5.676 | 1.655 | 2.989 | 12.821 | 26.535 | 39.356 | 122 | Bronze |
|  | Pāvels ZUBOVIČS | 3.023 | 4.350 | 5.286 | 3.455 | 5.923 | 2.464 | 0.500 | 0.189 | 0.000 | 0.168 | 7.373 | 17.985 | 25.358 | 200 |  |
|  | Jānis JERMAKS | 3.023 | 2.700 | 2.000 | 0.364 | 2.333 | 3.744 | 1.600 | 2.838 | 0.000 | 0.000 | 5.723 | 12.879 | 18.602 | 229 |  |
| Lithuania | Karolis LEONAVICIUS | 7.569 | 18.250 | 6.000 | 4.909 | 4.128 | 4.160 | 2.700 | 4.351 | 0.310 | 6.021 | 25.819 | 32.580 | 58.399 | 26 | Gold |
|  | Aurimas VYSNIAUSKAS | 11.083 | 12.800 | 6.429 | 6.909 | 4.487 | 4.160 | 4.200 | 2.649 | 0.621 | 4.758 | 23.883 | 34.212 | 58.095 | 28 | Gold |
|  | Bernardas MORKUNAS | 6.730 | 5.817 | 6.000 | 6.545 | 3.769 | 3.936 | 3.200 | 4.351 | 3.828 | 5.432 | 12.547 | 37.061 | 49.608 | 63 | Silver |
|  | Roberta POCEVICIUTE | 5.430 | 3.000 | 5.143 | 4.909 | 4.487 | 3.360 | 2.700 | 3.973 | 0.000 | 0.000 | 8.430 | 24.572 | 33.002 | 160 | HM |
| Malaysia | Jun Yan GOH | 7.890 | 17.300 | 5.571 | 1.091 | 4.487 | 2.176 | 1.700 | 2.459 | 0.000 | 0.379 | 25.190 | 17.864 | 43.054 | 102 | Bronze |
|  | Muhamad Azri Muhamad MARICAN | 7.326 | 8.750 | 5.143 | 4.182 | 1.974 | 3.040 | 1.000 | 3.405 | 0.672 | 1.768 | 16.076 | 21.185 | 37.261 | 137 | Bronze |
|  | Gah Hung LEE | 2.791 | 10.950 | 5.571 | 0.727 | 4.487 | 2.976 | 2.500 | 4.541 | 0.155 | 2.400 | 13.741 | 23.358 | 37.098 | 138 | Bronze |
|  | Aminatulmunirah KASIM | 7.817 | 6.400 | 2.857 | 0.909 | 2.692 | 2.400 | 1.000 | 2.459 | 0.414 | 2.189 | 14.217 | 14.921 | 29.138 | 186 |  |
| Mexico | Sergio Fonseca CHITICA | 1.628 | 11.350 | 3.571 | 1.091 | 3.949 | 4.800 | 2.100 | 3.689 | 0.414 | 0.421 | 12.978 | 20.035 | 33.013 | 159 | HM |
|  | Jose Enrique Robles SOTO | 8.153 | 0.900 | 4.714 | 1.091 | 3.949 | 3.840 | 1.200 | 5.676 | 1.966 | 0.674 | 9.053 | 23.109 | 32.162 | 169 |  |
|  | Juan Ivan GOMEZPERALTA | 1.977 | 7.300 | 1.714 | 0.727 | 4.846 | 3.200 | 1.900 | 1.703 | 0.362 | 0.505 | 9.277 | 14.958 | 24.234 | 210 |  |
|  | Carlos Leonel Ahumada MANUEL | 2.651 | 1.350 | 2.571 | 1.636 | 0.359 | 1.280 | 1.900 | 3.784 | 0.569 | 2.063 | 4.001 | 14.163 | 18.164 | 230 |  |
| Moldova | Vasile GRAUR | 8.030 | 18.610 | 5.000 | 4.000 | 3.769 | 4.640 | 1.600 | 2.081 | 0.000 | 2.063 | 26.640 | 23.153 | 49.793 | 62 | Silver |
|  | Veaceslav VIERU | 8.140 | 2.100 | 3.429 | 0.364 | 1.795 | 4.960 | 1.800 | 3.973 | 0.517 | 0.758 | 10.240 | 17.595 | 27.835 | 193 |  |
|  | Alexandru CARTALEANU | 2.519 | 2.533 | 3.286 | 0.000 | 2.513 | 3.520 | 2.800 | 3.027 | 0.310 | 1.895 | 5.053 | 17.351 | 22.403 | 218 |  |
|  | Leonid BIBIN | 4.891 | 0.000 | 6.000 | 0.000 | 3.590 | 2.976 | 1.200 | 1.892 | 0.000 | 0.000 | 4.891 | 15.658 | 20.549 | 223 |  |
| Mongolia | Javzansuren NORVANCHIG | 13.023 | 6.917 | 3.857 | 3.273 | 0.538 | 2.560 | 0.500 | 1.135 | 0.000 | 0.505 | 19.940 | 12.369 | 32.309 | 166 | HM |
|  | Urandelger TUVSHINDORJ | 0.000 | 15.717 | 2.286 | 2.727 | 2.513 | 0.768 | 1.000 | 1.514 | 0.724 | 0.000 | 15.717 | 11.531 | 27.248 | 195 |  |
|  | Battulga BYAMBASUREN | 0.698 | 6.950 | 2.000 | 1.818 | 1.615 | 3.680 | 1.200 | 2.270 | 0.414 | 0.253 | 7.648 | 13.250 | 20.898 | 222 |  |
|  | Uyanga DAGVADORJ | 2.093 | 0.000 | 1.857 | 0.727 | 0.359 | 2.080 | 1.000 | 0.378 | 0.310 | 0.000 | 2.093 | 6.712 | 8.805 | 247 |  |
| Netherlands | Raoul ROSENTHAL | 7.773 | 16.800 | 1.429 | 2.909 | 4.667 | 2.240 | 2.200 | 3.595 | 0.776 | 1.137 | 24.573 | 18.952 | 43.525 | 98 | Bronze |
|  | Mathijs de JONG | 4.372 | 12.950 | 2.143 | 1.818 | 3.590 | 4.160 | 1.500 | 3.784 | 0.000 | 0.126 | 17.322 | 17.121 | 34.443 | 153 | Bronze |
|  | Christiaan Alwin DOUMA | 8.558 | 3.333 | 5.143 | 0.727 | 3.231 | 4.288 | 1.500 | 2.459 | 1.086 | 1.474 | 11.891 | 19.908 | 31.800 | 173 |  |
|  | Jia CHEN | 7.173 | 6.583 | 4.000 | 0.182 | 2.692 | 2.112 | 1.700 | 2.459 | 0.517 | 3.411 | 13.756 | 17.073 | 30.830 | 177 |  |


| New Zealand | Jonathan LIN | 17.196 | 9.227 | 6.143 | 1.091 | 5.205 | 2.720 | 1.000 | 4.730 | 2.431 | 1.937 | 26.423 | 25.257 | 51.679 | 54 | Silver |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Chuan Zheng LEE | 5.221 | 16.000 | 6.143 | 0.182 | 3.769 | 3.520 | 1.200 | 4.919 | 0.000 | 6.147 | 21.221 | 25.880 | 47.101 | 74 | Silver |
|  | Thomas Ashton Christopher WONG | 2.605 | 12.560 | 5.429 | 0.909 | 3.769 | 2.240 | 2.700 | 4.730 | 0.414 | 2.400 | 15.165 | 22.590 | 37.755 | 131 | Bronze |
|  | Michael James PLUNKETT | 8.372 | 1.000 | 5.429 | 5.818 | 4.128 | 4.384 | 2.000 | 3.027 | 0.414 | 1.979 | 9.372 | 27.179 | 36.551 | 140 | Bronze |
| Norway | Henrik SOENSTEBY | 7.744 | 11.450 | 5.857 | 2.364 | 2.872 | 2.752 | 1.200 | 3.405 | 0.310 | 0.505 | 19.194 | 19.266 | 38.460 | 127 | Bronze |
|  | Geir Haakon BECKSTROEM | 8.013 | 3.200 | 4.714 | 2.182 | 4.487 | 3.680 | 1.300 | 2.270 | 1.914 | 0.800 | 11.213 | 21.347 | 32.560 | 165 | HM |
|  | Johan Yuan WANG | 0.233 | 2.650 | 5.286 | 5.091 | 3.590 | 2.560 | 1.200 | 2.649 | 0.362 | 1.137 | 2.883 | 21.874 | 24.756 | 207 |  |
|  | Camilla ESPEDAL | 5.482 | 0.800 | 4.714 | 0.182 | 0.538 | 0.480 | 0.500 | 1.892 | 0.000 | 0.674 | 6.282 | 8.980 | 15.262 | 233 |  |
| Pakistan | Shaina KHAN | 8.755 | 12.200 | 2.000 | 3.273 | 1.974 | 3.680 | 1.500 | 2.081 | 1.552 | 3.832 | 20.955 | 19.891 | 40.847 | 117 | Bronze |
|  | Anita PABANI | 8.937 | 7.010 | 4.000 | 0.909 | 3.410 | 4.800 | 1.500 | 2.649 | 1.086 | 0.632 | 15.947 | 18.986 | 34.933 | 149 | Bronze |
|  | Shahzad IQBAL | 3.209 | 0.800 | 4.571 | 1.091 | 2.513 | 3.328 | 1.000 | 2.838 | 0.414 | 1.305 | 4.009 | 17.060 | 21.069 | 220 |  |
|  | Hamza Khan SHAHBAZI | 1.186 | 2.050 | 5.429 | 1.091 | 2.692 | 1.120 | 1.000 | 3.216 | 0.310 | 1.516 | 3.236 | 16.374 | 19.610 | 226 |  |
| Peru | Luis Alberto Ypanaque ROCHA | 13.484 | 0.000 | 4.429 | 0.545 | 0.359 | 2.240 | 0.000 | 3.027 | 6.776 | 0.674 | 13.484 | 18.050 | 31.533 | 175 |  |
|  | Cristhian Luis Canari CHUMPITAZ | 0.000 | 10.133 | 1.714 | 0.364 | 6.282 | 3.776 | 1.600 | 3.595 | 0.931 | 0.674 | 10.133 | 18.935 | 29.069 | 187 |  |
|  | Joseph Hernan Pena ECHEVARRIA | 3.256 | 0.800 | 5.286 | 0.000 | 5.026 | 4.096 | 1.200 | 0.378 | 0.931 | 0.000 | 4.056 | 16.917 | 20.973 | 221 |  |
| Poland | Dawid Grzegorz LICHOSYT | 19.256 | 18.550 | 4.571 | 1.091 | 4.846 | 3.872 | 4.400 | 4.730 | 1.759 | 2.189 | 37.806 | 27.458 | 65.264 | 12 | Gold |
|  | Krzysztof Cezary KOSINSKI | 9.609 | 18.600 | 6.429 | 1.818 | 2.333 | 4.000 | 3.700 | 5.865 | 4.955 | 6.400 | 28.209 | 35.500 | 63.710 | 13 | Gold |
|  | Wojciech Dominik MAGON | 8.639 | 14.550 | 6.143 | 8.000 | 4.308 | 3.040 | 1.900 | 5.014 | 6.352 | 2.989 | 23.189 | 37.745 | 60.935 | 19 | Gold |
|  | Przemyslaw Krzysztof TREDAK | 10.667 | 8.910 | 5.571 | 8.000 | 4.128 | 6.240 | 2.300 | 4.730 | 0.931 | 6.105 | 19.577 | 38.006 | 57.582 | 30 | Gold |
| Portugal | Raul Joao de Sousa PEREIRA | 0.000 | 1.700 | 4.429 | 1.818 | 3.410 | 3.616 | 1.200 | 2.459 | 0.000 | 0.842 | 1.700 | 17.775 | 19.475 | 228 |  |
|  | Rui Emanuel Ferreira da SILVA | 0.814 | 3.050 | 3.286 | 1.091 | 1.256 | 2.240 | 1.000 | 0.000 | 0.000 | 0.842 | 3.864 | 9.715 | 13.579 | 239 |  |
|  | Rui Filipe Goncalves APOSTOLO | 4.170 | 0.600 | 0.571 | 1.091 | 0.897 | 2.656 | 0.700 | 1.135 | 0.414 | 0.253 | 4.770 | 7.717 | 12.487 | 241 |  |
|  | Rui Filipe Lebres LOPES | 0.000 | 1.450 | 3.000 | 2.182 | 1.077 | 0.320 | 0.000 | 0.946 | 0.000 | 0.337 | 1.450 | 7.862 | 9.312 | 246 |  |


| Romania | Ioan Teodor TROTUS | 11.231 | 0.800 | 5.714 | 7.455 | 4.128 | 5.600 | 4.000 | 4.162 | 0.517 | 5.137 | 12.031 | 36.713 | 48.744 | 67 | Silver |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Vlad Alexandru PUSCASU | 9.149 | 7.050 | 5.857 | 4.727 | 6.282 | 3.616 | 4.100 | 5.297 | 1.448 | 0.000 | 16.199 | 31.328 | 47.527 | 72 | Silver |
|  | Ionut Gabriel DUMITRU | 6.315 | 4.820 | 6.571 | 2.909 | 3.949 | 3.040 | 6.000 | 3.595 | 6.259 | 3.032 | 11.135 | 35.354 | 46.489 | 79 | Silver |
|  | Ingrid Cristiana VREJA | 2.093 | 6.500 | 6.286 | 3.091 | 5.744 | 2.080 | 3.500 | 4.919 | 0.828 | 2.568 | 8.593 | 29.015 | 37.608 | 134 | Bronze |
| Russian Federation | Leonid ROMASHOV | 19.256 | 13.300 | 6.143 | 7.273 | 3.949 | 3.526 | 5.600 | 5.108 | 3.776 | 4.337 | 32.556 | 39.712 | 72.267 | 3 | Gold |
|  | Vasiliy VOROBYEV | 13.340 | 14.860 | 6.000 | 4.000 | 3.769 | 7.360 | 3.700 | 5.865 | 6.103 | 6.611 | 28.200 | 43.408 | 71.609 | 4 | Gold |
|  | Stanislav TEREHOV | 13.464 | 11.750 | 5.429 | 5.455 | 4.846 | 4.800 | 3.100 | 7.000 | 3.103 | 3.832 | 25.214 | 37.564 | 62.778 | 15 | Gold |
|  | Eugeny NEKHOROSHEV | 9.191 | 3.800 | 6.857 | 5.818 | 4.487 | 5.440 | 7.200 | 6.432 | 6.983 | 5.263 | 12.991 | 48.481 | 61.472 | 18 | Gold |
| Saudi Arabia | Osamah Altaib SAFWAN | 0.000 | 0.450 | 1.714 | 0.727 | 1.256 | 0.013 | 1.500 | 1.230 | 0.414 | 0.379 | 0.450 | 7.233 | 7.683 | 248 |  |
|  | Mohammed Abdullah ALGASIM | 0.000 | 1.960 | 2.000 | 0.000 | 0.359 | 0.160 | 0.500 | 1.135 | 0.000 | 0.168 | 1.960 | 4.323 | 6.283 | 251 |  |
|  | Ibrahim Abdullah Ba JAAFR | 1.628 | 0.300 | 0.286 | 0.727 | 0.359 | 0.006 | 1.000 | 0.757 | 0.414 | 0.295 | 1.928 | 3.844 | 5.772 | 252 |  |
|  | Ataallah Naif ALHARBI | 0.000 | 1.150 | 1.143 | 0.000 | 0.359 | 0.006 | 1.000 | 1.703 | 0.000 | 0.379 | 1.150 | 4.590 | 5.740 | 253 |  |
| Singapore | Zeqi YANG | 12.015 | 4.383 | 6.143 | 0.182 | 4.487 | 4.960 | 4.800 | 4.730 | 5.586 | 5.305 | 16.398 | 36.193 | 52.591 | 51 | Silver |
|  | Benjamin CHEN | 5.824 | 10.493 | 5.857 | 2.182 | 3.949 | 2.944 | 4.500 | 3.405 | 2.586 | 4.168 | 16.318 | 29.592 | 45.909 | 84 | Silver |
|  | Guang Jun Joseph LIM | 2.326 | 9.100 | 5.857 | 1.818 | 4.308 | 3.840 | 3.300 | 4.351 | 4.707 | 2.737 | 11.426 | 30.918 | 42.344 | 108 | Bronze |
|  | Chin Heng GAN | 2.093 | 8.560 | 5.857 | 1.818 | 3.410 | 0.960 | 3.800 | 4.162 | 3.776 | 4.295 | 10.653 | 28.078 | 38.731 | 126 | Bronze |
| Slovakia | Martin LUKACISIN | 12.565 | 14.300 | 5.000 | 7.455 | 4.128 | 4.000 | 2.500 | 4.351 | 2.638 | 2.063 | 26.865 | 32.135 | 59.000 | 24 | Gold |
|  | Erik ANDRIS | 12.030 | 16.177 | 5.571 | 1.455 | 4.846 | 5.792 | 3.800 | 3.784 | 2.741 | 0.505 | 28.207 | 28.495 | 56.701 | 35 | Silver |
|  | Boris FACKOVEC | 9.535 | 12.950 | 6.571 | 3.636 | 4.128 | 3.520 | 3.800 | 4.919 | 4.397 | 1.389 | 22.485 | 32.361 | 54.846 | 44 | Silver |
|  | Lubica KRAUSKOVA | 3.561 | 11.733 | 5.000 | 2.364 | 4.487 | 3.296 | 1.000 | 3.405 | 0.000 | 1.642 | 15.294 | 21.194 | 36.488 | 141 | Bronze |
| Slovenia | Jan KOGOJ | 9.488 | 2.467 | 6.143 | 8.000 | 4.487 | 4.576 | 1.000 | 4.351 | 2.534 | 3.663 | 11.955 | 34.755 | 46.710 | 77 | Silver |
|  | Jan BITENC | 6.000 | 11.450 | 4.714 | 1.455 | 5.564 | 5.280 | 2.100 | 3.027 | 2.069 | 4.337 | 17.450 | 28.546 | 45.996 | 83 | Silver |
|  | Irena MATKOVIČ | 2.791 | 3.400 | 6.000 | 6.545 | 4.487 | 5.920 | 1.000 | 2.838 | 0.155 | 2.484 | 6.191 | 29.430 | 35.621 | 147 | Bronze |
|  | Miha Emerik HABIC | 2.907 | 6.200 | 5.571 | 1.818 | 3.051 | 2.400 | 1.000 | 3.027 | 0.724 | 2.358 | 9.107 | 19.950 | 29.057 | 188 |  |
| Spain | Victor Lopez FERRANDO | 10.716 | 5.560 | 5.571 | 3.273 | 2.154 | 5.440 | 0.500 | 2.081 | 0.517 | 0.337 | 16.276 | 19.873 | 36.149 | 144 | Bronze |
|  | Alberto Garcia BOSQUE | 2.837 | 8.050 | 5.286 | 1.818 | 1.436 | 3.840 | 1.000 | 5.486 | 0.310 | 1.726 | 10.887 | 20.903 | 31.790 | 174 |  |
|  | Andres Suarez VELAZQUEZ | 8.564 | 1.400 | 3.857 | 2.727 | 2.513 | 2.624 | 0.700 | 5.297 | 0.259 | 0.968 | 9.964 | 18.946 | 28.910 | 190 |  |
|  | Alberto Sanchez Molero | 7.720 | 1.833 | 1.143 | 1.818 | 0.718 | 4.800 | 1.000 | 1.892 | 0.000 | 0.968 | 9.554 | 12.339 | 21.893 | 219 |  |


| Sweden | Oscar Carl Gunnar GRANBERG | 8.140 | 15.350 | 5.571 | 3.818 | 5.744 | 0.480 | 1.000 | 3.878 | 0.517 | 1.179 | 23.490 | 22.188 | 45.677 | 86 | Silver |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Daria Ewa STRUSKA | 2.326 | 10.900 | 3.857 | 0.727 | 4.308 | 0.480 | 1.000 | 3.027 | 1.345 | 2.316 | 13.226 | 17.060 | 30.285 | 180 |  |
|  | Stella Lucie RIAD | 3.209 | 6.450 | 2.429 | 3.455 | 2.154 | 2.976 | 1.000 | 4.162 | 0.724 | 0.968 | 9.659 | 17.868 | 27.527 | 194 |  |
|  | Axel Nils Ola GOTTFRIES | 5.875 | 4.250 | 5.000 | 0.909 | 2.513 | 3.040 | 0.500 | 1.703 | 0.000 | 1.137 | 10.125 | 14.801 | 24.927 | 205 |  |
| Switzerland | Lucia Domenica MEIER | 7.442 | 15.200 | 3.571 | 3.091 | 3.590 | 3.200 | 0.700 | 3.595 | 0.000 | 1.895 | 22.642 | 19.641 | 42.283 | 110 | Bronze |
|  | Max HAFLIGER | 5.936 | 0.000 | 6.143 | 2.545 | 4.667 | 1.984 | 1.500 | 3.405 | 5.069 | 3.326 | 5.936 | 28.640 | 34.575 | 151 | Bronze |
|  | Andreas FRUTIGER | 7.922 | 10.000 | 4.714 | 0.000 | 2.333 | 3.200 | 1.000 | 1.892 | 0.310 | 1.389 | 17.922 | 14.839 | 32.761 | 162 | HM |
|  | Frederic COTTIER | 1.395 | 6.133 | 5.000 | 0.727 | 2.872 | 1.760 | 1.500 | 2.459 | 0.155 | 0.505 | 7.529 | 14.979 | 22.508 | 217 |  |
| Tajikistan | Khursand YOROV | 1.395 | 5.067 | 4.286 | 6.909 | 5.385 | 6.720 | 2.200 | 4.824 | 0.000 | 0.926 | 6.462 | 31.250 | 37.712 | 133 | Bronze |
|  | Umed BOLTAEV | 5.581 | 1.000 | 3.286 | 2.364 | 3.410 | 4.960 | 2.000 | 3.595 | 4.914 | 1.095 | 6.581 | 25.623 | 32.204 | 167 | HM |
|  | Saidullo SULAYMONZODA | 0.000 | 0.200 | 4.000 | 2.818 | 4.487 | 2.368 | 1.200 | 4.351 | 0.776 | 0.000 | 0.200 | 20.001 | 20.201 | 225 |  |
|  | Khusrav OLIMI | 1.395 | 6.300 | 1.286 | 0.364 | 0.718 | 2.176 | 1.200 | 2.649 | 1.086 | 0.000 | 7.695 | 9.478 | 17.174 | 231 |  |
| Thailand | Bavorn HONGSRICHINDA | 14.186 | 17.950 | 6.143 | 3.636 | 4.128 | 4.832 | 3.200 | 4.351 | 1.190 | 2.021 | 32.136 | 29.501 | 61.638 | 17 | Gold |
|  | Tanatorn KHOTAVIVATTANA | 4.461 | 11.750 | 6.429 | 5.455 | 5.923 | 3.680 | 2.800 | 5.392 | 5.328 | 5.853 | 16.211 | 40.858 | 57.069 | 33 | Silver |
|  | Pornchai KAEWSAPSAK | 4.186 | 10.400 | 6.714 | 4.545 | 5.923 | 3.526 | 6.000 | 6.149 | 0.517 | 2.484 | 14.586 | 35.859 | 50.445 | 56 | Silver |
|  | Techin CHULADESA | 9.070 | 3.033 | 5.286 | 4.364 | 4.487 | 5.280 | 3.500 | 5.014 | 2.793 | 2.821 | 12.103 | 33.544 | 45.647 | 87 | Silver |
| Turkey | Hande BOYACI | 18.067 | 8.867 | 4.714 | 4.909 | 5.205 | 3.936 | 2.600 | 4.162 | 2.379 | 5.053 | 26.934 | 32.959 | 59.893 | 21 | Gold |
|  | Ahmet Selim HAN | 9.767 | 4.633 | 4.857 | 5.273 | 4.487 | 3.680 | 4.900 | 0.757 | 2.534 | 2.484 | 14.401 | 28.972 | 43.373 | 99 | Bronze |
|  | Dogukan DIKMEN | 0.930 | 3.800 | 5.143 | 3.091 | 5.205 | 4.416 | 2.500 | 4.541 | 3.983 | 2.063 | 4.730 | 30.941 | 35.672 | 146 | Bronze |
|  | Mehmet VURAL | 1.860 | 2.910 | 5.571 | 2.182 | 1.974 | 2.560 | 3.500 | 3.973 | 3.103 | 1.937 | 4.770 | 24.801 | 29.571 | 185 |  |
| Turkmenistan | Serdar ROZYYEV | 1.977 | 15.250 | 5.000 | 1.727 | 1.795 | 5.600 | 2.900 | 2.838 | 2.431 | 1.347 | 17.227 | 23.638 | 40.865 | 116 | Bronze |
|  | Batyr Garlyyev | 9.847 | 1.800 | 4.714 | 1.091 | 5.205 | 3.872 | 2.500 | 4.730 | 2.638 | 2.358 | 11.647 | 27.108 | 38.755 | 125 | Bronze |
|  | Muradov NURMUHAMMET | 0.000 | 7.700 | 4.286 | 3.636 | 5.564 | 3.040 | 0.500 | 4.730 | 1.914 | 2.021 | 7.700 | 25.691 | 33.391 | 157 | Bronze |
|  | Sohbet HOJAMUHAMMEDOV | 0.000 | 0.000 | 1.143 | 1.091 | 0.000 | 0.640 | 1.100 | 0.378 | 0.000 | 0.000 | 0.000 | 4.352 | 4.352 | 255 |  |
| Ukraine | Ostap CHERVAK | 2.849 | 14.110 | 6.714 | 3.273 | 5.564 | 5.280 | 3.600 | 6.622 | 2.534 | 4.842 | 16.959 | 38.429 | 55.388 | 39 | Silver |
|  | Volodymyr TKACHENKO | 2.698 | 10.333 | 5.286 | 0.364 | 5.564 | 5.280 | 2.500 | 3.595 | 5.948 | 2.316 | 13.031 | 30.852 | 43.883 | 94 | Bronze |
|  | Kirill POLISCHUK | 5.018 | 3.100 | 5.714 | 6.727 | 5.923 | 6.176 | 5.200 | 0.000 | 2.690 | 1.937 | 8.118 | 34.367 | 42.485 | 106 | Bronze |
|  | Olha BALABON | 5.426 | 1.500 | 6.143 | 5.818 | 4.487 | 3.456 | 5.000 | 3.973 | 0.931 | 3.663 | 6.926 | 33.471 | 40.398 | 119 | Bronze |


| United Kingdom | Matthew James CLIFFE | 9.070 | 5.860 | 5.286 | 6.182 | 5.205 | 4.672 | 3.300 | 6.811 | 1.552 | 5.137 | 14.930 | 38.144 | 53.074 | 50 | Silver |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Frederick Robert William Meath MANNERS | 7.105 | 10.793 | 6.857 | 8.000 | 4.128 | 4.480 | 1.200 | 3.027 | 5.586 | 1.263 | 17.898 | 34.542 | 52.440 | 53 | Silver |
|  | Derek Steven Hung-Che CHAN | 4.885 | 5.900 | 6.143 | 7.273 | 5.205 | 5.760 | 1.900 | 4.730 | 0.517 | 2.484 | 10.785 | 34.012 | 44.797 | 91 | Bronze |
|  | Jaroslav ZAK | 6.275 | 1.850 | 5.714 | 7.364 | 4.128 | 1.280 | 2.900 | 5.865 | 0.310 | 0.505 | 8.125 | 28.067 | 36.191 | 143 | Bronze |
| United States | Brian Kihoon LEE | 5.440 | 9.650 | 5.286 | 2.182 | 3.769 | 5.760 | 5.300 | 4.162 | 7.086 | 6.611 | 15.090 | 40.156 | 55.246 | 40 | Silver |
|  | Justin KOH | 8.791 | 16.650 | 5.000 | 1.091 | 5.564 | 4.160 | 1.100 | 6.243 | 2.069 | 4.253 | 25.441 | 29.480 | 54.921 | 43 | Silver |
|  | Kenneth BREWER | 2.151 | 12.500 | 5.571 | 7.273 | 6.641 | 3.680 | 1.600 | 5.108 | 0.000 | 4.337 | 14.651 | 34.210 | 48.861 | 65 | Silver |
|  | Sofia IZMAILOV | 9.128 | 3.150 | 4.286 | 1.727 | 4.846 | 2.656 | 1.500 | 3.595 | 0.931 | 2.653 | 12.278 | 22.193 | 34.471 | 152 | Bronze |
| Uruguay | Joaquin GRASSI | 2.791 | 0.900 | 2.143 | 1.818 | 0.538 | 0.320 | 1.200 | 2.743 | 0.724 | 0.000 | 3.691 | 9.487 | 13.178 | 240 |  |
|  | Sebastian BARCARDAL | 2.326 | 0.000 | 2.429 | 0.727 | 0.000 | 0.704 | 1.000 | 1.514 | 0.310 | 0.505 | 2.326 | 7.189 | 9.515 | 245 |  |
|  | Diego OTERO | 2.488 | 0.900 | 0.286 | 0.364 | 0.718 | 1.280 | 0.200 | 1.419 | 0.000 | 0.000 | 3.388 | 4.266 | 7.655 | 249 |  |
|  | Sebastian FIAMENE | 2.326 | 0.000 | 0.286 | 0.727 | 0.000 | 1.120 | 1.000 | 0.568 | 0.310 | 0.000 | 2.326 | 4.011 | 6.336 | 250 |  |
| Venezuela | Gabriel Eduardo Sanoja LOPEZ | 11.734 | 15.100 | 3.143 | 3.273 | 3.769 | 2.880 | 1.000 | 2.838 | 1.448 | 0.000 | 26.834 | 18.351 | 45.185 | 88 | Bronze |
|  | Daniel Enrique Cardenas ARMAS | 10.465 | 6.850 | 4.571 | 3.273 | 7.000 | 1.408 | 1.300 | 0.946 | 0.000 | 2.189 | 17.315 | 20.688 | 38.003 | 129 | Bronze |
| Vietnam | Minh Nguyen Thi NGOC | 2.698 | 8.500 | 5.857 | 7.091 | 7.000 | 7.040 | 5.000 | 5.676 | 7.190 | 2.189 | 11.198 | 47.043 | 58.241 | 27 | Gold |
|  | Ha Phan Tran HONG | 8.605 | 3.400 | 5.857 | 7.818 | 6.282 | 5.440 | 3.500 | 5.770 | 6.672 | 1.095 | 12.005 | 42.435 | 54.439 | 45 | Silver |
|  | Linh Bui LE | 11.121 | 1.450 | 4.143 | 5.455 | 4.128 | 5.440 | 5.800 | 5.297 | 1.759 | 1.853 | 12.571 | 33.874 | 46.445 | 80 | Silver |
|  | Manh Le DINH | 3.047 | 1.000 | 5.857 | 4.636 | 5.205 | 5.286 | 4.000 | 1.324 | 2.276 | 0.000 | 4.047 | 28.585 | 32.632 | 163 | HM |

## Comparative Analysis of the IChO Results from 1990 to 2007

| Year | Country | First <br> Gold | Last <br> Gold | $\boldsymbol{\Delta ( \text { Gold/Silver) }}$ | First <br> Silver | Last <br> Silver | $\Delta$ (Silver/Bronze) | First <br> Bronze | Last <br> Bronze | $\boldsymbol{\Delta}$ (Bronze/Non- <br> Medalists) | First <br> Non- <br> Medalist |
| :--- | :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1990 | France | 82 | 65 | 2.75 | 62.25 | 57.25 | 1.25 | 56 | 42.5 | 1.5 | 41 |
| 1991 | Poland | 94.75 | 87.25 | 1.25 | 86 | 77 | 0.75 | 76.25 | 61.5 | 1.5 | 60 |
| 1992 | USA | 96.42 | 90.42 | 0.38 | 90.04 | 85.85 | 0.44 | 85.41 | 78.01 | 0.39 | 77.62 |
| 1993 | Italy | 83.5 | 75.5 | 2.5 | 73 | 64.5 | 0.5 | 64 | 49.5 | 1.5 | 48 |
| 1994 | Norway | 83.87 | 79.14 | 0.714 | 78.426 | 72.49 | 0.705 | 71.785 | 58.936 | 0.326 | 58.61 |
| 1995 | China | 95.541 | 82.115 | 0.32 | 81.795 | 73.027 | 0.322 | 72.705 | 60.124 | 0.002 | 60.122 |
| 1996 | Russia | 92.251 | 79.717 | 1.135 | 78.582 | 67.133 | 0.128 | 67.005 | 53.151 | 0.459 | 52.692 |
| 1997 | Canada | 81.25 | 72.5 | 0.5 | 72 | 65.75 | 0.75 | 65 | 54.5 | 0.5 | 54 |
| 1998 | Australia | 95.49 | 88.36 | 0.22 | 88.14 | 80.17 | 0.65 | 79.52 | 65.6 | 0.86 | 64.74 |
| 1999 | Thailand | 94.118 | 81.609 | 1.249 | 80.36 | 70.061 | 0.145 | 69.916 | 53.158 | 0.203 | 52.955 |
| 2000 | Denmark | 94.46 | 80.313 | 0.468 | 79.845 | 71.914 | 0.341 | 71.573 | 58.201 | 0.5 | 57.701 |
| 2001 | India | 92.31 | 82.91 | 1.1 | 81.81 | 68.61 | 0.27 | 68.34 | 50.13 | 0.73 | 49.4 |
| 2002 | Netherlands | 92.5 | 81.35 | 2.23 | 79.12 | 72.14 | 0.3 | 71.84 | 61.45 | 0.51 | 60.94 |
| 2003 | Greece | 96.43 | 87.83 | 0.3 | 87.53 | 80.07 | 1.04 | 79.03 | 65.13 | 0.99 | 64.14 |
| 2004 | Germany | 88.7 | 72.1 | 1.1 | 71 | 60 | 0.4 | 59.6 | 47 | 0.9 | 46.1 |
| 2005 | Taiwan | 96.75 | 90.6 | 0.89 | 89.71 | 80.62 | 0.54 | 80.08 | 64.07 | 0.85 | 63.22 |
| 2006 | Korea | 93.43 | 70.61 | 0.48 | 70.13 | 56.71 | 0.32 | 56.39 | 39.41 | 0.17 | 39.24 |
| 2007 | Russia | 76.71 | 57.423 | 0.229 | 57.194 | 45.647 | 0.462 | 45.185 | 33.335 | 0.322 | 33.013 |

The 39th IChO Organizers acknowledge Dr. Wolfgang Hampe for the idea of the statistical analysis and contribution of the data

## List of Mentors, Observers, and Guests

| Country | Role | Name |
| :---: | :---: | :---: |
| Argentina | HM | Jorge Alberto Onofrio Bruno |
|  | M | Maria Laura Uhrig |
| Armenia | HM | Lida Sahakyan |
|  | M | Artak Tovmasyan |
| Australia | HM | Anthony Edward Phillips |
|  | M | Alex Chit Hei Wong |
|  | SO | Mark John Ellison |
| Austria | HM | Manfred Kerschbaumer |
|  | M | Lisbeth Berner |
| Azerbaijan | HM | Vaqif Abbasov |
|  | M | Mutellim Abbasov |
|  | SO | Yusif Abdullayev |
|  | SO | Nasim Ajdar Abishov |
| Belarus | HM | Viktar Khvaluk |
|  | M | Aliaksandr Rahoisha |
| Belgium | HM | Sebastien Delfosse |
|  | M | Hans L.S. Vanhoe |
|  | SO | Cedric Pascal Patrick Malherbe |
| Brazil | HM | Sergio Maia Melo |
|  | M | Jose Arimateia Dantas Lopes |
|  | SO | Lucia Souza Carvalho Melo |


| Bulgaria | HM | Donka Nikolova Tasheva |
| :---: | :---: | :---: |
|  | M | Penka Vasileva Tsanova |
| Canada | HM | Andrew Paul Dicks |
|  | M | Stanislaw Skonieczny |
| China | HM | Lianyun Duan |
|  | M | Ke-qing Zhao |
|  | SO | Ying-xia Wang |
|  | SO | Bi-qin Wang |
| Chinese Taipei | G | Tai-Shan Fang |
|  | G | I-Hsing Chen |
|  | HM | I-Jy Chang |
|  | M | Bih-Yaw Jin |
|  | SO | Tun-Cheng Chien |
|  | SO | Ya-Ling Chen |
| Croatia | HM | Branka Zorc |
|  | M | Tomislav Cvitas |
| Cuba | HM | Luis Enrique Guerra Castano |
| Cyprus | HM | Anaxagoras Hadjiosif |
|  | M | Stella Ioannou-Loucaides |
| Czech Republic | HM | Eva Muchova |
|  | M | Petr Slavicek |
| Denmark | HM | Kurt Bjoenager Nielsen |
|  | M | Hanne Busk |
|  | SO | Morten Foverskov |
| Estonia | HM | Uno Maeorg |
|  | M | Vladislav Ivanishtshev |
| Finland | HM | Jorma Kullervo Koskimies |
|  | M | Markku Rafael Sundberg |
|  | SO | Nina Helmi Katariina Aremo |


| France | HM | Adrien Sebastien Meglio |
| :---: | :---: | :---: |
|  | M | Guillaume Meriguet |
|  | SO | Vincent Tejedor |
| Germany | HM | Sabine Ingeborg Nick |
|  | M | Wolfgang Hampe, StD |
|  | SO | Carsten Schmuck |
| Greece | HM | Anastasia Detsi |
|  | M | Dimitrios Chiniadis |
| Hungary | HM | Gyorgy Tarczay |
|  | M | Szilard Varga |
|  | SO | Laszlo Turi |
|  | SO | Attila Villanyi |
|  | SO | Andras Kotschy |
| Iceland | HM | Gisli Holmar Johannesson |
|  | M | Sigurdur Vidir Smarason |
|  | SO | Margret Lilja Bjornsdottir |
| India | HM | Dilip Kumar Maity |
|  | M | Sambasivan Venkat Eswaran |
|  | SO | Swapna Mahesh Narvekar |
| Indonesia | HM | Riwandi Sihombing |
|  | M | Djulia Onggo |
|  | SO | Ismunaryo Moenandar |
| Iran | HM | Mansour Abedini |
|  | M | Ebrahim Kianmehr |
|  | SO | Seyed Ali Seyedi Esfahani |
|  | SO | Mahin Jabalameli |


| Ireland | HM | Paraic James |
| :---: | :---: | :---: |
|  | M | Wesley Richard Browne |
| Israel | HM | Moris S. Eisen |
|  | M | Iris Barzilai |
| Italy | HM | Mario Anastasia |
|  | M | Pietro Allevi |
| Japan | HM | Yoshiyuki Sugahara |
|  | M | Noriyuki Yonezawa |
|  | SO | Keijiro Taga |
|  | SO | Masatada Matsuoka |
| Kazakhstan | HM | Kurmangali Bekishev |
|  | M | Rassima Sadakbayeva |
| Korea Republic | G | Eui seo Park |
|  | G | Duckhwan Lee |
|  | G | Sookyon, Yeo Lee |
|  | HM | Jung Hag Park |
|  | M | Tai Jong Kang |
|  | SO | Seonghoon Lee |
|  | SO | Hee Gweon Woo |
| Kuwait | M | Barak Mehdi Hadi |
|  | M | Fotouh Alshamali |
| Kyrgyzstan | HM | Minira Batkibekova |
|  | M | Raina Asakeeva |
| Latvia | HM | Ināra Akmene |
|  | M | Skaidrite Pakule |
| Lithuania | HM | Rimantas Raudonis |
|  | M | Edvinas Orentas |


| Malaysia | G | Mohd Shah Noriah |
| :---: | :---: | :---: |
|  | G | Turiman Punia |
|  | HM | Mohd Jamil Maah |
|  | M | Noorsaadah A. Rahman |
|  | SO | Mei Leng Lee |
| Mexico | HM | Carlos Mauricio CastroAcuna |
|  | M | Eugenio Octavio Reyes Salas |
| Moldova | HM | Nadejda Gheorghe Velisco |
|  | M | Andrei Mihail Bunescu |
| Mongolia | HM | Dorj Daichaa |
|  | M | Nyamgerel Choijilsuren |
|  | SO | Davaasuren Sandag |
| Netherlands | HM | Peter de Groot |
|  | M | Emiel de Kleijn |
|  | SO | Cornelis Beers |
| New Zealand | HM | Suzanne Margaret Boniface |
|  | M | David Salter |
| Nigeria | G | Olayemi Albert Bamikole |
|  | G | Grace Oni Ojo |
|  | SO | Sunday Asher Adedeji |
| Norway | HM | Hans-Petter Hersleth |
|  | M | Kristian Vestli |
| Pakistan | HM | Khalid Mohammed Khan |
|  | M | Muhammad Shaiq Ali |


| Peru | HM | Bertha Beatriz Flores Alor |
| :---: | :---: | :---: |
|  | M | Galina Shevtsova |
| Poland | HM | Marek Orlik |
|  | M | Janusz Stepinski |
| Portugal | HM | Diana Claudia Gouveia Alves Pinto |
|  | M | Maria do Amparo Ferreira Faustino |
|  | SO | Alzira Pinto Rebelo |
| Romania | HM | Marius Andruh |
|  | M | Mihaela Maria Hillebrand |
|  | SO | Daniela Elisabeta Bogdan |
| Russian Federation | HM | Sergey Igorevich Kargov |
|  | M | Alexandr Belov |
|  | SO | Alexey Zeifman |
| Saudi Arabia | G | Mohammed Abdulkarim Ibrahim |
|  | HM | Ghanem Saad AIGhanem |
|  | M | Hadi Ali Bahari |
|  | SO | Hassan Ahmed Masslouf |
| Singapore | HM | Karen K.W. Mak |
|  | M | Basheer Chanbasha |
|  | SO | Loy Chuan Chua |
| Slovakia | HM | Anton Sirota |
|  | M | Marta Salisova |
|  | SO | Jan Reguli |
| Slovenia | HM | Darko Dolenc |
|  | M | Andrej Godec |


| Spain | HM | Juan Antonio Rodriguez Renuncio |
| :---: | :---: | :---: |
|  | M | Maria Carmen Cartagena Causape |
|  | SO | Fernando Latre David |
| Sweden | HM | Per Henning Lindgren |
|  | M | Ulf Charles Jaglid |
|  | so | Anna Cecilia Stenberg |
| Switzerland | HM | Maurice Cosandey |
|  | M | Thomas Engeloch |
| Tajikistan | HM | Abdufatokh Hotamov |
|  | M | Golibsho Takdirovich Nasymov |
| Thailand | G | Narongsil Thooppanom |
|  | HM | Vudhichai Parasuk |
|  | M | Yongsak Sritana-Anant |
|  | SO | Amarawan Intasiri |
|  | SO | Ekasith Somsook |
| Turkey | HM | Jale Hacaloglu |
|  | M | Cihangir Tanyeli |
| Turkmenistan | HM | Guvanchmyrat Paytakov |
|  | M | Aman Begliyev |
| Ukraine | HM | Galyna Malchenko |
|  | M | Yuriy Kholin |
| United Kingdom | HM | Charles Stuart McCaw |
|  | M | Timothy Graham Hersey |
|  | SO | Henneli Greyling |
|  | SO | William Peter Nolan |


| United States | G | Katherine Ringland Kotz |
| :--- | :---: | :--- |
|  | G | Ronald Edward Monson |
|  | HM | John Carl Kotz |
|  | M | Kara Anne Pezzi |
| Venezuela | SO | John Leon Kiappes |
| Uruguay | HM | William Stebniki |
| Vietnam | HM | Amalia Torrealba |
|  | M | Eliseo Silva |
|  | G | Hung Pham Tuan |
|  | G | Nga Nguyen Thi |
|  | HM | Hue Tran thanh |
|  | M | Hien Pham dinh |
|  | SO | Dau Nguyen Van |

IChO-2007 BUDGET

| US \$ |  |  |
| :---: | :---: | :---: |
| 1. | Total Budget of the IChO-2007 | 2956200 |
| 1.1. | Governmental source | 1813600 |
| 1.2. | Sponsors | 1070000 |
| 1.3. | Participation fees | 72600 |
| 2. | Expenditures of the IChO-2007 | 2956200 |
| 2.1. | Examination preparation | 1111700 |
| 2.1.1. | Equipment | 595500 |
| 2.1.2. | Reagents | 203200 |
| 2.1.3. | Practical and theoretical preparatory and examination tasks | 65000 |
| 2.1.4. | Facilities for the International Jury meetings and translation | 248000 |
| 2.2. | Accomodation and Food | 860000 |
| 2.2.1. | Students | 380000 |
| 2.2.2. | Mentors | 480000 |
| 2.3. | Transportation | 154700 |
| 2.3.1. | Students | 98000 |
| 2.3.2. | Mentors | 56700 |
| 2.4. | Opening and Closing Ceremonies | 120000 |
| 2.5. | Cultural program | 68000 |
| 2.5.1 | Students | 44000 |
| 2.5.2. | Mentors | 24000 |
| 2.6. | Secretariat and operation | 178600 |
| 2.6.1. | Staff costs | 162800 |
| 2.6.2. | Equipment and services | 15800 |
| 2.7. | Guides | 42000 |
| 2.8. | Public relations | 207200 |
| 2.8.1. | Catalyzer | 60000 |
| 2.8.2. | Souvenirs | 81200 |
| 2.8.3. | Presentations, mass media | 66000 |
| 2.9. | The 39th IChO web-server | 34100 |
| 2.10. | Final report | 16000 |
| 2.11. | Consumables | 12300 |
| 2.12. | Other | 151600 |

Participation fees for the IChO-2007

| No. | Country | Amount, US $\$$ |
| :---: | :--- | ---: |
| 1 | Argentina | 1300 |
| 2 | Armenia | 200 |
| 3 | Australia | 800 |
| 4 | Austria | 2000 |
| 5 | Azerbaijan | 800 |
| 6 | Belarus | 1200 |
| 7 | Belgium | 2000 |
| 8 | Brazil | 900 |
| 9 | Bulgaria | 2000 |
| 10 | Canada | 1000 |
| 11 | China | 1200 |
| 12 | Chinese Taipei | 200 |
| 13 | Croatia | 800 |
| 14 | Cuba | 1600 |
| 15 | Cyprus | 1800 |
| 16 | Czech Republic | 1500 |
| 17 | Denmark | 700 |
| 18 | Estonia | 1400 |
| 19 | Finland | 1900 |
| 20 | France | 1700 |
| 21 | Germany | 300 |
| 22 | Greece | 400 |
| 23 | Hungary | 2000 |
| 24 | Iceland | 600 |
| 25 | India | 600 |
| 26 | Indonesia | 800 |
| 27 | Iran | 1500 |
| 28 | Ireland | 1100 |
| 29 | Israel | 200 |
| 30 | Italy | 1400 |
| 31 | Japan | 500 |
| 32 | Kazakhstan | 1000 |
| 33 | Korea | 100 |
| 34 | Kuwait | 1500 |
|  |  |  |


| 35 | Kyrgyzstan | 800 |
| :---: | :---: | :---: |
| 36 | Latvia | 1700 |
| 37 | Lithuania | 1700 |
| 38 | Malaysia | 200 |
| 39 | Mexico | 1600 |
| 40 | Moldova | 100 |
| 41 | Mongolia | 200 |
| 42 | Netherlands | 500 |
| 43 | New Zealand | 1600 |
| 44 | Nigeria |  |
| 45 | Norway | 1300 |
| 46 | Pakistan | 200 |
| 47 | Peru | 400 |
| 48 | Poland | 1600 |
| 49 | Portugal | 500 |
| 50 | Romania | 2000 |
| 51 | Russia | 0 |
| 52 | Saudi Arabia | 200 |
| 53 | Singapore | 1800 |
| 54 | Slovakia | 1500 |
| 55 | Slovenia | 1700 |
| 56 | Spain | 1200 |
| 57 | Sweden | 2000 |
| 58 | Switzerland | 2000 |
| 59 | Tajikistan | 400 |
| 60 | Thailand | 800 |
| 61 | Turkey | 1400 |
| 62 | Turkmenistan | 600 |
| 63 | U.S.A. | 1500 |
| 64 | Ukraine | 1400 |
| 65 | United Kingdom | 2000 |
| 66 | Uruguay |  |
| 67 | Venezuela | 1500 |
| 68 | Vietnam | 1200 |
|  | Total Amount | 72600 |

## Preparations

2005
January- Choose the Venue: Chemistry Department, M.V. Lomonosov Moscow State University

February - Choose the Period of the IChO
December - Participation in the International Steering Committee Meeting, Korea

## 2006

February - Science Committee started its work
July, 4 - Order of Prime-Minister of Russian Federation
July - visit to the 38th IChO in Yeungnam University, Korea
September - Order of Ministry of Education and Science, Russian Federation
October - Order of Rector of M.V. Lomonosov Moscow State University
October, 20 - Internet-site launched
December, 7-10 - International Steering Committee Meeting, Moscow
December - IChO 2007 Tentative Program

## 2007

January - Official Invitation
January - Budget Funding from State Budget
January-April - Laboratory Renovation
February, 1 - Upload Preparatory Problems on Internet
February - On-Line Registration Launched
February-June - On-Line Registration
February - Select Guides and Staff
July, 15 to 24 - IChO
December - Report to the International Steering Committee, Budapest

## People who made the IChO-2007 possible

## Organizing Committee ${ }^{1}$

Petr Anisimov (Federal Agency for Education, RF)
Grigorii Balykhin (Federal Agency for Education, RF)
Tatiana Beshenenko (Federal Agency for Education, RF)
Nikolai Bulaev (State Duma, RF)
Evgenii Butko (Federal Agency for Education, RF)
Svetlana Demidova (Federal Agency for Education, RF)
Vadim Eremin
Elena Eremina
Andrei Fursenko - Chairman, Minister of Education and Science, RF
Alexander Gladilin
Isaak Kalina (Ministry of Education and Science, RF)
Lyudmila Kokhanova
Nikolai Kuz'menko
Valerii Lunin - President of the IChO-2007
Vladimir Mironov (Vice-Rector, MSU)
Elena Pazyuk
Victor Shtepa
Lyubov' Strel'nikova (Chief Editor, Khimiya I Zhizn')
Vladimir Terenin

## Science Committee

Ivan Babkin
Yurii Barbalat
Svetlana Bendrysheva
Zhanna Boeva
Andrei Cheprakov
Bulat Garifullin (Bashkirian Medical
State University)
Alexander Gladilin, Co-Chair
Eugene Karpushkin

Anna Bacheva
Mikhail Beklemishev
Anna Berkovitch
Alexander Bogachev
Vadim Eremin, Co-Chair
Andrei Garmash
II'ya Glebov
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[^0]Mikhail Korobov
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Kirill Oskolok
Valery Putlyaev
Marina Rozova
Irina Seregina
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Marina Reshetova
Igor Sedov (Kazan' State University,
A.Butlerov Institute of Chemistry)

Sergey Seryakov
Boris Tarasevich
Igor Tyulkov
Andrei Vedernikov (Univ. of Maryland)

## Secretariat

Anna Bacheva
Anastasiya Chekanova
Elena Pazyuk
Mikhail Tabunov (web)

Anna Berkovich
Elena Eremina
Boris Pokrovskii (web)
Ekaterina Yakubovich

## Technical Committee

| M. Belyakov | A. Bibin | M. Chudakova |
| :--- | :--- | :--- |
| A. Demidova | A. Ezhov | M. Galkin |
| An. Gladilin | D. Ivanov | K. Ivanova |
| P. Kebets | A. Marinchuk | A. Natikan |
| M. Nikitina | A. Poteryaev | E. Rodina |
| M. Steklov | V. Valaeva | S. Vatsadze |

A. Veresov

## Lab instructors

| N. Aryutkina | P. Binevskiy | P.Chelushkin |
| :--- | :--- | :--- |
| A. Chemagin | M. Chernobrovkin | G. Dudina |
| O. Fedyanina | V. Figurovskaya | E. Ivanainen |
| S. Ivanova | S. Kurzeev | M. Livantsov |
| L. Livantsova | I. Men'shikova | I. Naperova |
| O. Popova | V. Sergeeva | I. Shender |
| O. Starostina | T. Suslenkova | G. Ushakov |
| S. Vatsadze | Yu. Volkova | I. Zorov |

## Lab assistants

G. Demchuk
T. Klimashina
P. Kudan
T. Lyskova
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L. Sergeeva
M. Tereshina
A. Druzhinina
D. Dzhigailo
N. Krutova
S. Kubyshev
L. Lukanina
O. Lukanina
S. Matusova
T. Matyushina
O. Monogarova
N. Potapova
L. Shadskaya
L. Shimko
K. Yablotskiy
A. Zatirakha

## Spectrophotometer operators

| O. Anikina | O. Bogomolova | V. Bugrin |
| :--- | :--- | :--- |
| D. Davydov | A. Filatov | L. Filatova |
| E. Gerasimova | A. Gopin | N. Gruzinskaya |
| A. Kislukhin | M. Kondrashov | N. Kovaleva |
| D. Maltseva | M. Nemykh | D. Pavlov |
| I. Protasov | E. Sbrueva | T. Semashko |
| V. Skorkin | Yu. Smirnova | M. Smolov |
| A. Sokolyuk | V. Spiridonov | S. Uglanova |
| V. Vasil'yev | A. Zhirnov |  |

## "Catalyzer" team

A. Agaeva
E. Bredina
K. Davydova
M. Eremina
A. Galieva
M. Kokhanova
A. Kravtsova
A. Lobus (photo)
A. Lukichev (head)
I. Lukichev
M. Nefedieva
A. Pomerantseva
I. Salynkina
S.Sobolev
V. Turin

Opening and Closing Ceremonies designed by Victor Shiryaev

Doctors - Olga Eremina and Tatiana Pogorelova

## Guides

| Argentina | Anna Kovrigina |
| :--- | :--- |
| Armenia | David Ayrapetyan |
| Australia | Nadezhda Kolesnik |
| Austria | Daniil Zaonegin |
| Azerbaijan | Eldar Rizaev |
| Belarus | Vitaliy Sushkevich |
| Belgium | Alexey Rozov |
| Brazil | Kate Abramova |
| Bulgaria | Georgi Valeriev Stoychev |
| Canada | Artem Kovalenko |
| China P.R. | Jin Zhao |
| Chinese Taipei | Anna Lyamina |
| Croatia | Anastasiya Galanina |
| Cuba | Anna Kalyushnaya |
| Cyprus | Elena Ivanova |
| Czech Republic | Kate Zaharevich |
| Denmark | Nadezhda Ogneva |
| Estonia | Eugenia Tamyar |
| Finland | Alexey Shikhantsov |
| France | Etienne Richard |
| Germany | Zhenya Kazanova |
| Greece | Anton Tunin |
| Hungary | Alexei Kulagin |
| Iceland | Sasha Yovcheva |
| India | Svetlana Khoronenkova |
| Indonesia | Sergey Kovalevskiy |
| Iran | Marina Frolova |
| Ireland | Tatiana Kononova |
| Israel | Maxim Abakumov |
| Italy | Ksenia Sarycheva |
| Japan | Marina Ulanovskaya |
| Kazakhstan | Maria Khrenova |
| Korea Republic | Natalia Leshakova |
| Kyrgyzstan | Aatvia |


| Malaysia | Alexandra Malishkina |
| :--- | :--- |
| Mexico | Nina Kozhemyakina |
| Moldova | Andrey Istrate |
| Mongolia | Ganbaatar Tsetserleg |
| Netherlands | Elena Galysheva |
| New Zealand | Kate Yakubovich |
| Norway | Natalia Morukova |
| Pakistan | Alexander Kuznetsov |
| Peru | Lidia Bogatyreva |
| Poland | Evgeniya Zhukovskaya |
| Portugal | Valentina Pyatickh |
| Romania | Alexey Godina |
| Russian Federation | Oleg Chernov |
| Saudi Arabia | Samir Zheltisov |
| Singapore | Mila Shtepa |
| Slovakia | Yana Kresan |
| Slovenia | Maria Kuleshova |
| Spain | Olga Usovich |
| Sweden | Kate Zakharevich |
| Switzerland | Daniil Troshinkin |
| Tajikistan | Ulmas Zhumaev |
| Thailand | Diana Kfuri |
| Turkey | Kyiyalbek Kaparov |
| Turkmenistan | Anton Reshetnyak |
| Ukraine | Maxim Zabilskiy |
| United Kingdom | Mikhail Sheybe |
| United States | Daria Tsareva |
| Uruguay | Azalia Korunbaeva |
| Venezuela | Anastasiya Nevokshanova |
| Vietnam | Nguen Din Tyyong |
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| mentors | Anna Dyachenko |
| mentors | Alexandr Veresov |
| mentors | Igor Tyulkov |
| mentors | Oleg Brilev |
|  |  |
| guests | Aleksandra Prokhorova |
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[^0]:    ${ }^{1}$ Affiliation by default: Chemistry Department of MSU

