IChO 2020 Report

23-30/07/2020

Istanbul, TURKEY



52nd IChO 2020 International Chemistry Olympiad

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Foreword



With each passing year, the International Chemistry Olympiad has grown in size, and consequently, the number of participants has increased. In addition, this year we hosted International Chemistry Olympiad for the second time since 2011. We wish we could have welcomed you in Istanbul as our honorable guests.

Unfortunately, the year 2020 did not start as we expected. The current COVID-19 pandemic has resulted in high rates of infection and death, as well as widespread social disruption and a reduction in access to healthcare services and support. In light of the current worldwide COVID-19 pandemic, one of our options was to cancel IChO 2020 and take no further actions. As an alternative plan, the IChO 2020 Organizing Committee decided to introduce a remotely-conducted competition where we could still provide selected students with opportunities to showcase their abilities and encounter new aspects of chemistry. We decided to make voting in April 2020. The responses about organizing a remote IChO received from the participating countries were rather positive. Fifty out of 61 countries voted positively for a remote theoretical examination and the green light occurred.

Although the world has been upside down for several months, Remote IChO 2020 allowed us to keep the continuity of the Chemistry Olympiad. Students have been working for this Olympiad for years and we did not want their efforts to be wasted. On this occasion, we hope that we have managed to bring another generation of students to the chemistry lovers club.

"Chemistry for A Better Tomorrow" is the theme that brought us all together this year and our students are the chemists that will create a better future for humanity as a whole. Chemistry is the energy of life and a cross-cutting discipline in support of the future that we want to see. Chemistry provides contributions to biotechnology, molecular biology, pharmacy, environmental and material sciences, among many others. This final report gathers the theoretical examination and its solution as well as the statistics and results of the 235 candidates who attended the contest. And it also includes information on all those who gave a lot of time and energy preparing and conducting the event.

We would like to thank to;

- OlyExams for doing a great job in adapting the OLY-Software to the IChO 2020 in such a short time. In this way, we used a software for the first time in the Chemistry Olympiads.
- Steering Committee of IChO, for supporting us during the whole process.
- Scientific Committee and Organization Committee for their valuable contributions.
- All the staff who worked 7/24 for the success of IChO 2020.
- Our digital agency for making a very creative closing online ceremony. We felt ourselves in a real conference center during the ceremony.

IChO 2020 Team

52nd IChO Overview



Official Date

23th - 30th July 2020 (Closing Ceremony was held on 30th July 2020)

Participants

235 Students (231 of them have written the exam)

62 Head Mentor

108 Mentor

Teams

60 Participating Countries

8 Observing Countries

Results

26 Gold Medals

50 Silver Medals

73 Bronze Medals

15 Honorable Medals

Host Organization

Ministry of Industry and Technology

The Scientific and Technological Research Council of Turkey (TÜBİTAK)

Organizers and Hosts

Ministry of Industry and Technology

Ministry of Industry and Technology is a government ministry office of the Republic of Turkey, responsible for industrial and technological affairs in Turkey.



The Scientific and Technological Research Council of Turkey (TÜBİTAK)

TÜBİTAK, The Scientific and Technological Research Council of Turkey is a national agency of Turkey whose stated aim is to develop science, technology, and innovation, to support and conduct research and development, and to "play a leading role in the creation of a science and technology culture" in the country.



Participating Teams

NO	PARTICIPATING TEAMS	NO	PARTICIPATING TEAMS
1	Armenia	31	Lithuania
2	Australia	32	Mexico
3	Austria	33	Montenegro
4	Azerbaijan	34	Netherlands
5	Belgium	35	Nigeria
6	Brazil	36	NorthernMacedonia
7	Bulgaria	37	Norway
8	Canada	38	Pakistan
9	China	39	Philippines
10	Chinese Taipei	40	Poland
11	CzechRepublic	41	Portugal
12	Denmark	42	RussianFederation
13	ElSalvador	43	SaudiArabia
14	Estonia	44	Serbia
15	Finland	45	Singapore
16	France	46	Slovakia
17	Georgia	47	Slovenia
18	Germany	48	SriLanka
19	Greece	49	Switzerland
20	Hungary	50	Syria
21	Iceland	51	Tajikistan
22	Indonesia	52	Thailand
23	Iran	53	Turkmenistan
24	Ireland	54	Türkiye
25	Israel	55	UnitedKingdom
26	Japan	56	UnitedStatesofAmerica
27	Kazakhstan	57	Uruguay
28	Korea	58	Uzbekistan
29	Kyrgyzstan	59	Venezuela
30	Latvia	60	Vietnam

Observing Teams:

Afghanistan, Albania, Ecuador, Bangladesh, Nepal, Oman, Paraguay, Trinidad and Tobago

Welcome Messages



Dear Participants of IChO 2020,

It gives me great pleasure to welcome you all to the 52nd International Chemistry Olympiads (IChO) in Istanbul. I hope you will enjoy your stay in Turkey and take back nice memories with you. Chemistry as a science has been studied and applied for centuries in these lands; therefore, holding such an important event in İstanbul makes it even more meaningful.

You are all welcome to Istanbul, the beautiful city of two continents. As you all know, Istanbul is the only city in the world lying across continents, with one arm reaching out to Asia and the other to Europe. For more than 1500 years, it has been the capital of three Empires: Roman, Byzantine, and the Ottoman Empires. Setting aside its magnificent historical heritage thanks to its glorious past, Istanbul is the international center of finance and economy offering services in banking, telecommunications, industry, technology, marketing, engineering, and tourism. There are more than 60 universities in Istanbul and thousands of international students prefer to study in these universities.

In international competitions such as IChO, the contestants' achievements are striking in two respects. Firstly; it builds up our hopes for the future through their performance, demonstrating what mankind is capable of intellectually. Secondly, it is striking to witness that the universality of chemistry reasoning is reflected in the work of the students despite the wide cultural diversities prevailing among them. I consider it as the reaffirmation of the fact that chemistry reasoning is one of the highest and most universal values that the human intellect has created so far.

Needless to say; fostering and promoting friendly relations among young chemists in the world would contribute to the establishment of multi-dimensional scientific cooperation, which we value very much as the Ministry of Industry and Technology of Turkey. I sincerely believe that IChO 2020 will serve as a platform where participants from all over the world could establish long-lasting friendships, which – in the end – will result in the creation of a more peaceful world as well as mutual understanding between our countries. I am very honored by your presence in my country and wish you success in the Olympiads.



It is a great honor for Turkey to host the 52nd International Chemistry Olympiad (IChO) in Istanbul Technical University (ITU). ITU is one of the oldest technical universities in the world. As ITU provides an international environment, it offers many opportunities for students to gain international experience. I am very happy to express that the Scientific and Technological Research Council of Turkey (TUBITAK) is coordinating the organization of this event. I would like to extend my warm welcome to all participants from every part of the world!

Chemistry is commonly referred to as the central science not only due to its connections with other scientific disciplines but also owing to its impact on our lives. The knowledge derived from chemistry allows us to appreciate the world we live in, as well as understand how to change and improve it. Therefore, it is very exciting to host the most talented young chemists who will take part in shaping the future of chemistry as well as our world. More than 300 IChO contestants from nearly 80 countries on five continents believing in "chemistry for a better tomorrow" will have ten days of magnificent experiences.

In addition to scientific experiences, our guests will also enjoy various activities and experience amazing opportunities in Istanbul, which is a city of fantastic history, culture, and beauty. Istanbul is the financial center of Turkey and it retains its metropolitan status: the city's population is more than 14 million people, making it one of the largest cities in the world. The days you will spend in Istanbul will be unforgettable in

all - scientific, cultural and educational terms. The city of Istanbul, where most activities will take place, will surely offer you fascinating perspectives and memorable experiences. So please enjoy your time here.

We look forward to welcoming all participants of the 52nd International Chemistry Olympiad to participate in this great scientific event. Let's meet in Istanbul where the continents and cultures "**Bond**".



It is my great pleasure to greet you all at this special science summit in Istanbul, a beautiful city and a historical crossroads between continents and civilizations. This is also the city where I fell in love with chemistry and I received my fundamental chemistry education that many years later led to a Nobel Prize in Chemistry. You have come together from different backgrounds to spend time with one another and compete to earn one of the medals in recognition of your love for chemistry. I know you have worked very hard to achieve the honor of representing your home country at this Olympiad. However, you are not representing just your homeland but you are also representing the hope of humanity for a better world where science is supreme and is used to help build a just and prosperous world for all people regardless of national origin, ethnicity, or personal beliefs. If you choose to pursue this scientific journey, this will be just the beginning. You must continue to work hard as I believe strongly that hard work is the most important key to success. I also believe that the honor of being an Olympian, which all of you share, goes hand in hand with the responsibility of serving humanity. You are our hope for a better and a just future for mankind.

Chemistry defines the way a substance changes and reacts with other substances. Thus, learning chemistry helps you better understand the nature of relations between individuals. This will lead you to contribute to the well-being of humanity and to a better world.

I wish you all good luck at the Istanbul Chemistry Olympiad.

Program

- 15th of July 2020:
- 21st of July 2020:
- 23rd of July 2020:

- Deadline to register student information, invigilator form, make payment and send signed formal documents.
- Oly-Exams Software training for the country mentors • and invigilators between 01:00 -03:00 pm (Istanbul Time)
- Exam software opening at 07:00 am Istanbul Time. •
- Problems available to mentors (available also for . translations).
- International jury meeting via Zoom in two separate • (starting time of the sessions: 04:00 pm Istanbul Time).
- 24th of July 2020:
- 25th of July 2020

26th of July 2020

27th of July 2020

Invigilators were able to get the printout after 09.00 am • on 25th of July 2020.

Submission of the translations on the software.

•

- Theoretical exam; conducted in each country. Exams • were observed over zoom cameras.
- Scanned answer sheets were uploaded to Oly-Exams. •
- Gradings were done by the academic committee. •
- Grades of the students were announced at 03.00 pm. •
- The delegations specifies their requests on having a • moderation or not via Oly-Exams.
- The IChO 2020 Team informed all delegations regarding • the time of their arbitration's meeting via telegram.
- 28th of July 2020
- Arbitrations were conducted via zoom between 09 am -• 6 pm.
- Arbitration time for each delegation were arranged • according to the time zones of countries.
- Each arbitration session were planned to take up to 15 • minutes.
- The final results were announced via an online closing . ceremony at 3 pm (IST Time).
- 30th of July 2020

Theoretical Examination with Solution and Grading Schemes



International Chemistry Olympiad

Istanbul, Turkey

CHEMISTRY FOR A BETTER TOMORROW

July 25, 2020









Instructions

- Only write with pen. Your calculator should be non-programmable.
- This examination has **9 problems**.
- You will have **5 hours** to solve the exam.
- Begin only when the START command is given.
- All results must be written in the appropriate boxes in pen in the designated areas on the **answer sheets**. Use the back of the exam sheets if you need scratch paper. Remember that answers written outside the answer boxes will not be graded.
- Write relevant calculations in the appropriate boxes when necessary. Full marks will be given for correct answers only when your work is shown.
- The invigilator will announce a **30-minute** warning before the Stop command.
- You **must stop** working when the **STOP** command is given. Failure to stop writing will lead to the nullification of your exam.
- The official English version of this examination is available on request only for clarification.
- You are not allowed to leave your working place without permission. If you need any assistance (broken calculator, need to visit a restroom, etc), raise hand and wait until an invigilator arrives.

GOOD LUCK!

Problems & Grading Information

Problem	Title	Total Score	% of Total Score
1	Two Beauties of Turkey: the Van Cat and the Ankara Cat	24	8
2	A Tale of a Reactive Intermediate	77	10
3	(±)-Coerulescine	51	8
4	Symmetry Does Matter!	66	10
5	Konya, Carrot, Beta-Carotene, Vitamin-A, Immune System, Vision	100	14
6	Thermodynamics through an Interstellar Journey	80	12
7	Phthalocyanines	85	12
8	Boron Compounds and Hydrogen Storage	58	14
9	Quantification of Heavy Metal Ions	100	12
	TOTAL	641	100

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Problem 5. Konya, Carrot, Beta-Carotene, Vitamin-A, Immune System, Vision	61
Problem 6. Thermodynamics through an Interstellar Journey	69
Problem 7. Phthalocyanines	82
Problem 8. Boron Compounds and Hydrogen Storage	90
Problem 9. Quantification of Heavy Metal Ions	100

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Physical Constants and Equations

Avogadro's number, $N_A = 6.0221 \times 10^{23} mol^{-1}$ Boltzmann constant, $k_B = 1.3807 \times 10^{-23} J K^{-1}$ Universal gas constant, $R = 8.3145 JK^{-1}mol^{-1} = 0.08205 atm L K^{-1}mol^{-1}$ Speed of light, $c = 2.9979 \times 10^8 m s^{-1}$ Planck's constant, $h = 6.6261 \times 10^{-34} I s$ Faraday's constant, $F = 9.6485 \times 10^4 C mol^{-1}$ Mass of electron, $m_e = 9.1093 \times 10^{-31} kg$ Standard pressure, $P = 1 bar = 10^5 Pa$ Atmospheric pressure, $P_{atm} = 1.01325 \times 10^5 Pa = 760 mmHg = 760 torr$ Zero of the Celsius scale, 273.15 K 1 picometer (pm) = $10^{-12} m$; $1\text{\AA} = 10^{-10} m$; 1 nanometer (nm) = $10^{-9} m$ $1 eV = 1.6 \times 10^{-19} J$ 1 cal = 4.184 J $1 amu = 1.6605 \times 10^{-27} kg$ Charge of an electron: $1.6 \times 10^{-19} C$ Ideal gas equation: PV = nRTEnthalpy: H = U + PVGibbs free energy: G = H - TS $\Delta G = \Delta G^{0} + RT lnQ$ $\Delta_r G^0 = -RT lnK = -nF E_{cell}^0$ Entropy change: $\Delta S = \frac{q_{rev}}{r}$, where q_{rev} is heat for the reversible process

 $E = E^{0} + \frac{RT}{nF} ln \frac{C_{oxidation}}{C_{reduction}}$

 $\Delta S = nRln \frac{V_2}{V_1}$ (for isothermal expansion of an ideal gas)

Nernst equation:

Energy of a photon: $E = \frac{hc}{\lambda}$

Integrated rate law

Zeroth-order:	$[A] = [A]_0 - kt$			
First-order:	$ln[A] = ln[A]_0 - kt$			
Second order:	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$			
Arrhenius equation:	$k = Ae^{-E_a/RT}$			
Equation of linear calibi	Tation curve: $y = mx + n$			
Lambert–Beer equation: $A = \varepsilon lc$				

1																	18
1 H 1.008	2	_	ato S ate	omic num Symbo omic weig	ber Ol ght							13	14	15	16	17	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 TI 204.4	82 Pb 207.2	83 Bi 209.0	⁸⁴ Po -	85 At	⁸⁶ Rn
87 Fr	⁸⁸ Ra	89-103	104 Rf	105 Db -	106 Sg	107 Bh -	108 Hs	¹⁰⁹ Mt	110 Ds	111 Rg	¹¹² Cn	113 Nh	114 FI	¹¹⁵ Mc	116 Lv -	117 Ts	118 Og

Periodic Table of Elements

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
138.9	140.1	140.9	144.2	-	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0	175.0
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Ра	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
-	232.0	231.0	238.0	-	-	-	-	-	-	-	-	-	-	-





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¹H-NMR Chemical Shifts



Chemical shift (δ) ppm



Typical Coupling Constants

¹³C-NMR Chemical Shifts



L

Functional Group	Type of Vibration	Absorption Frequency Region (cm ⁻¹)	Intensity		
Alcohol	I	I			
O-H	(stretch, H- bonded)	3600–3200	strong, broad		
	(stretch, free)	3700–3500	strong, sharp		
C0	(stretch)	1150–1050	strong		
Alkane					
C_H	stretch	3000–2850	strong		
0 11	bending	1480–1350	variable		
Alkene					
-С-Н	stretch	3100–3010	medium		
-0 11	bending	1000–675	strong		
C=C	stretch	1680–1620	variable		
Alkyl Halide	I	I			
C–F	stretch	1400–1000	strong		
C-CI	stretch	800–600	strong		
C–Br	stretch	600–500	strong		
C–I	stretch	500	strong		
Alkyne	I				
C-H	stretch	3300	strong, sharp		
C≡C	stretch	2260–2100	variable, not present in symmetrical		
			alkynes		
Amine					
N-H	stretch	3500–3300	medium (primary amines have two bands; secondary amines have one band, often very weak)		
C–N	stretch	1360–1080	medium-weak		

IR Absorption Frequency Table

N–H	bending	1600	medium
Aromatic	1		
C-H	stretch	3100–3000	medium
C=C	stretch	1600–1400	medium-weak, multiple bands
Carbonyl			
C=O	stretch	1820–1670	strong
Acid	•		•
C=O	stretch	1725–1700	strong
O-H	stretch	3300–2500	strong, very broad
C0	stretch	1320–1210	strong
Aldehyde	1		
C=0	stretch	1740–1720	strong
C-H	stretch	2850–2820 & 2750– 2720	medium, two peaks
Amide			
C=0	stretch	1690–1640	strong
N-H	stretch	3500–3100	unsubstituted have two bands
	bending	1640–1550	
Anhydride	l		l
C=0	stretch	1830–1800 &1775– 1740	two bands
Ester			
C=0	stretch	1750–1735	strong
C0	stretch	1300–1000	two bands or more
Ketone			
acyclic	stretch	1725–1705	strong
	stretch	3-membered - 1850	strong
cyclic	stretch	4-membered - 1780	strong
	stretch	5-membered - 1745	strong

	stretch 6-membered - 1715 stro		strong
	stretch	7-membered - 1705	strong
α,β - unsaturated	stretch	1685–1665	strong
	conjugation move	es absorptions to lower wa	venumbers
aryl ketone	stretch	1700–1680	strong
Ether	•		
C0	stretch 1300–1000 (1150– 1070) strong		strong
Nitrile			
C≡N	stretch	2260–2210	medium
Nitro	•		
N-O	stretch	1560–1515 &	strong two bands
		1385–1345	energ, the sando

Problem 1	Question	1.1	1.2	1.3	Total
8% of the total	Points	14	4	6	24

Problem 1. Two Beauties of Turkey: the Van Cat and the Ankara Cat



The most beautiful of cats, the Van cat is a pure breed living only in Lake Van basin. Another endemic cat breed is the Ankara cat. They are called Angora cats. Their most important feature is their two different eye colors.

Van cat



Ankara cat



Nepeta cataria (catnip)



Just like people, cats can sometimes be stressed and angry. Just as people are made happy by melatonin, the stress of cats can be reduced and they can be made happy thanks to a natural product. Nepetalactone is an organic compound isolated from the plant catnip (*Nepeta cataria*), which acts as a cat attractant. Nepetalactone is a ten-carbon bicyclic monoterpenoid compound derived from isoprene with two fused rings: a cyclopentane and a lactone.

Cat eating catnip in the garden





Cat's dream



Nepetalactone

Total synthesis of nepetalactone:



1.1. The above scheme describes the total synthesis of nepetalactone. <u>Draw</u> structures of A-G, without stereochemical details.

Hints:

- Compound **A** has strong and sharp band at 3300 cm⁻¹ in the IR spectrum.
- A, B, and F are monocyclic, while C, D, E, and G are bicyclic compounds.
- **F** has one doublet at ~ 9.8 ppm in the ¹H-NMR spectrum.

Reactions of nepetalactone:



The above scheme includes a few reactions of one of the enantiopure nepetalactone 1 isomers. Three of the reaction products (5, 6, and J) are used as insect repellents in industry.

1.2. For the relationship between **5** and **6**, which of the following is/are true? <u>Tick</u> the box next to the correct answer(s) on your answer sheets.

Enantiomers
Diastereomers
Identical
Stereoisomers

Reaction of **1** with DDQ gives highly conjugated compound **H**. Also, thermal reaction of compound **H** with p-quinone gives **I** with molar mass of 226.28 g/mol.

1.3. <u>Draw</u> the structures of H, I, and J indicating stereochemistry.

Hints:

- During the formation of I, sequential pericyclic reactions and an oxidation reaction (due to the presence of O₂) take place, and a well-known gas forms during the reaction.
- J has a strong and very broad band between 3300 and 2500 cm⁻¹ in the IR spectrum.

Solution:

Total synthesis of nepetalactone:



1.1. <u>Draw</u> the structures of A–G without stereochemical details.







Reactions of nepetalactone:



1.2. For the relationship between 5 and 6, which of the following is/are true? Tick the box next to the correct answer(s).

Diastereomers points for each correct answer).	wers (2
Same compounds 2 points (total) if there is one mistake.	
Stereoisomers 0 points if there are more than one mist	akes.

1.3. <u>Draw</u> the structures of H, I, and J indicating stereochemistry.



Problem 2	Question	2.1	2.2	2.3	2.4	2.5	2.6	2.7	Total
10% of the total	Points	7	9	8	16	5	4	28	77

Problem 2. A Tale of a Reactive Intermediate

Arynes constitute a special class of reactive intermediates. The first experimental evidence for the structure of an aryne (benzyne) was demonstrated in 1953 via the elegant labeling experiments by John D. Roberts and coworkers.

In one such experiment, chlorobenzene, whose carbon at position 1 was labeled with radioactive ¹⁴C, was reacted with KNH₂ in liquid NH₃ to give nearly equal amounts of isotopic isomers **A** and **B** along with the inorganic salt **C**. This reaction proceeds via the formation of aryne intermediate **D**.



2.1. <u>Draw</u> the structure of **A**, **B** and **D**, and provide the formula of **C**. Indicate the position(s) of ¹⁴C-labeled carbon(s) with an asterisk (*) whenever applicable."

Analysis of the ¹⁴C-labeled product(s) was achieved via degradation experiments (the ¹⁴C-labeled carbons are not shown on the structures). Radioactivities of the intermediates and final products were examined.



2.2. <u>Tick</u> the appropriate boxes on the answer sheet for the intermediates and products that you expect to exhibit radioactivity.

Considering only A:	Considering only B :
Compound 1	Compound 1
□ BaCO ₃ (Batch 1)	\Box BaCO ₃ (Batch 1)
Compound 2	Compound 2
\Box BaCO ₃ (Batch 2)	\Box BaCO ₃ (Batch 2)

With the aim of facilitating aryne formation, Kobayashi and co-workers developed a fluoride-induced aryne generation protocol. Using this method, benzene derivative 3 is reacted with furan (4) in the presence of CsF, resulting in the formation of E, F, and G.



- Combustion analysis of **E** revealed the following atom content: 75.8% carbon, 5.8% hydrogen, and 18.4% oxygen.
- E does not have a proton that is exchangeable with D₂O in ¹H-NMR spectroscopy.
- **F** is an ionic compound.

2.3. <u>Determine</u> the structures of E, F, and G (without stereochemical details).

In the absence of a nucleophile or a trapping agent, arynes can undergo [2+2]-type cyclodimerization or [2+2+2]-type cyclotrimerization reactions under suitable conditions. The aryne derivative that is obtained when **3** is treated with one equivalent of CsF in MeCN can give, in principle, four different dimerization and trimerization products (H–K).

- H has two planes of symmetry.
- I is expected to exhibit 21 signals in its ¹³C-NMR spectrum.
- I and J both exhibit an m/z value of 318.1 in their mass spectra.

2.4. <u>Determine</u> the structures of H–K.

When **5** is reacted with β -ketoester **6** in the presence of 2 equivalents of CsF at 80 °C, **L** is obtained as the major product. The ¹H-NMR and ¹³C-NMR data for **L**, in CDCl₃, are as follows:

- ¹H-NMR: δ 7.79 (dd, J = 7.6, 1.5 Hz, 1H), 7.47–7.33 (m, 2H), 7.25–7.20 (m, 1H), 3.91 (s, 2H), 3.66 (s, 3H), 2.56 (s, 3H) ppm.
- ¹³C-NMR: δ 201.3, 172.0, 137.1, 134.4, 132.8, 132.1, 130.1, 127.5, 51.9, 40.2, 28.8 ppm.



2.5. Determine the structure of L.

2.6. In the reaction shown in task 2.5, which of the statement(s) in the answer sheet describe(s) the function of CsF?

• The pK_a values of HF and β -ketoester **6** in dimethyl sulfoxide (DMSO) are about 15 and 14, respectively.

\Box F ⁻ hydrolyzes the trifluoromethanesulfonate (O ₃ SCF ₃) group of 5 .
\Box F ⁻ attacks the –SiMe ₃ group of 5 .
\Box F ⁻ acts as a base to deprotonate 6 .
\Box F ⁻ acts as a nucleophile and attacks the ester group of 6.

Diazapyrone derivative **8** was shown to be a useful reactant for the construction of a variety of cyclic frameworks. Its preparation from phenylglyoxylic acid (**7**) and its use in two different reactions are described below.

- **Q** and **T** are gases under ambient conditions.
- **O** and **P** are constitutional isomers.
- **Q** does not have any signals in its IR spectrum.
- Heating 1 mol of **R** at 85 °C generates 1 mol of reactive intermediate **S**.
- Reaction of 8 with two equivalents of S gives U, Q, and T.



Note:

equiv= equivalent

cat= catalyst
2.7. <u>Determine</u> the structures of M–U.

Solution:



2.1. <u>**Draw**</u> the structures of **A**–**D**. Indicate the position(s) of ¹⁴C-labeled carbon(s) with an asterisk (*) whenever applicable.



С	D
KCI or K ⁺ : CI :	
	2 points.
1 point. 0 points if only cation or anion is written.	 2 points for different resonance forms of A including the circle representation for aromaticity. 1 point if labeled carbon is not shown or if its position is incorrect.

2.2. <u>Tick</u> the appropriate boxes on the answer sheet for the intermediates and products that you expect to exhibit radioactivity.

Considering only A:	Considering only B:
	Compound 1
⊠ BaCO₃ (Batch 1)	□ BaCO ₃ (Batch 1)
Compound 2	Compound 2
□ BaCO ₃ (Batch 2)	⊠ BaCO ₃ (Batch 2)
Solution: only BaCO ₃ (Batch 1)	Solution: Compound 1 and BaCO ₃ (Batch 2)
3 points for the correct answer.	6 points (total) for the two correct answers (3 points
0 points for one or more mistakes.	for each correct answer).
	3 points (total) if there is one mistake.
	0 points if there are more than one mistakes.

Note: The answer to this task will depend on the student's structural assignment of compounds **A** and **B** in task **2.1**



2.3. <u>Determine</u> the structures of E, F, and G (without stereochemical details).

E	F
MeO	CsO₃SCF₃ or Cs⁺ CF₃SO₃⁻ or CsOTf
4 points.	2 points.
2 points if the product of [2+2] reaction between aryne and furan is written.	
0 points if ring-opened naphthol product is written.	
G	
(CH ₃) ₃ SiF or Me ₃ SiF	
2 points.	

2.4. <u>Determine</u> the structures of H–K.



2.5. <u>Determine</u> the structure of L.



2.6. In the reaction shown in task 2.5, which of the statement(s) in the answer sheet describe(s) the function of CsF?







2.7. <u>Determine</u> the structures of M–U.







Problem 3	Question	3.1	3.2	3.3	3.4	3.5	3.6	3.7	Total
8% of the total	Points	8	16	4	8	5	5	5	51

Problem 3. (±)-Coerulescine

A spiro compound is typically an organic compound containing rings linked together by one common atom (spiroatom) as carbon atom with bold in figure below. The spiro[pyrrolidin-3,3'-oxindole] ring system is a structural framework incorporated in several cytostatic alkaloids and unnatural compounds. Coerulescine (1) and horsfiline are the simplest prototype members of this subfamily that can be synthesized by the route shown below.

C;

Claisen rearrangement, which is a [3,3]-sigmatropic rearrangement, is a powerful carbon–carbon bond-forming reaction in which an allyl vinyl ether is converted thermally to an unsaturated carbonyl compound as shown in the Scheme below. When compound **A** is heated, it undergoes Claisen rearrangement to give carbonyl compound **B**.

For this entire task, your answers can be given without any stereochemical details.





3.1. <u>Draw</u> the structures of A and B.

- A is an inseparable mixture of *cis/trans* isomers.
- **B** has IR absorption at 1726 cm⁻¹.

3.2. <u>Draw</u> structures for C, D, E, and F.

• **D**–**F** have a bicyclic structure.

3.3. <u>Choose</u> the correct order of steps for the transformation of **F** to **G**.

 $\hfill\square$ Imine formation, then reduction, then amidation

 $\hfill\square$ Amidation, then imine formation, then reduction

 $\hfill\square$ Reduction, then amidation, then imine formation

3.4. <u>Draw</u> structures for G and H (both spiro compounds).

3.5. <u>**Draw**</u> the structure of the intermediate produced by treatment with *n*-BuLi in the step $H \rightarrow$ **coerulescine (1)**.

Coerulescine (1), on treatment with *N*-bromosuccinimide (NBS), gives the bromo derivative, which upon heating with sodium methoxide in the presence of cuprous iodide gives **horsfiline (I)** in 60% yield.

3.6. <u>Choose</u> the correct structure for compound I consistent with the following selected ¹H-NMR data: δ 7.05 (d, *J* = 1.4 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.72 (dd, *J* = 8.0, 1.4 Hz, 1H) ppm.



3.7. When the allyl ether of 2 naphthol is heated a sigmatropic rearrangement is initiated. <u>Write</u> the structure of major product isolated from this reaction.



Solution:



3.1. <u>**Draw**</u> the structures of **A** and **B**.



3.2. <u>Draw</u> structures for C, D, E, and F.





3.3. <u>Choose</u> the correct reaction order for the transformation of F to G.

☑ Imine formation, then reduction, then amidation	
\Box Amidation, then imine formation, then reduction	4 points for correct answer.
\Box Reduction, then amidation, then imine formation	0 points for incorrect answer.

3.4. Draw structures for G and H.



3.5. <u>**Draw**</u> the structure of the intermediate for the reaction with *n*-BuLi in the step $H \rightarrow coerulescine$.



3.6. <u>Choose</u> the correct structure for compound I consistent with the following selected ¹H-NMR data: δ 7.05 (d, J = 1.4 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.72 (dd, J = 8.0, 1.4 Hz, 1H) ppm.





3.7. When the allyl ether of 2 naphthol is heated a sigmatropic rearrangement is initiated. **Write** the structure of major product isolated from this reaction.





Problem 4	Question	4.1	4.2	4.3	4.4	4.5	4.6	4.7	Total
10% of the total	Points	12	6	6	16	9	9	8	64

Problem 4. Symmetry Does Matter!

There are numerous reactions in organic chemistry that proceed through cyclic transition states and these are classified as pericyclic reactions. Woodward–Hoffmann rules, developed by Robert B. Woodward and Roald Hoffmann, are used to rationalize stereochemical aspects and the activation energy of pericyclic reactions.



Woodward-Hoffmann rules								
	Electrocyclic I	reactions	Cycloa	dditions				
Number of electrons	Thermal (Δ)	Photochemical (hv)	Thermal (∆)	Photochemical (hv)				
4 <i>n</i> (n = 1, 2,)	Conrotatory (con)	Disrotatory	Disfavored	Favored				
4 <i>n</i> +2 (n = 1, 2,)	Disrotatory (dis)	Conrotatory	Favored	Disfavored				

4.1. <u>Fill</u> in the table for reactions (i)–(iii) or products 2–5:

Reaction	Product	[? + ?] cycloaddition	Δ or hv
i	2		
ii	3		
iii	4		
	5		

There are three possible benzotropone isomers. Although two of the benzotropone isomers were isolated, 3,4benzotropone (1) has not been isolated. Its instability is attributed to the *o*-quinoidal structure of 1 because it has no sextet electron system in the benzene ring.

4.2. <u>**Draw**</u> the structures of stable benzotropone isomers **A** (with 6 signals in its ¹³C-NMR) and **B** (with 11 signals in its ¹³C-NMR).

4.3. When the following tetraene is reacted under photochemical conditions, symmetry-allowed product(s) of three different ring sizes can form according to the Woodward–Hoffmann rules. <u>Tick</u> the correct answer in each row.

$$\overset{\mathsf{D}}{\overbrace{}}\overset{\mathsf{hv}}{\overbrace{}}?$$

D,D	D
	D



Prof. Dr. Aziz Sancar

The Nobel Prize in Chemistry 2015 was awarded jointly to the Turkish scientist Aziz Sancar, Swedish scientist Tomas Lindahl, and American scientist Paul Modrich for their "mechanistic studies of DNA repair". Pyrimidine bases found in DNA may undergo a photochemical **[2+2]-cycloaddition reaction** (see above figure) with UV light that reaches a person's skin, causing damage to DNA, which may ultimately lead to skin cancer. The research by Professor Aziz Sancar focused on the DNA repair mechanism for this type of damage.

Thymine (\mathbf{T}) is one of the nucleobases that can undergo such a photochemical reaction with UV light. Let us assume that we have a solution of free thymine that was subjected to UV irradiation.



4.4. Considering stereochemistry, <u>draw</u> the structures of <u>all possible products</u> of this reaction between two free thymine (T) molecules. <u>Circle</u> the compound(s) which is/are chiral. Drawing only one enantiomer of an enantiomeric pair is sufficient. Please note that only C=C bonds participate in this reaction.

A broad range of halogenated derivatives of norbornadiene (**N**) are known in the literature. Tribromo-norbornadiene ($C_7H_5Br_3$) has six achiral isomers. Three of these isomers (**6**, **7**, and **8**) are given below.



4.5. How many signals do you expect from the ¹³C-NMR spectra of **6**, **7**, and **8**? <u>Fill in</u> the following boxes.



4.6. <u>Draw</u> structures of the remaining achiral tribromo-norbornadiene ($C_7H_5Br_3$) isomers (**C**, **D**, and **E**) in addition to 6–8 over the given figures in the boxes.



The NMR spectrum of ether **9** is complex. Two MeO– groups are different as are all the hydrogen atoms on the rings. However, diphenol **10** has a very simple NMR spectrum and there are only three types of protons (marked as a, b, and c). A reasonable average structure responsible for all resonance structures and its symmetry is shown as **11**.







Solution:



4.1. <u>Fill</u> in the table for reactions (i)–(iii) or products 2–5:

Reaction	Product	[? + ?] cycloaddition	Δ or hv
i	2	 [10 + 10] ([6 + 6] is also acceptable). 2 points. 	hv 1 point.
ii	3	 [8 + 2] ([4 + 2] is also acceptable). 2 points. 	Δ 1 point.
iii	4	 [10 + 8] ([6 + 4] is also acceptable). 2 points. 	Δ 1 point.
	5	 [10 + 8] ([6 + 4] is also acceptable). 2 points. 	Δ 1 point.

4.2. <u>**Draw**</u> the structures of stable benzotropone isomers **A** (with 6 signals in its ¹³C-NMR) and **B** (with 11 signals in its ¹³C-NMR).



4.3. When the following tetraene is reacted under photochemical conditions, symmetry-allowed product(s) can form according to the Woodward–Hoffmann rules. <u>Tick</u> the correct answer(s).





4.4. Considering stereochemistry, <u>draw</u> the structures of <u>all possible products</u> of this reaction. <u>Circle</u> the compound(s) which is/are chiral. Drawing only one enantiomer of an enantiomeric pair is sufficient. Please note that only C=C bonds participate in this reaction.



4 points (in total) for the correct determination of chirality for the two chiral compounds (2 points each).
2 points if there is one mistake in the determination of chirality.
0 points if there is more than one mistake in the determination of chirality.

4.5. How many signals do you expect from the ¹³C-NMR spectra of **6**, **7**, and **8**? <u>Fill in</u> the following boxes.



4.6. <u>**Draw**</u> open structures of the remaining achiral (meso) tribromo-norbornadiene ($C_7H_5Br_3$) isomers (**C**, **D**, and **E**) in addition to 6–8 over the given figures in the boxes.



4.7. How many signals do you expect from the ¹³C- and ¹H-NMR spectra of **12** and **13**?



Problem 5	Question	5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	Total
14% of the total	Points	13	13	15	8	12	10	17	12	100

Problem 5. Konya, Carrot, Beta-Carotene, Vitamin-A, Immune System, Vision



Mevlana (Rumi) was a great mystic and Sufi poet who lived out his days in Konya in the 13th century. The indirect relevance of Konya to chemistry is that the city provides 65% of the country's carrot production, from which one of the essential vitamins (vitamin A) is obtained.

Carrot is an important source of β -carotene, which gives the vegetable its orange color. This molecule is a red-orange pigment naturally found in plants and fruits and is a provitamin A carotenoid. It is converted to vitamin A, which is essential for normal growth and development, the immune system, and vision function.



Figure 1. Ball and stick representation of the structure of β -carotene. The gray and white spheres represent the carbon and hydrogen atoms, respectively. The numbered carbon atoms belong to the linear conjugated π -segment of the molecule.

 β -Carotene has an extended polyene chain of 22 carbon atoms. It is a conjugated π -system, having alternating single and double bonds. Its experimental maximum absorption wavelength (λ_{max}) is 455 nm. We assume that all the bonds between C₁ and C₂₂ are conjugated bonds. There are 22 π -electrons in the molecule (Figure 1).

To a crude approximation, the electrons in the $C-2p_z$ orbitals, which are perpendicular to the molecular plane, are assumed to move along the entire molecule, without interacting with each other. They are like independent particles confined in a molecule moving along the x-axis in one dimension. These characteristics of π -electrons make them eligible for being treated by the simplest model called the **particle in one-dimensional box** model.

The wave function and the energies of the quantized levels for an electron moving in a one-dimensional box with infinite potential walls are given as follows:

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$
Eq.1

where n is the quantum number, $n=1,2,3,4,...,\infty$, and L is the box length.

$$E_n = \frac{n^2 h^2}{8m_e L^2}$$
 Eq.2

In two dimension, within the framework of independent particle approximation, the wavefunction is expressed as a product of one-dimensional wavefunctions, and the energy is expressed as a sum of one-dimensional energies. The energy levels of the two dimensional rectangular box is given as follows:

$$E_{n_x,n_y} = \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right] \left\{\frac{h^2}{8m_e}\right\}$$
 Eq. 3

where n_x , n_y are the quantum numbers and they are positive integers. L_x , L_y are the dimensions of the box in the 2D model. They are positive numbers.

5.1. Which two of the sentences given below are correct? <u>Tick</u> only one answer which includes correct sentences in your answer sheet.

The β -carotene molecule is orange in color because

- i) it absorbs in the visible region of the electromagnetic spectrum.
- ii) HOMO \rightarrow LUMO transition occurs by absorption of IR photon.
- iii) the spacing between the 22nd and the 23rd energy levels is equal to the energy of the IR photon at the orange wavelength.
- iv) it absorbs green/blue light and it transmits red/yellow color.
- v) it absorbs in the UV-Vis region since the molecule has no net dipole moment.

Although it is highly unrealistic, let us assume that the conjugated segment of the molecule is linear and treated with the particle in a one-dimensional box model as shown in figure 2. In this case, the length of the box can be approximated as L=1.40×n_c (in Å), where n_c is the number of carbon atoms in the conjugated segment.

Use this information to answer the questions 5.2–5.6.



Figure 2. Schematic representation of the conjugated line segment made up carbon atoms of β -carotene in a one-dimensional box of length L.

5.2. <u>Calculate</u> the energies (in J) of the lowest two energy levels

5.3. <u>Draw</u> the wavefunctions of the lowest two energy levels with proper labelling the x-axis.

5.4. <u>Sketch</u> the energy level diagram up to n = 4 showing the relative spacing.

5.5. What is the total π -energy (in J) of the molecule?

5.6. <u>Calculate</u> the wavelength (in nm) at which the transition between the highest occupied and lowest unoccupied energy levels occurs.

Use the particle in a two-dimensional box model to answer questions 5.7–5.8.





Assume that the conjugated segment is made up of conjugated bonds that are all-*trans* to each other. The motion of the π -electrons is studied in the two-dimensional rectangular box with the dimensions L_x = 26.0 Å, L_y = 3.0 Å (Figure 3).

5.7. <u>Calculate</u> the energies (in J) of the highest occupied and the lowest unoccupied energy levels and the wavelength (in nm) at which the transition between these energy levels occurs.

5.8. What should be the L_x value (in Å) in order for the molecule to absorb light at the experimental λ_{max} =455 nm if L_y is kept constant at 3.0 Å. (Assume that the quantum numbers for homo and lumo are the same as in the question 5.7.)

Solution:

5.1. Which two of the sentences given below are correct? <u>Tick</u> only one answer which includes correct sentences in your answer sheet.

□ a) i and ii	□ b) i and iii	⊠ c) i and iv	□ d) i and v
🗆 e) ii and iii	☐ f) ii and iv	□ g) ii and v	□ h) iii and iv
□ j) iii and v	\Box k) iv and v		
13 points for the cor	rrect answer.		

5.2. <u>Calculate</u> the energies (in J) of the lowest two levels.

Calculation:

$$L = 1.40 \times 22 = 30.8 \text{ Å}$$

$$E_n = \frac{n^2 h^2}{8m_e L^2} = n^2 (6.351 \times 10^{-21}) \text{ J}$$

$$E_1 = 6.351 \times 10^{-21} \text{ J}$$

$$E_2 = 2.540 \times 10^{-20} \text{ J}$$
13 points. 3 points for correct box length, 5 points for each correct energy value.
No partial credit will be given.



5.3. <u>**Draw**</u> the wavefunctions of the lowest two energy levels with proper labelling the x-axis.

5.4. <u>Sketch</u> the energy level diagram up to n = 4 showing the relative spacing.



5.5. Calculate the total π -energy (in J) of the molecule?



5.6. <u>Calculate</u> the wavelength (in nm) at which the transition between the highest occupied and lowest unoccupied energy levels occurs.

Calculation:
The quantum numbers for the highest occupied and lowest unoccupied energy levels are 11 and 12,
respectively. $\Delta E = E_{12} - E_{11} = E_n = \frac{12^2 h^2}{8m_e L^2} - \frac{11^2 h^2}{8m_e L^2} = \frac{23h^2}{8m_e L^2} = \frac{hc}{\lambda}$ then, $\lambda = \frac{8m_e cL^2}{23h} = 1360$ nm10 points for the correct answer.
If wavelength expression is written correctly but the result is calculated wrongly then 3 points will
be deducted.
1 point will be deducted for incorrect unit.

5.7. <u>Calculate</u> the energies (in J) of the highest occupied and the lowest unoccupied energy levels and the wavelength (in nm) at which the transition between these energy levels occurs.

Calculation:

$$E_{n_x,n_y} = \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right] \left\{\frac{h^2}{8m_e}\right\} = \left[\frac{n_x^2}{26^2} + \frac{n_y^2}{3^2}\right] 6.025 \times 10^{-18} \text{ J}, \text{ where } L_x \text{ and } L_y \text{ should be in Å.}$$
The quantum numbers and the energies of the highest occupied and the lowest unoccupied energy levels are:
 $n_x = 11, n_y = 1 \text{ and } n_x = 12, n_y = 1$
 $E_{11,1} = \left[\frac{11^2}{26^2} + \frac{1^2}{3^2}\right] 6.025 \times 10^{-18} \text{ J} = 17.48 \times 10^{-19} \text{ J}$

 $\mathbf{E}_{12,1} = \left[\frac{12^2}{26^2} + \frac{1^2}{3^2}\right] \mathbf{6.025 \times 10^{-18} J} = \mathbf{19.53 \times 10^{-19} J}$



5.8. What should be the L_x value (in Å) in order for the molecule to absorb light at the experimental λ_{max} if L_y is kept constant at 3.0 Å. (Assume that the quantum numbers for homo and lumo are the same as in the question 5.7.)

Calculation:

$$\Delta E = \left[\frac{12^2}{L_x^2} + \frac{1^2}{L_y^2} - \frac{11^2}{L_x^2} - \frac{1^2}{L_y^2}\right] \left\{\frac{h^2}{8m_e}\right\} = \left[\frac{23}{L_x^2}\right] 6.025 \times 10^{-18} = \frac{1.386 \times 10^{-18}}{L_x^2} (L_x \text{ is in } \text{Å})$$

$$\Delta E = E_{\text{photon}} = (\text{hc})/\lambda \rightarrow \frac{1.386 \times 10^{-18}}{L_x^2} = \frac{6.626 \times 10^{-34} \times 2.998 \times 10^8}{455 \times 10^{-9}}$$

$$L_x = 1.782 \times 10^{-9} \text{ m} \quad L_x = 17.82 \text{ Å}$$
12 points for the correct answer.
No partial credit will be given.
1 point will be deducted for incorrect unit.

Problem 6 Question	6.1	6.2	6.3	6.4	6.5	6.6	6.7	6.8	Total
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12% of the total	Points	5	12	6	3	6	6	5	3	80
	Question	6.9	6.10	6.11	6.12	6.13				
	Points	8	6	6	8	6				

Problem 6. Thermodynamics through an Interstellar Journey

Part 1

In a hypothetical universe, an unknown amount of diborane participates in the following reaction:

 $B_2H_6(g) + 6 H_2O(l) \rightarrow 2 H_3BO_3(s) + 6 H_2(g)$

Assume that in this hypothetical universe, $H_3BO_3(s)$ obtained from this reaction was completely sublimed at 300 K. The necessary energy for sublimation was obtained through work released by **one cycle** of an ideal heat engine in which one mole of monoatomic perfect gas flows through the cycle described in the pressure (p) – volume (V) diagram below:

- A \rightarrow B; isothermal reversible expansion receiving 250 J by heat transfer (q_H) at a temperature of 1000 K (T_H) from a hot source.
- $B \rightarrow D$; reversible adiabatic expansion.
- D→C; isothermal reversible compression at a temperature of 300 K (T_C) releasing some amount of heat (q_C) to a cold sink.
- $C \rightarrow A$; reversible adiabatic compression.



After heat transfers, the remaining energy is released as work (w). Also, q_H and q_C are related to T_C and T_H as follows:

$$\frac{|q_H|}{|q_C|} = \frac{T_H}{T_C}$$

The efficiency of the cycle can be found by work released by cycle (w) divided by heat absorbed by cycle (q_H).

You are provided with the change in enthalpies of the following reactions at 300 K.

(1) $B_2H_6(g) + 6 \operatorname{Cl}_2(g) \rightarrow 2 \operatorname{BCl}_3(g) + 6 \operatorname{HCl}(g)$	$\Delta_{\rm r} {\rm H}(1) = -1326 {\rm kJ} {\rm mol}^{-1}$
(2) $BCI_3(g) + 3 H_2O(I) \rightarrow H_3BO_3(g) + 3 HCI(g)$	$\Delta_r H(2) = -112.5 \text{ kJ mol}^{-1}$
(3) $B_2H_6(g) + 6 H_2O(I) \rightarrow 2 H_3BO_3(s) + 6 H_2(g)$	$\Delta_r H(3) = -493.4 \text{ kJ mol}^{-1}$
$(4) \frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow HCl(g)$	$\Delta_r H(4) = -92.3 \text{ kJ mol}^{-1}$

6.1. <u>Calculate</u> the molar enthalpy of sublimation (in kJ mol⁻¹) for H₃BO₃ at 300 K.

6.2. <u>Calculate</u> the $\Delta_r U$ (internal energy) in terms of kJ mol⁻¹ at 300 K for the reactions (2) and (4) given above (assume ideal gas behavior for each gaseous species in each reaction).

6.3. <u>Calculate</u> the amount of overall work produced by a heat engine (|w|) in terms of J and the amount of overall heat released to the cold sink ($|q_c|$) in terms of J.

6.4. <u>Calculate</u> the efficiency of the heat engine described above.

6.5. <u>Calculate</u> the entropy change (Δ S) for A \rightarrow B and D \rightarrow C processes in the heat engine in terms of J K⁻¹.

6.6. <u>Calculate</u> the Gibbs energy change (Δ G) in terms of J for A \rightarrow B and D \rightarrow C processes in the heat engine.

6.7. <u>Calculate</u> the ratio of pressure at point A to the pressure at point B in the cycle (standard pressure: 1 bar).
6.8. <u>Calculate</u> the amount of $H_2(g)$ (in moles) produced according to the reaction given at the beginning of the task for one cycle of the engine.

Part 2

Interstellar journeys can be done by using diborane as rocket fuel. Combustion of diborane is shown below:

$$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$$

Combustion of diborane is experimented in a 100 L closed container at different temperatures and the equilibrium amounts were recorded.

	8930 K	9005 K
B ₂ H ₆ (g)	0.38 mol	0.49 mol
H ₂ O(g)	0.20 mol	0.20 mol

Partial pressure of O_2 (g) was stabilized to 1 bar and kept constant at all conditions. Assume that in this hypothetical universe; $\Delta_r S^\circ$ and $\Delta_r H^\circ$ are independent of temperature, the standard molar entropy (S°) of B₂O₃(s) does not change with pressure, all the gas species behave as an ideal gas, and all species remain in the same phase, without any further decomposition before or after reaction, at all temperatures then:

6.9. <u>Calculate</u> K_p (pressure based equilibrium constant) at 8930 K and 9005 K.

6.10. <u>Calculate</u> $\Delta_r G^\circ$ of the reaction in terms of kJ mol⁻¹ at 8930 K and 9005 K. (If you failed to find K_p, please use K_p (8930 K) =2, K_p (9005 K) = 0.5)

6.11. <u>Calculate</u> $\Delta_r G^{\circ}$ (in terms of kJ mol⁻¹), $\Delta_r H^{\circ}$ (in terms of kJ mol⁻¹), and $\Delta_r S^{\circ}$ (in terms of J mol⁻¹K⁻¹) of the combustion reaction at 298 K. (If you failed to find K_p, please use K_p (8930 K) =2, K_p (9005 K) = 0.5)

6.12. <u>Tick</u> the correct answer in the table by determining whether combustion reactions are favored or not at given T below under standard pressure (1 bar).

	favored	Unfavored
298 K		
8930 K		
9005 K		

9100 K	

6.13. <u>Calculate</u> the $\Delta_f H$ (kJ mol⁻¹) and S°(kJ mol⁻¹ K⁻¹) of H₂O(g) using the values given in the table below. ($\Delta_f H$ = enthalpy of formation, S° = standard entropy)

(If you fail to find $\Delta_r H^\circ$ and $\Delta_r S^\circ$ of the combustion, please use ΔH° = 1000 kJ mol⁻¹, ΔS° = 150 J K⁻¹ mol⁻¹)

	ΔH _f (298 K)	S° (298 K)
$B_{2}H_{6}(g)$	36.40 kJ mol ⁻¹	0.23 kJ mol ⁻¹ K ⁻¹
O ₂ (g)	0.00 kJ mol ⁻¹	0.16 kJ mol ⁻¹ K ⁻¹
$B_2O_3(s)$	–1273 kJ mol ^{–1}	0.05 kJ mol ⁻¹ K ⁻¹

Solution:

^{6.1.} <u>Calculate</u> the molar enthalpy of sublimation (in kJ mol⁻¹) for H₃BO₃ at 300 K.

Calculation:
Hess rule:
$\Delta H(3) - 2 \times \Delta H(2) + 12 \times \Delta H(4) - \Delta H(1) = -2 \times \Delta H_{sub} (H_3 BO_3)$
$\Delta H_{sub} (H_3 BO_3) = 25 kJ mol^{-1}$
5 points.
2 points will be deducted if student forgets to divide by 2 in last step 3 points will be deducted if Hess rule is applied correctly, but the answer is incorrect due to miscalculation.
If the answer is incorrect due to any other reason, Zero point will be given If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

6.2. <u>Calculate</u> the $\Delta_r U$ (internal energy) in terms of kJ mol⁻¹ at 300 K for the reactions (2) and (4) given above (assume ideal gas behavior for each gaseous species in each reaction).

Calculation:
$\Delta U = \Delta H - \Delta (PV) = \Delta H - (\Delta n_{gas})RT$ $RT = 8.3145 J mol^{-1} K^{-1} \times 300 K = 2.494 kJ mol^{-1}$ $\Delta U = \Delta H - (\Delta n_{gas}) \times 2.494 kJ mol^{-1}$ $\Delta U(2) = -112.5 kJ - (3 mol) \times 2.494 kJ mol^{-1} = -120.0 kJ$ $\Delta U(4) = -92.3 kJ - (0) \times 2.494 kJ mol^{-1} = -92.3 kJ$
6x2=12 points. For each calculation considering that the logic for solving this question is correctly established; 1 point will be deducted if the answer is not correct in due to miscalculation. If the logic for solving this question is not established correctly, no points will be given. If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

6.3. <u>Calculate</u> the amount of work produced by a heat engine (w) in terms of J and the amount of heat released to the cold sink (q_c) in terms of J.

Calculation:

 $\frac{|q_H|}{|q_C|} = \frac{T_H}{T_C} \rightarrow \frac{250 \, J}{q_C} = \frac{1000 \, K}{300 \, K} \rightarrow |q_C| = 75 \, J$ $|w| = q_H - |q_C| = 250 \, J - 75 \, J = 175 \, J$

For w=3 points, for $3 q_c=3$ points, in total **6 points**. If q_c is incorrect due to miscalculation, 1 point will be deducted. If w is incorrect due to miscalculation, 1 point will be deducted. If w is incorrect due to incorrect q_c calculated in this section, zero point will be deducted. If w is incorrect due to incorrect q_c calculated in this section and there are miscalculations, 1 point will be deducted. If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

6.4. <u>Calculate</u> the efficiency of the heat engine described above.

6.5. <u>Calculate</u> the entropy change (Δ S) for A \rightarrow B and D \rightarrow C processes in the heat engine in terms of J K⁻¹.

Calculation: $\Delta S = \frac{dq_{reversible}}{T}$ For A \rightarrow B $\Delta S_{A \rightarrow B} = \frac{250 J}{1000 K} = 0.25 J K^{-1}$ For D \rightarrow C $\Delta S_{B \rightarrow C} = \frac{-75 J}{300 K} = -0.25 J K^{-1}$ 3 points for A \rightarrow B, 3 points for D \rightarrow C, in total 6 points. If $\Delta S_{A \rightarrow B}$ is incorrect due to miscalculation, 1 points will be deducted. Since q_H is provided in the question, If $\Delta S_{A \rightarrow B}$ is incorrect due to any other reason, no points will be given If $\Delta S_{D \rightarrow C}$ is incorrect due to miscalculation, 1 points will be deducted. If $\Delta S_{D \rightarrow C}$ is incorrect due to miscalculation, 1 points will be deducted. If $\Delta S_{D \rightarrow C}$ is incorrect due to incorrect q_c obtained in 6.3, Zero point will be deducted. However, if there are miscalculations, 1 points will be deducted. If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

6.6. <u>Calculate</u> the Gibbs energy change (Δ G) in terms of J for A \rightarrow B and D \rightarrow C processes in the heat engine.

Calculation:
$\Delta G = \Delta H - T\Delta S$, for isothermal processes $\Delta H = 0$, then $\Delta G = -T\Delta S$
$\Delta G_{A \to B} = -0.25 J K^{-1} \times 1000 K = -250 J$
$\Delta G_{D \to C} = -(-0.25 J K^{-1}) \times 300 K = 75 J$
3 points for $A \rightarrow B$, 3 points for $D \rightarrow C$, in total 6 points . If $\Delta G_{A \rightarrow B}$ is incorrect due to miscalculation, 1 points will be deducted. If $\Delta G_{D \rightarrow C}$ is incorrect due to miscalculation, 1 points will be deducted. If $\Delta G_{A \rightarrow B}$ is incorrect due to incorrect $\Delta S_{A \rightarrow B}$ obtained in 6.5, zero point will be deducted. But if there are miscalculations, 1 points will be deducted. If $\Delta G_{a \rightarrow B}$ is incorrect due to incorrect $\Delta S_{A \rightarrow B}$ obtained in 6.5, zero point will be deducted. But if there are miscalculations, 1 points will be deducted.
miscalculations, 1 points will be deducted. If AH is not considered to be zero, no points will be given.
If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

6.7. <u>Calculate</u> the ratio of pressure at point A to the pressure at point B in the cycle.

Calculation:

$$\Delta S = \frac{dq_{reversible}}{T} = nRln \frac{V_B}{V_A}$$

$$0.25 J K^{-1} = 1 mol \times 8.314 J mol^{-1}K^{-1}ln \frac{V_B}{V_A}$$

$$ln \frac{V_B}{V_A} = 0.03007 \rightarrow \frac{V_B}{V_A} = 1.03$$

$$\frac{V_B}{V_A} = \frac{P_A}{P_B} \rightarrow \frac{P_A}{P_B} = 1.03$$

5 points.

5 points. If student can find up to $ln \frac{V_B}{V_A}$ with correct value and calculate no further, 3 points will be deducted If student can find up to $ln \frac{V_B}{V_A}$ with incorrect value and calculate no further, 3.5 points will be deducted If student can find up to $\frac{V_B}{V_A}$ with correct value and calculate no further, 2 points will be deducted If student can find up to $\frac{V_B}{V_A}$ with incorrect value and calculate no further, 2.5 points will be deducted If student gets incorrect $\frac{P_A}{P_B}$ due to miscalculation, 1.5 points will be deducted. If student uses incorrect ΔS obtained from 6.5 or given in the question, no points will be deducted. If any unit is used in the answer, 0.5 points will be deducted.

6.8. <u>Calculate</u> the amount of H₂(g) (in moles) produced during the formation of boric acid.

Calculation:

 $\frac{0.175 \ kJ}{25 \ kJ \ mol^{-1}} = 7 \ \times 10^{-3} moles \ of \ H_3BO_3 \ is \ sublimated$

 $(7 \times 10^{-3}) \times 3 = 21 \times 10^{-3}$ moles of H_2 is generated

3 points.

If student gives incorrect answer due to miscalculation in any step, no points will be given. If student gives incorrect answer due to incorrect w obtained in 6.3, no points will be deducted. If there are miscalculations, the grading scheme given above will be applied. If student gives incorrect answer due to incorrect sublimation enthalpy obtained in 6.1, no points will be deducted. If there are miscalculations, the grading scheme given above will be applied. If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

6.9. <u>Calculate</u> K_p (pressure based equilibrium constant) at 8930 K and 9005.

Calculation:

$$PV = nRT \rightarrow P = \frac{nRT}{V} \rightarrow P = \frac{n \times 0.08205 \ L \ atm \ mol^{-1}K^{-1} \times T}{100 \ L}$$
At 8930 K,

$$For \ B_2H_6(g) \rightarrow P_{B_2H_6(g)} = \frac{0.38 \ mol \times 0.08205 \ L \ atm \ mol^{-1}K^{-1} \times 8930 \ K}{100 \ L} = 2.784 \ atm = 2.821 \ bar$$

$$For \ H_2O(g) \rightarrow P_{H_2O(g)} = \frac{0.20 \ mol \times 0.08205 \ L \ atm \ mol^{-1}K^{-1} \times 8930 \ K}{100 \ L} = 1.465 \ atm = 1.484 \ bar$$
At 9005 K,

$$For \ B_2H_6(g) \rightarrow P_{B_2H_6(g)} = \frac{0.49 \ mol \times 0.08205 \ L \ atm \ mol^{-1}K^{-1} \times 9005 \ K}{100 \ L} = 3.618 \ atm = 3.666 \ bar$$

$$For \ H_2O(g) \rightarrow P_{H_2O(g)} = \frac{0.20 \ mol \times 0.08205 \ L \ atm \ mol^{-1}K^{-1} \times 9005 \ K}{100 \ L} = 3.618 \ atm = 3.666 \ bar$$

$$For \ H_2O(g) \rightarrow P_{H_2O(g)} = \frac{0.20 \ mol \times 0.08205 \ L \ atm \ mol^{-1}K^{-1} \times 9005 \ K}{100 \ L} = 1.478 \ atm = 1.498 \ bar$$

$$K_p \ at \ 8930 \ K = \frac{(P_{H_2O(g)})^3}{(P_{O_2(g)})^3 \times P_{B_2H_6(g)}}}{\frac{(1.484)^3}{(1)^3 \times 2.821}} = 1.159$$

$$K_p \ at \ 9005 \ K = \frac{(P_{H_2O(g)})^3}{(P_{O_2(g)})^3 \times P_{B_2H_6(g)}}}{\frac{(1.498)^3}{(1)^3 \times 3.666}} = 0.917$$

$$2x4 \ points \ for \ K_p.$$
For each calculation of K_p.
If answer is incorrect due to miscalculation, 1 point will be deducted.
If answer is incorrect due to incorrect $P_{B_2H_6(g)}$ calculated in this part, no points will be deducted. However, if there are miscalculation, 1 point will be deducted.

If answer is incorrect due to incorrect K_p calculated in this part, no points will be deducted. If answer is incorrect due to miscalculation and incorrect K_p , 1 point will be deducted.

6.10. <u>Calculate</u> $\Delta_r G^\circ$ of the reaction in terms of kJ mol⁻¹ at 8930 K and 9005 K (use three decimal places for your result).

(If you failed to find K_p , please use K_p (8930 K) =2, K_p (9005 K) = 0.5)

Calculation:

The equilibrium constant is determined by gaseous species, K_p is going to be used to calculate ΔG° :

 $\Delta G^{\circ} = -RT ln K_p$

 ΔG° at 8930 K = -8.3145 J mol⁻¹ K⁻¹ × 8930 K ln1.159 = -10.956 kJ mol⁻¹

 ΔG° at 9005 K = -8.3145 J mol⁻¹ K⁻¹ × 9005 K ln0.917 = 6.488 kJ mol⁻¹

3 points for each ΔG° , in total **6 points**. For each ΔG° ; If ΔG° is incorrect due to miscalculation, 1 points will be deducted. If student uses incorrect value for K_p obtained from 6.9 or provided in this question, no points will be deducted. If there are miscalculations, if there are miscalculations, 1 point will be deducted. If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

6.11. <u>Calculate</u> $\Delta_r G^{\circ}$ (in terms of kJ mol⁻¹), $\Delta_r H^{\circ}$ (in terms of kJ mol⁻¹), and $\Delta_r S^{\circ}$ (in terms of J mol⁻¹K⁻¹) of the combustion reaction at 298 K.

(If you failed to find $K_p,$ please use K_p (8930 K) =2, K_p (9005 K) = 0.5)

Calculation:
$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$
$\Delta G^{\circ}(8930 \ K) = -10956 \ J \ mol^{-1} = \Delta H^{\circ} - 8930 \ K \times \Delta S^{\circ}$
$\Delta G^{\circ}(9005 K) = 6488 J mol^{-1} = \Delta H^{\circ} - 9005 K \times \Delta S^{\circ}$
$\Delta S^{\circ} = -249.1 J mol^{-1} K^{-1}$
$\Delta H^{\circ} = -2237.1 \ kJ \ mol^{-1}$
$\Delta G^{\circ}(298 \text{K}) = -2237.1 \text{kJ} \text{mol}^{-1} - 298 \text{K} \times (-0.2491 \text{kJ} \text{mol}^{-1} \text{K}^{-1}) = -2162.9 \text{kJ} \text{mol}^{-1}$
2 points for °, 2 points for ΔH° , 2 points for $\Delta G^\circ(298 \text{ K})$, in total 6 points. For ΔS° and ΔH° , if student gives incorrect answer due to miscalculation, 1 point will be deducted.
Students may calculate ΔS° after finding ΔH° by using;
$lnK = -\frac{\Delta_r H^{\circ}}{\Delta_r S^{\circ}} + \frac{\Delta_r S^{\circ}}{\Delta_r S^{\circ}}$
RT - R
If student gives incorrect answer due incorrect AH° obtained by in this part, zero point will be deducted.
there are miscalculations 1 point will be deducted

For ΔG° , if student gives incorrect answer due to miscalculation, 1 point will be deducted.
For ΔG° , if student gives incorrect answer due to incorrect ΔS° obtained in this part, zero point will be
deducted. If there are miscalculations, 1 point will be deducted.
For ΔG° , if student gives incorrect answer due to incorrect ΔH° obtained in this part, zero point will be
deducted. If there are miscalculations, 1 point will be deducted.
For ΔG° , if student gives incorrect answer due to incorrect ΔS° and ΔH° obtained in this part, zero point
will be deducted. If there are miscalculations, 1 point will be deducted.
If atudant uses any incorrect value for 40° and/or K, obtained from 6.0 and 6.10 or given in this guestion
In student uses any incorrect value for ΔG and/or κ_p obtained from 0.9 and 0.10 or given in this question,
The points will be deducted. If there are miscalculations, if there are miscalculations, it point will be deducted.
Students who solved this problem by using;
$ln\frac{K_2}{m} = -\frac{\Delta_r H^{\circ}}{m}(\frac{1}{m} - \frac{1}{m})$
$K_1 = R T_2 T_1^2$
for AH° 2 points for $AC^{\circ}(298 K)$
However
For ΔH° if student gives incorrect answer due to miscalculation. 1 point will be deducted

For ΔH° , if student gives incorrect answer due to miscalculation, 1 point will be deducted. For ΔS° , if student gives incorrect answer due to miscalculation, 1 point will be deducted. For ΔS° , if student gives incorrect answer due incorrect ΔH° obtained by using equation above, zero point will be deducted. If there are miscalculations, 1 point will be deducted.

Students may calculate ΔS° after finding ΔH° by using;

$$lnK = -\frac{\Delta_r H^{\circ}}{RT} + \frac{\Delta_r S}{R}$$

If student gives incorrect answer due to miscalculation, 1 point will be deducted. If student gives incorrect answer due incorrect ΔH° obtained by in this part, zero point will be deducted. If there are miscalculations, 1 point will be deducted.

For ΔG° , if student gives incorrect answer due to miscalculation, 1 point will be deducted.

For ΔG° , if student gives incorrect answer due to incorrect ΔH° obtained in this part, zero point will be deducted. If there are miscalculations, 1 point will be deducted.

For ΔG° , if student gives incorrect answer due to incorrect ΔS° obtained in this part, zero point will be deducted. If there are miscalculations, 1 point will be deducted.

For ΔG° , if student gives incorrect answer due to incorrect ΔS° and ΔH° obtained in this part, zero point will be deducted. If there are miscalculations, 1 point will be deducted.

If student uses any incorrect value for ΔG° and/or K_p obtained from 6.9 and 6.10 or given in this question, no points will be deducted. If there are miscalculations, the grading scheme above will be applied

If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

6.12. <u>Tick</u> the correct answer on the table by determining whether combustion reactions are favored or not at given T below under standard pressure (1 bar).

	Favored	Unfavored				
298 K						
8930 K						
9005 K						
9100 K 🗆 🖂						
8 points. Each correct answer is 2 points.						

6.13. Calculate the $\Delta_f H$ (kJ mol⁻¹) and S°(kJ mol⁻¹ K⁻¹) of H₂O(g) using the values given in the table below. ($\Delta_f H =$

enthalpy of formation, S° = standard entropy)

(If you fail to find $\Delta_r H^\circ$ and $\Delta_r S^\circ$ of the combustion, please use $\Delta H^\circ = 1000 \text{ kJ mol}^{-1}$, $\Delta S^\circ = 150 \text{ J K}^{-1} \text{ mol}^{-1}$)

Calculation:

$$B_{2}H_{6}(g) + 3O_{2}(g) \rightarrow B_{2}O_{3}(s) + 3H_{2}O(g)$$

$$\Delta H^{\circ} = \left[\Delta H_{f}(B_{2}O_{3}(s)) + 3 \times \Delta H_{f}(H_{2}O(g))\right] - \left[\Delta H_{f}(B_{2}H_{6}(g)) + 3 \times \Delta H_{f}(O_{2}(g))\right]$$

$$\Delta S^{\circ} = \left[S^{\circ}(B_{2}O_{3}(s)) + 3 \times S^{\circ}(H_{2}O(g))\right] - \left[S^{\circ}(B_{2}H_{6}(g)) + 3 \times S^{\circ}(O_{2}(g))\right]$$

$$\Delta H_{f}(H_{2}O(g)) = -309.2 \ kJ \ mol^{-1}$$

$$S^{\circ}(H_{2}O(g)) = 0.137 \ kJ \ mol^{-1} \ K^{-1}$$

$$3 \ points \ for \ \Delta H_{f}(H_{2}O(g)), \ 3 \ points \ for \ S^{\circ}(H_{2}O(g)), \ in \ total \ 6 \ points.$$
If \(\Delta H_{f}(H_{2}O(g))) \text{ is in correct due to miscalculation, 2 points will be deducted.}
If \(\Delta H_{f}(H_{2}O(g))) \text{ is in correct due to miscalculation, 2 points will be deducted.}
No points will be deducted if wrong values are obtained for \(\Delta H^{\circ}\) and \(\Delta S^{\circ}\) from \(6.11) or the values here. If there are miscalculations, 2 points will be deducted for each.

If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

provided

Broblom 7	Question	7.1	7.2	7.3	7.4	7.5	7.6	7.7	7.8	7.9	Total
12% of the total	Points	4	8	6	8	8	14	19	12	6	85

Problem 7. Phthalocyanines





Emeritus Professor Özer Bekaroğlu

The term phthalocyanine (Pc) takes its origin from the Greek "naphtha", which means rock oil, and "cyanine", which means dark blue. Turkish scientist Özer Bekaroğlu can be regarded as the pioneer of Pc chemistry in Turkey.

Metal-free phthalocyanine (1, H_2Pc) is a large planar macrocyclic compound with the formula ($C_8H_4N_2$)₄ H_2 .

7.1. How many π -electrons are there in the bold region of the H₂Pc molecule in compound **1** shown above?



Pcs containing one or two metal ions are called metallo-phthalocyanines (MPcs) and they exhibit different geometries as given above.

7.2. <u>Complete</u> the table in your answer sheet by determining the coordination number of central ions in 2–5.

Central ion	Copper ion	Titanium ion	Silicon ion	Cerium ion
Coordination number				

7.3. <u>Complete</u> the table in your answer sheet by determining the oxidation number of each metal (Cu, Ti, and Ce) in **2**, **3**, and **5**.

Metal in compounds	2	3	5
Oxidation number			

7.4. <u>Complete</u> the table in your answer sheet by determining the geometry of compounds 2–5.

Geometry	Compound
Octahedral	
Square prism	
Square pyramidal	
Square planar	

7.5. <u>Complete</u> the table in your answer sheet by determining the magnetic property of compounds 2–5.

• Use the letter "**p**" for paramagnetic property and letter "**d**" for a diamagnetic property.

Compound	Magnetic property
2	
3	
4	
5	

7.6. <u>Write</u> the ground-state electron configuration of the silicon (Si) ion in the compound **4** and <u>find</u> all the quantum numbers for the 2p electrons in its ground state.

Electron configuration:

	п	l	m_1	m_s
Quantum numbers for 2p electrons:				

Metal-free phthalocyanine $(1, H_2Pc)$ is commonly formed through the cyclotetramerization of phthalonitriles. On the other hand, Pcs having different substituents are called asymmetric, which can be prepared by the statistical cyclization of two different phthalonitriles. This method has no selectivity and the product is a mixture of all possible isomers.

7.7. <u>Draw</u> the possible products that may occur in the statistical cyclization method by using **F** and **G**. If there are any stereoisomers label as *cis*- or *trans*-.

- F and G represent two different symmetrical phthalonitriles.
- One of the products is F_4 as given below.
- Draw other products similar to the format of F₄.



Pcs are used as photosensitizers in the photodynamic therapy (PDT) of cancer due to their strong absorption in the visible spectrum and high molar absorption coefficients. PDT consists of three essential components: **photosensitizer**, light, and oxygen. None of these is individually toxic, but together they initiate a photochemical reaction resulting in the generation of cytotoxic singlet oxygen (¹O₂) that can destroy cancer cells.



- The multiplicity of an energy level is defined as 2S+1
- If the two spins are parallel ($\uparrow\uparrow$), S = 1, and if the two spins are antiparallel ($\uparrow\downarrow$), S = 0.

7.8. <u>Draw</u> the molecule orbital (MO) diagram of the lowest energy singlet state of dioxygen (¹O₂) and calculate bond order.

• There are no unpaired electrons in that state!

7.9. If the wavelength of the light needed to excite triplet oxygen into singlet oxygen is 1270 nm, <u>calculate</u> the energy (in kJ/mol) needed for this transition process.

Solution:

7.1. How many π -electrons are there in the bold region of the H₂Pc molecule in compound **1** shown above?

The number of π -electrons in an H₂Pc: **18** π -electrons

4 points for correct answer.

0 points if the number of electrons is not correct.

7.2. <u>Complete</u> the table in your answer sheet by determining the coordination number of central ions in 2–5.

Central ion	Copper ion	Titanium ion	Silicon ion	Cerium ion		
Coordination number	4	5	6	8		
2 points for each correct answer (8 points in total).						
0 points if the answer is not correct.						

7.3. <u>Complete</u> the table in your answer sheet by determining the oxidation number of each metal (Cu, Ti, and Ce) in **2**, **3**, and **5**.

Metal in compounds	2	3	5			
Oxidation number	+2	+4	+4			
2 points for each correct answer (6 points in total).						
0 points if the answer is not correct.						

7.4. <u>Complete</u> the table in your answer sheet by determining the geometry of compounds 2–5.

Geometry	Compound
Octahedral	4
Square prism	5
Square pyramidal	3
Square planar	2
2 μ	points for each correct answer (8 points in total). 0 points if the answer is not correct.

7.5. <u>Complete</u> the table in your answer sheet by determining the magnetic property of compounds 2–5.

Compound	Magnetic property

2	p			
3	d			
4	d			
5	d			
2 points for each correct answer (8 points in total). 0 points if the answer is not correct.				

7.6. <u>Write</u> the ground-state electron configuration of the silicon (Si) ion in the compound **4** and <u>find</u> all the quantum numbers for the 3p electrons in its ground state.

Electron configuration: Si ⁴⁺ : [He] 2 <i>s</i> ² 2 <i>p</i> ⁶ 2 points for writing electron configuration.	(0 points if the ele	ectron configura	ation is not corre	ect.)	
	n	l	m_1	ms	
	2	1	+1	+1/2	
	2	1	0	+1/2	
	2	1	-1	+1/2	
Quantum numbers for 2p electrons:	2	1	+1	-1/2	
	2	1	0	-1/2	
	2	1	-1	-1/2	
	2 points for each correct quantum set (12 points in total). 0 points if one of the quantum number is not correct in the set.				

7.7. <u>Draw</u> the possible products that may occur in the statistical cyclization method by using **F** and **G**. If there are any stereoisomers label as *cis*- or *trans*-.



7.8. <u>Draw</u> the molecule orbital (MO) diagram of the lowest energy singlet state of dioxygen (¹O₂) and calculate bond order.



7.9. If the wavelength of the light needed to excite triplet oxygen into singlet oxygen is 1270 nm, <u>calculate</u> the energy (in kJ/mole) needed for this transition process.

Calculation:

1 *nm* = 1 × 10⁻⁹ m and 1270 *nm* = 1.270 × 10⁻⁶ m
$$E = h \times c \div \lambda$$

 $E = (6.6261 \times 10^{-34} \text{ J s}) (2.9979 \times 10^8 \text{ ms}^{-1}) \div 1.270 \times 10^{-6} \text{ m} = 1.564 \times 10^{-19} \text{ J and}$

1.564 × 10^{−22} kJ

4 points.

For 1 mol, multiply by Avogadro's constant = $(1.564 \times 10^{-22} \text{ kJ}) (6.0221 \times 10^{23} \text{ mol}^{-1})$

= 94.19 kJ/mol

2 points. 0 points if the calculation is not correct.

	Question	8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	Total
	Points	3	3	4	4	4	4	6	3	
Problem 8	Question	8.9	8.10	8.11	8.12	8.13	8.14	8.15	8.16	
14% of the total	Points	2	3	2	4	4	4	2	2	58
	Question	8.17								
	Points	4								

Problem 8. Boron Compounds and Hydrogen Storage



Sodium borohydride ($NaBH_4$) and ammonia borane (BNH_6) are the most studied chemical hydrogen storage materials. In this question, you will explore the chemistry of boron and the use of boron compounds as hydrogen storage materials.

Borax $(Na_2B_4O_7 \cdot nH_2O)$ is a boron mineral that is produced by ETI Mining Company in Turkey. $NaBH_4$ can be synthesized by the reduction of anhydrous borax with metallic sodium under high-pressure hydrogen gas in the presence of silicon dioxide (silica) at 700 °C, namely the Bayer process. In this process, all hydrogen is stored in NaBH₄. On the other hand, it has been shown that ammonia borane (BNH₆) can be synthesized by the reaction of NaBH₄ and ammonium sulfate in dry tetrahydrofuran (THF) at 40 °C (**Hint:** BNH₆ synthesis must be conducted in a well-ventilated fume-hood because flammable gas is generated as one of the by-products). While NaBH₄ is an ionic compound, ammonia borane is a Lewis acid–base adduct.

8.1. <u>Write</u> a balanced chemical equation for the synthesis of $NaBH_4$ from anhydrous borax.

8.2. Write a balanced chemical equation for the synthesis of ammonia borane from NaBH4.

8.3. <u>**Draw**</u> the molecular geometry of the BH_4^- ion and BNH_6 molecule.

8.4. <u>Calculate</u> the hydrogen content of $NaBH_4$ and BNH_6 as a percentage by mass (wt%).

The hydrogen stored in both compounds can be released via hydrolysis reactions in the presence of a suitable catalyst at room temperature. Upon the hydrolysis reactions, 4 and 3 moles of H_2 gas are released from the hydrolysis of 1 mole of $NaBH_4$ and BNH_6 , respectively, along with metaborate anion including B-O bonds.

8.5. <u>Write</u> the balanced chemical equations for the hydrolysis of $NaBH_4$ and BNH_6 .

One of the simplest stable borates is diboron trioxide (B_2O_3). Higher borates such as $B_3O_6^{3-}$ having cyclic structures containing B-O-bonds can be formed. Since B_2O_3 is an acidic compound, it is easily reacted with water to produce boric acid (H_3BO_3). On the other hand, the high temperature and high-pressure reaction of B_2O_3 with ammonia yields two-dimensional boron nitride, which consists of planar graphite-like sheets of alternating B and N atoms.

8.6. <u>Write</u> the balanced chemical equations for the synthesis of boric acid and boron nitride.

8.7. <u>Draw</u> the molecular structures of the $B_3 0_6^{3-}$ ion, boric acid, and a single two-dimensional boron nitride sheet. **Hint:** show at least 10 B atoms in the boron nitride structure.

Furthermore, B-H compounds, called boranes, are an important class of boron compounds. The simplest stable borane is diborane (B_2H_6) and many of the higher boranes can be prepared by the pyrolysis of diborane. Diborane can be synthesized via metathesis of a boron halide and a hydride source.

8.8. <u>Write</u> a balanced chemical equation for the synthesis of diborane from the reaction of BF_3 and $LiBH_4$. Hint: both products are boron compounds.

8.9. <u>Draw</u> the molecular geometry of the diborane molecule. **Hint:** there is no B-B bond in the structure.

 BH_3 (borane) is an unstable and highly reactive molecule. Therefore, it is not possible to isolate it as BH_3 under ordinary conditions. However, it can be stabilized via its reaction with carbon monoxide to yield borane carbonyl (BH_3CO) compound, which is an adduct of borane. The preparation of BH_3CO plays an important role in exploring the chemistry of boranes as it indicates the likely existence of the borane molecule.

8.10. <u>Sketch</u> the Lewis dot structure of $BH_3 - CO$ molecule by showing the formal charges.

8.11. Which of the statements given in your answer sheet is observed in the C – 0 bond of a CO molecule upon the bond formation between BH₃ and CO? <u>Tick</u> the correct box.

 \Box It gets longer because there will be π -back donation from BH₃ to CO.

 \Box It gets longer because CO donates π -bonding electrons to BH₃.

- □ No or slight change on it because CO donates its mainly non-bonding electrons to BH₃.
- \Box It gets shorter because CO donates π^* anti-bonding electrons to BH_{3.}

Borazine consists of single and double bonded cyclic B - N units and hydrogen atoms attached to these atoms with the molecular formula $B_3N_3H_6$ and is isostructural to benzene. Borazine can be synthesized by using a two-step procedure including the synthesis of symmetrically trisubstituted chlorine derivatives of borazine ($B_3N_3H_3Cl_3$) from the reaction of ammonium chloride and boron trichloride, and then reduction of $B_3N_3H_3Cl_3$ with LiBH₄ in THF.

8.12. <u>Write</u> the balanced chemical equations for the two-step synthesis of borazine starting from ammonium chloride in THF (tetrahydrofuran). **Hint:** THF stabilizes one of the products by forming a Lewis acid-base adduct.

8.13. <u>Draw</u> the molecular structures of borazine and its symmetrically trisubstituted chlorine derivative.

Catalysts are substances that accelerate the rate of reactions by allowing them to proceed in a lower energy pathway. The catalytic activity of the catalysts is generally determined by the turnover frequency (TOF), which is calculated by dividing the molar amount of the product to the mole of active catalyst and the time (TOF = mole product/(mole catalyst x time)). A typical hydrolysis of BNH₆ was carried out in 10.0 mL of water by using 100.0 mM BNH₆ and 5.0 mg of CuPt/C catalyst (CuPt alloy nanoparticles supported on carbon black containing 8.2 wt% Pt atom). 67.25 mL of hydrogen gas was generated in 5 minutes.

8.14. Assuming the catalytic reaction is performed under standard conditions (1 atm and 273.15 K), <u>calculate</u> the TOF (min^{-1}) of the CuPt/C catalyst <u>in terms of only Pt atoms</u> in the hydrolysis of BNH₆ by considering the volume of the hydrogen gas generated.

As a result of detailed crystal analysis of a synthesized Cu_xPt_y alloy nanoparticles (the subscripts indicate molar percentages of the atoms in the alloy structure), it was determined that the face centered cubic (fcc) unit cell was formed by Pt atoms and the Pt atoms on the face of the fcc unit cell are supposed to be replaced with Cu atoms to form Cu_xPt_y displacement alloy nanoparticles. According to this information, answer the following questions.

8.15. <u>Determine</u> the composition of the alloy nanoparticles by finding x and y in the Cu_xPt_y .

8.16. <u>Sketch</u> the shape of the described crystal unit cell of Cu_xPt_y alloy nanoparticles by showing the position of all atoms on the unit cell.

8.17. Another alloy has a Cu_2Pt_1 composition. Assume that this alloy also has a fcc unit cell with an edge length of 380 pm, but the Cu and Pt atoms are randomly distributed in the atomic positions. <u>Calculate</u> the density of this alloy in g/cm³.

Solution:

8.1. <u>Write</u> a balanced chemical equation for the synthesis of NaBH₄ from anhydrous borax.

 $Na_2B_4O_7 + 16Na + 8H_2 + 7SiO_2 \rightarrow 4NaBH_4 + 7Na_2SiO_3$ (3 points) No partial point will be given if the stoichiometry is incorrect No penalty will be given for writing another silicate product if the balanced chemical equation is correct.

8.2. <u>Write</u> a balanced chemical equation for the synthesis of ammonia borane (BNH₆) from NaBH₄.

 $2NaBH_4 + (NH_4)_2SO_4 \rightarrow 2BNH_6 + 2H_2 + Na_2SO_4$ (3 points) No partial point will be given if the stoichiometry is incorrect. -1 point if molecular formula of the side product (Na₂SO₄) is written incorrectly. -1 points if the hydrogen gas is not written in the product side

8.3. <u>Draw</u> the molecular geometry of the BH_4^- ion and BNH_6 molecule



8.4. <u>Calculate</u> the hydrogen content of $NaBH_4$ and BNH_6 as a percentage by mass (wt%).

 $wt\% H (NaBH_4) = \frac{4 \times (A_w(H))}{M_w(NaBH_4)} \times 100 = \frac{4.032}{37.83} = 10.65\%$ (2 points) $wt\% H (BNH_6) = \frac{6 \times (A_w(H))}{M_w(BNH_6)} \times 100 = \frac{6.048}{30.87} = 19.59\%$ (2 points) No partial point given if any mistake occurs. 8.5. Write the balanced chemical equations for the hydrolysis of NaBH₄ and BNH₆.

 $NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$ (2 points) $BNH_6 + 2H_2O \rightarrow NH_4BO_2 + 3H_2$ (2 points)

No partial points will be given if the total stoichiometry is incorrect No penalty for writing NaBO₂ as Na⁺ + BO₂⁻ or NH₄BO₂ as NH₄⁺ + BO₂⁻ No penalty for writing other borates if the stoichiometry is correct

8.6. <u>Write</u> the balanced chemical equations for the synthesis of boric acid and boron nitride.

 $B_2O_3 + 3H_2O \rightarrow 2H_3BO_3$ (2 points) $B_2O_3 + 2NH_3 \xrightarrow{high T/high P} 2BN + 3H_2O$ (2 points) No partial points will be given if the total stoichiometry is incorrect. No penalty if the high T/high P on the reaction arrow is missed.

8.7. <u>Draw</u> the molecular structures of the $B_3 0_6^{3-}$ ion, boric acid, and a single two-dimensional boron nitride sheet (**Hint:** show at least 10 B atoms).



B ₃ 0 ³⁻ Boric acid Boron nitride			
	$B_3 O_6^{3-}$	Boric acid	Boron nitride

8.8. <u>Write</u> a balanced chemical equation for the synthesis of diborane from the reaction of BF_3 and $LiBH_4$. (Hint: both products are boron compounds)

 $3LiBH_4 + 4BF_3 \rightarrow 2B_2H_6 + 3LiBF_4$ (3 points) No partial point will be given if the stoichiometry is incorrect -1 point if molecular formula of the side product (LiBF₄) is written incorrectly.

8.9. Draw the VSEPR molecular geometry of the diborane molecule (Hint: there is no B-B bond in the structure).



8.10. <u>Sketch</u> the Lewis dot structure of BH₃CO molecule by showing the formal charges.



8.11. Which of the following statements is observed in the C - O bond of a CO molecule upon the bond formation between BH_3 and CO?

 \Box It gets longer because there will be π -back donation from BH₃ to CO.

 \Box It gets longer because CO donates π -bonding electrons to BH₃. \boxtimes No or slight change on it because CO donates its mainly non-bonding electrons to BH₃.

 \Box It gets shorter because CO donates π^* anti-bonding electrons to BH_{3.}

(2 points) No point if more than one box is clicked.

8.12. <u>Write</u> the balanced chemical equations for the two-step synthesis of borazine starting from ammonium chloride in THF. (Hint: THF stabilizes one of the products).

 $3NH_4Cl + 3BCl_3 \rightarrow B_3N_3H_3Cl_3 + 9HCl (2 \text{ points})$ $B_3N_3H_3Cl_3 + 3LiBH_4 \xrightarrow{THF} B_3N_3H_6 + 3LiCl + 3THF \cdot BH_3 (2 \text{ points})$ No partial point will be given if the total stoichiometry is wrong. -1 point for each if molecular formula of the side products is written incorrectly.

8.13. <u>Draw</u> the molecular structures of borazine and its symmetrically trisubstituted chlorine derivative.



-1 point for each molecule if the cyclic structure is shown but the double bonds are not Mesomeric structures will also be accepted

8.14. Assuming the catalytic reaction is performed under standard conditions, <u>calculate</u> the TOF of the CuPt/C catalyst <u>in terms of only Pt atoms</u> in the hydrolysis of BNH_6 by considering the volume of the hydrogen gas generated.

moles of
$$H_2$$
 gas generated = $\frac{67.25 \ mL}{22.41 \ mL}$ = 3.0 mmol = 3 × 10⁻³ mol (1 point)
moles of $Pt = \left[\left(\frac{0.005 \times 8.2}{100} \right) / 195.1 \right] = 2.1 \times 10^{-6} \ mol$ (1 point)
 $TOF = \frac{3 \times 10^{-3} \ mol \ H_2}{(2.1 \times 10^{-6} \ mol \ Pt) \times 5.0 \ min} = 286 \ min^{-1}$ (2 points)
(4 points in total)
No partial point given if any mistake occurs in the calculation of TOF.

8.15. <u>Determine</u> the composition of the alloy nanoparticles by finding x and y in the Cu_xPt_y

In a regular fcc unit cell, $Corners = \frac{8 \times 1}{8} = 1 Pt atom$ $Faces = \frac{6 \times 1}{2} = 3 Pt atoms$ After the replacement surface Pt atoms with Cu atoms, $Corners = \frac{8 \times 1}{8} = 1 Pt atom (1 point)$ $Faces = \frac{6 \times 1}{2} = 3 Cu atoms (1 point)$ Alloy composition = Cu_3Pt (2 points), $Cu_{75}Pt_{25}$ is also accepted (4 points in total) No penalty will be given if the calculation of Pt atoms in a regular fcc unit cell or after replacements is not shown.

8.16. <u>Sketch</u> the shape of the described crystal unit cell of CuxPty alloy nanoparticles by showing the position of all atoms on the unit cell.



8.17. Another alloy has a Cu_2Pt_1 composition. Assume that this alloy also has a fcc unit cell with an edge length of 380 pm, but the Cu and Pt atoms are randomly distributed in the atomic positions. <u>Calculate</u> the density of this alloy in g/cm³.

Actual unit cell composition: $Cu_{2.66}Pt_{1.33}$ (1 point) $V = A^3$ $a = 380 \ pm = 3.80 \times 10^{-8} cm$ $V = (3.80 \times 10^{-8})^3 = 54.87 \times 10^{-24} \ cm^3$ (1 point) $d = \frac{m}{V} = \frac{\left[(2.66 \times (A_w(Cu)) + 1.33(A_w(Pt)]/N_A}{54.87 \times 10^{-24} \ cm^3}\right] = \frac{\left[(2.66 \times (63.54) + (195.1)x_{1.33}\right]/6.02 \times 10^{23}}{54.87 \times 10^{-24}}$ $= 12.97 \ g/cm^3$ (2 points) (4 points in total) 1 point will be given if the density is calculated by not considering the actual alloy composition of $Cu_{2.66}Pt_{1.33}$ in the given fcc unit cell.

Problem 9	Question	9.1	9.2	9.3	9.4	9.5	9.6	9.7	9.8	Total
12% of the total	Points	5	5	8	16	5	6	25	30	100

Problem 9. Quantification of Heavy Metal Ions

For the quantitative analysis of heavy metal ions in a factory's wastewater pool, the following steps have been applied by an analyzer at 298 K:

Step 1) 10-mL samples of each were obtained from five different regions in a wastewater pool, mixed in a 100-mL beaker, and then stirred for 5 minutes using a magnetic stirrer.

Step 2) 10-mL of sample solution was taken from the 100-mL beaker and 142 mg of Na₂SO₄ was added while stirring, followed by transfer to a three-electrode cell as seen in Figure 1a. In this electrochemical cell, Pt wire, Ag/AgCl (3 M KCl), and Pt foil served as the working, reference, and counter electrodes, respectively.

Step 3) These electrodes were connected to a potentiostat and a constant potential of -0.50 V vs. Ag/AgCl for 14 minutes was applied as seen in Figure 1b (horizontal line). It is assumed that 14 min. is sufficient to complete the expected electrochemical reactions.



Figure 1. a) Electrochemical cell design; 1) Working electrode (Pt wire), 2) reference electrode (Ag/AgCl, 3M KCl), 3) counter electrode (Pt foil), 4) cell tap, 5) electrochemical cell, 6) 10-mL of sample solution. **b)** Potential change of working electrode as a function of time. y-axis: potential/V vs Ag/AgCl, x-axis: time/min.

Step 4) The electrodes were rinsed with distilled water, placed into another electrochemical cell including 10mL of 0.1 M H₂SO₄ solution, and potential was scanned between -0.50 and +0.50 V as seen in Figure 1b (downward sloping line in 2 min.). Current vs. potential data for this step are presented in Figure 2a, which is like an excellent view of *Mount Ararat (Ağrı Dağı*), the highest mountain in Turkey (Figure 2b).



Figure 2. a) Potential scan of the working electrode as a function of current in 0.1 M H₂SO₄ solution after keeping it constant at a potential of -0.50 V in 10-mL of wastewater sample as seen in Figure 1b (horizontal line). y-axis: current/ μ A, x-axis: potential/V vs Ag/AgCl, b) A view of *Great and Little Ararat* peaks.

Step 5) Another 10-mL of the sample solution prepared in *step 1* was taken and the processes explained in *steps 2 and 3* were applied in that order. The electrodes were rinsed with distilled water and placed into 10-mL of 0.1 M H_2SO_4 solution. Then the potential of the working electrode was kept constant at +0.05 V for 14 minutes. It is assumed that 14 min. is sufficient to complete the expected electrochemical reactions.

Step 6) After *step 5* was performed, the solution in the electrochemical cell was placed in a suitable oven to evaporate at 150 °C until dry solid was obtained.

Step 7) 5-mL of ethylenediaminetetraacetic acid (EDTA, H₄Y) (Figure 3) solution was added to the solid obtained in *step 6* and it was shaken to dissolve. It is known that 1-mL of EDTA solution is equivalent to 3.85 mg/mL BaCO₃. Then, pH of the solution was adjusted to 10.0. Excess EDTA was titrated with standard 0.0010 M Ni(NO₃)₂ solution and it was observed that 95.60 mL of Ni(NO₃)₂ solution was consumed up to the endpoint.



Figure 3. Chemical structure of EDTA (H₄Y).

- In water saturated with H₂S, equilibrium concentration of [H₂S] is 0.1 M.
- K_{sp}(NiS) = 4.0 × 10⁻²⁰; K_{sp}(CuS) = 1.0 × 10⁻³⁶
- $K_{a1}(H_2S) = 9.6 \times 10^{-8}; K_{a2}(H_2S) = 1.3 \times 10^{-14}$

Reaction	E°/V (at 298 K)
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	-0.24
$2H^+(aq) + 2e^- \rightarrow H_2(q)$	0.00
$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$	+0.34
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.23

9.1. Which of the following can be considered for peak 1 and peak 2 in Figure 2a, respectively? <u>Tick</u> the correct box on the answer sheet.

9.2. Which of the statements is expected, if the potential is applied as -1.2 V instead of -0.5 V at the first step (horizontal line) in Figure 1b? <u>Tick</u> the correct box on the answer sheet.

9.3. <u>Calculate</u> the scan rate of data presented in Figure 2a as mV/s at 298 K.

The potential of the following cell is measured as 0.437 V.

 $Pt, H_2(0.92 \ bar) | HCl(1.50 \times 10^{-2} \ M), AgCl(sat) | Ag$

9.4. <u>Calculate</u> the standard electrode potential value (V) of half-cell of $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$ at 298 K. <u>Note:</u> You must show all works.

9.5. Which of the statements is the main purpose of *step 5* in this analysis? <u>Tick</u> the correct box on the answer sheet.

9.6. <u>Write</u> net ionic equations for the complexation and the back titration reaction of *step 7* on the answer sheet

9.7. <u>Calculate</u> Ni²⁺ concentration as mg/L in the wastewater of the factory. <u>Note</u>: You must show all works.

9.8. <u>Calculate</u> the minimum pH value for starting the precipitation of Ni²⁺ ions in the solution obtained in *step 5* by passing H₂S gas into the solution until saturation. If you cannot solve question **9.7**, use 20 *mg/L Ni*²⁺ *sample* for this question. <u>*Note*</u>: You must show all works.

Solution:

9.1. Which of the following can be considered for peak 1 and peak 2 in Figure 2a, respectively? <u>Tick</u> the correct box on the answer sheet.

□ Peak 1: electrochemical reduction of Ni / Peak 2: electrochemical reduction of Cu

□ Peak 1: electrochemical reduction of Cu / Peak 2: electrochemical reduction of Ni

□ Peak 1: electrochemical reduction of Ni / Peak 2: electrochemical oxidation of Cu

Peak 1: electrochemical oxidation of Ni / Peak 2: electrochemical oxidation of Cu

□ Peak 1: electrochemical oxidation of Cu / Peak 2: electrochemical oxidation of Ni

5 points for correct answer.

9.2. Which of the statement is expected, if the potential is applied as -1.2 V instead of -0.5 V at the first step (horizontal line) in Figure 1b? <u>Tick</u> the correct box on the answer sheet.

\Box NO evolution	
\square NO ₂ evolution	
\Box Nitrogen evolution	5 points for correct answer.
\Box Oxygen evolution	
⊠ Hydrogen evolution	

9.3. <u>Calculate</u> the scan rate of data presented in Figure 2a as mV/s.

Calculation:	
We can calculate the scan rate using the slope of Figure 1b (downward sloping line)	
Scan rate = 1000 mV/120 s = 8.33 mV/s	
8 points.	

9.4. <u>Calculate</u> the standard electrode potential value of half-cell of $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$. <u>Note:</u> You must show all works.

Calculation:

$$E_{cell} = E_{right} - E_{left} (3 \text{ point})$$

$$Half - reactions;$$

$$AgCl(s) + e^{-} \rightarrow Ag(s) + Cl^{-}(aq)$$

$$2H^{+}(aq) + 2e^{-} \rightarrow H_{2}(g)$$

$$E_{cell} = (E_{AgCl/Ag}^{o} - 0.0592 \log[Cl^{-}]) - (E_{H^{+}/H_{2}}^{o} - \frac{0.0592}{2} \log \frac{P_{H_{2}}}{[H^{+}]^{2}}) (7 \text{ points})$$

$$0.437 = (E_{AgCl/Ag}^{o} - 0.0592 \log 1.5 \times 10^{-2}) - (0.00 - \frac{0.0592}{2} \log \frac{0.92}{(1.5 \times 10^{-2})^{2}}) (4 \text{ points})$$

$$E_{AgCl/Ag}^{o} = 0.22 \vee (2 \text{ point})$$

$$-2 \text{ points for each calculation error.}$$

$$-2 \text{ points for each wrong unit.}$$

9.5. Which of the statements is the main purpose of *step 5* in this analysis? <u>Tick</u> the correct box on the answer sheet.

 \Box Modification of Pt wire with Ni–Cu alloy film

 \Box Modification of Pt wire with Ni film

Electrochemical stripping of both Cu and Ni from Cu–Ni-modified Pt wire to the solution

□ Electrochemical stripping of Cu from Cu–Ni-modified Pt wire to the solution

Electrochemical stripping of Ni from Cu–Ni-modified Pt wire to the solution

5 points for correct answer.
9.6. <u>Write</u> net ionic equations for the complexation and the back titration reaction of *step 7* in your answer sheet.

Complexation: $Ni^{2+}(aq) + Y^{4-}(aq) \rightarrow NiY^{2-}(aq)$ or $Ni^{2+}(aq) + HY^{3-}(aq) \rightarrow NiHY^{-}(aq)$ Back titration: $Ni^{2+}(aq) + Y^{4-}(aq) \rightarrow NiY^{2-}(aq)$ or $Ni^{2+}(aq) + HY^{3-}(aq) \rightarrow NiHY^{-}(aq)$ 3 points for each correct answer.

9.7. <u>Calculate</u> Ni²⁺ concentration as mg/L in the wastewater of the factory. <u>Note</u>: You must show all works.

Calculation:

5 pieces of 10-mL samples were collected and the total sample volume is 50-mL. 10-mL of the part was taken from this 50-mL sample. (2 point)

EDTA titration; 3.85 mg BaCO₃/mL EDTA

$$Ba^{2+}(aq) + Y^{4-}(aq) \rightarrow BaY^{2-}(aq)$$

 $[EDTA] = \frac{\frac{3.85 \text{ mg BaCO}_3}{197 \text{ mg BaCO}_3} \times \frac{1 \text{ mmol EDTA}}{1 \text{ mmol BaCO}_3}}{1 \text{ mmol BaCO}_3} = 0.01954 \text{ M EDTA} (8 \text{ points})$

$$Ni^{+2}(aq) + Y^{-4}(aq) \rightarrow NiY^{-2}(aq)$$

 $mmol_{Ni^{+2}} = \left[\left(\frac{0.01954 \ mmol \ EDTA}{1 \ mL \ EDTA} \times 5.00 \ mL \ EDTA \right) - \left(\frac{0.0010 \ mmol \ Ni^{2+}}{1 \ mL \ Ni^{2+}} \times 95.60 \ mL \ Ni^{2+} \times \frac{1 \ mmol \ EDTA}{1 \ mmol \ Ni^{2+}} \right) \right] \times \frac{1 \ mmol \ Ni^{2+}}{1 \ mmol \ EDTA} = 0.0021 \ mmol \ Ni^{2+} \ (12 \ points)$

$$C_{Ni^{2+}} = \frac{\left(0.0021 \, mmol \, Ni^{2+} \times \frac{58.7 \, mg \, Ni^{2+}}{1 \, mmol \, Ni^{2+}}\right) \times \frac{50 \, mL}{10 \, mL}}{0.05 \, L \, sample} = 12.33 \, mg/L \, \text{(3 points)}$$

-3 points for each calculation error.

-3 points for each wrong unit.

-3 points for each wrong conversion factor.

9.8. <u>Calculate</u> the minimum pH value for starting the precipitation of Ni²⁺ ions in the solution obtained in *step 5* by passing H₂S gas into the solution until saturation. If you cannot solve question **9.7**, use 20 *mg/L Ni*²⁺ *sample* for this question. <u>*Note*</u>: You must show all works.

Calculation:

$$[Ni^{2+}] = \frac{0.0021 \text{ mmol } Ni^{2+}}{10 \text{ mL sample}} = 2.1 \times 10^{-4} \text{M or } [Ni^{2+}] = \frac{0.01233 \text{ g/Ni}^{2+}}{11 \text{ sample}} = 2.1 \times 10^{-4} \text{M}$$
(6 points)

$$NiS \Rightarrow Ni^{2+}(aq) + S^{2-}(aq)$$

$$4.0 \times 10^{-20} = 2.1 \times 10^{-4} \times [S^{2-}]$$

$$[S^{2-}] = 1.905 \times 10^{-16} \text{ M (6 points)}$$

$$H_2S + H_2O \Rightarrow HS^- + H_3O^+ \text{ Ka}_1 = 9.6 \times 10^{-8} = \frac{[HS^-][H_3O^+]}{[HS^-]} (1 \text{ point})$$

$$HS^- + H_2O \Rightarrow S^{2-} + H_3O^+ \text{ Ka}_2 = 1.3 \times 10^{-14} = \frac{[S^{2-}][H_3O^+]}{[HS^-]} (1 \text{ point})$$

$$0.1 = [H_2S] + [HS^-] + [S^{2-}] (1 \text{ points})$$

$$[H_2S] \gg [HS^-] + [S^{-2}] \text{ and } [H_2S] = 0.1 \text{ M (1 points)}$$

$$Ka_1 \times Ka_2 = 1.25 \times 10^{-21} = \frac{[S^{2-}][H_3O^+]^2}{(H_2S)^2} (7 \text{ points})$$

$$1.25 \times 10^{-21} = \frac{1.905 \times 10^{-16} [H_3O^+]^2}{0.1} (4 \text{ points})$$

$$[H_3O^+] = 8.1 \times 10^{-4} \text{ M}$$

$$pH = 3.09 (3 \text{ points})$$

If Ni²⁺ concentration is taken 20 mg/L, the result is pH = 2.99

- -3 points for each calculation error.
- -3 points for each wrong unit.
- -3 points for each wrong conversion factor.

Exam Statistics & Overall Results

Task 1 - Two Beauties of Turkey: the Van Cat and the Ankara Cat

Mean: 15.79

Standard deviation: 7.48





Task 2 - A Tale of a Reactive Intermediate

Mean: 42.07

Standard deviation: 26.23





Task 3 - (±)-Coerulescine

Mean: 34.55

Standard deviation: 16.41





Task 4 - Symmetry Does Matter!

Mean: 35.48

Standard deviation: 18.63





Task 5 - Konya, Carrot, Beta-Carotene, Vitamin-A, Immune System, Vision

Mean: 70.30

Standard deviation: 29.36





Task 6 - Thermodynamics through an Interstellar Journey

Mean: 42.56

Standard deviation: 25.84





Task 7 – Phthalocyanines

Mean: 64.77

Standard deviation: 19.56





Task 8 – Boron Compounds and Hydrogen Storage

Mean: 36.27

Standard deviation: 15.54





Task 9 – Quantification of Heavy Metal Ions

Mean: 36.78

Standard deviation: 37.31





Overall Results



Mean: 60.06

Standard deviation: 24.42





IChO 2020 Results



GOLD MEDAL

Rank	Name	Surname	Country	Total	Medal
1	Alex Zihan	Li	United States of America	99,07	gold
2	Mugyeom	Jeon	Korea	98,60	gold
3	Yuntian	Gu	China	98,07	gold
4	Zhuo Yang	Zhang	China	97,07	gold
5	Dang Hai	Ly	Vietnam	96,97	gold
6	Letian	Li	China	96,55	gold
7	Şebnem	Gül	Turkey	96,48	gold
8	Alec Chen	Zhu	United States of America	95,98	gold
9	Duong Hoang	Nguyen	Vietnam	94,08	gold
10	Mohammad Shahabaddin	Daneshvar	Iran	93,51	gold
11	Jan	Oboril	Czech Republic	93,23	gold
12	Ananthan	Sadagopan	United States of America	92,98	gold
13	Agustin Alejandro	Lorusso Notaro Francesco	United Kingdom	92,71	gold
14	Sean	Leong	Singapore	92,62	gold
15	Anh Quoc Trung	Pham	Vietnam	92,50	gold
16	Heng-Jui	Chang	Chinese Taipei	92,42	gold
17	Junha	Hong	Korea	92,15	gold
18	Deniz	Güner	Turkey	92,15	gold
19	Ilia Dmitrievich	Chaika	Russian Federation	92,11	gold
20	Richard Yanzhou	Huang	Australia	92,01	gold
21	Shih Peng	Huang	Chinese Taipei	91,99	gold
22	Trang Minh Thi	Dam	Vietnam	91,38	gold
23	Charles Jordi	Windle	Singapore	91,31	gold
24	Anugrah George	Chemparathy	United States of America	91,29	gold
25	Jovan	Liau	Singapore	90,92	gold
26	Roi	Peer	Israel	90,35	gold

SILVER MEDAL

Rank	Name	Surname	Country	Total	Medal
27	Meng-Fu	Chen	Chinese Taipei	89,89	silver
28	Tomasz Jan	Slusarczyk	Poland	89,85	silver
29	Junha	Park	Korea	89,61	silver
30	Teng Wei	Ngwan	Singapore	89,59	silver
31	Mirakbarov Xodjiakbar O G Li	Mirumid	Uzbekistan	89,27	silver
32	Haonan	Sun	China	88,91	silver
33	Jan	Vavrin	Czech Republic	88,90	silver
34	Ygor De Santana	Moura	Brazil	88,73	silver
35	Evgeniy Yurievich	Epifanov	Russian Federation	88,67	silver
36	Chien-Yi	Wu	Chinese Taipei	88,34	silver
37	Nikita	Zoglo	Estonia	88,23	silver
38	Magdalena	Lederbauer	Austria	87,02	silver
39	Worawit	Tangamornchaipattana	United Kingdom	86,95	silver
40	Maximilian	Mittl	Germany	86,43	silver
41	Mohammadaryan	Taghvaeearabi	Iran	86,20	silver
42	Kamil	Kubanychbek	Kyrgyzstan	85,44	silver
43	Vasilisa Vadimovna	Kislitsyna	Russian Federation	84,98	silver
44	Avca Melis	Keskin	Turkey	83.95	silver
45	Alexander Ramsey	Thew	United Kingdom	83.34	silver
46	Ron	Shorints	Israel	83.31	silver
47	Akito	Ai	Japan	83.23	silver
48	Maximilian	Spitaler	Austria	82.66	silver
49	David	Benko	Huppary	82,60	silver
50	Bar	Sheffer	Israel	81.80	silver
51	Levon	Kharatyan	Armenia	81.15	silver
52	Dilshodakhon Kamolkhon Kizi	Isaeva	Uzhekistan	81.04	silver
53	Minicong	lee	Korea	80.45	silver
56	Martin	Brokes	Slovakia	80.37	silver
55	Filio	Koldzie	Serbia	80.35	silver
56	Avealrem	Durmus	Turkey	80.29	eilver
57	Wasin	Tiarawut	Thailand	80.20	silver
58	Ptvik	Patel	United Kingdom	80.00	silver
50	Viima	Vochida	Janan	79.72	eilver
60	Pamin	Assembour	Iran	79.61	eilver
61	Zarko	lykovic	Serbia	79.62	silver
62	Michael Cole Moises	Tantoco	Philippines	79.27	eilver
63	Viktor Gennadievich	Neeov	Princippines Russian Enderation	79.16	eilver
66	Filin	Hulek	Czech Republic	78.99	ellver
45	Chapanthorn	Arceiri	Thailand	78.51	eilver
66	lvan Candra	Gunawan	Indonesia	78,51	eilver
67	licanat	Pulicavak	Thailand	78,49	eilver
68	Khanim	Yaoublu	Azerbaijan	78.43	silver
40	Frederik Laurin	Walter	Germany	78,45	silver
70	Abbichava	Tungwongkitsiri	Thailand	78.30	eilver
70	Jovan	Maskavie	Corbia	70,37	silver
20	Pinako	Havashi	Janan	77.07	elluer
72	Peo	Chihavama	Japan	77.00	eilvor
75	Mark	Coesanto	Japan	77.40	eilvor
74	Damuan Stevanov	Econtracy	Pulaasia	77,47	silver
75	Ellies	Patubbau	Estenia	77,30	silver
76	Flupp	retunnov	Estonia	77,08	sitver

BRONZE MEDAL

Rank	Name	Surname	Country	Total	Medal
77	Michal Piotr	Lipiec	Poland	75,47	bronze
78	Linus Albert	Schwarz	Germany	75,40	bronze
79	Caleb Hsien-Yen	Hsiung	Australia	75,03	bronze
80	Kevin Arturo	Urrutia Alvarez	El Salvador	74,89	bronze
81	Amir	Mahboubi	Iran	74,75	bronze
82	Hung	Nguyen	Canada	74,13	bronze
83	Pedro Yudi	Honda	Brazil	73,80	bronze
84	Khaidar	Kairbek	Kazakhstan	73,38	bronze
85	Azhdar	Farzullazade	Azerbaijan	73,00	bronze
86	Steven	William	Indonesia	72,93	bronze
87	Osama	Alali	Saudi Arabia	72,73	bronze
88	Uvindu Praveen	Sumanasekara	Sri Lanka	72,63	bronze
89	Thiago Jose Veloso	De Souza	Brazil	71,65	bronze
90	Pavel Atanasov	Nikolov	Bulgaria	71,11	bronze
91	Istvan David	Ficsor	Hungary	70,62	bronze
92	Adam Szymon	Sukiennik	Poland	70,27	bronze
93	Fernando Juan Jose	Rodriguez	Venezuela	70,01	bronze
94	Abilmansur	Muzhubayev	Kazakhstan	69,68	bronze
95	Nathan Wayne Fontanilla	Ariston	Philippines	69,08	bronze
96	Kamil	Mambetov	Kyrgyzstan	68,73	bronze
97	Teodor Svilenov	Maslyankov	Bulgaria	68,43	bronze
98	Stefan Marcus Ang	Ong	Philippines	68,27	bronze
99	Samuel	Novak	Slovakia	68,08	bronze
100	Andrej	Kovacs	Slovakia	67,86	bronze
101	Shahzod	Nazirov	Tajikistan	67,60	bronze
102	Davi Medeiros Fortunato	Catanhede	Brazil	67,50	bronze
103	Wojciech Jan	Michalski	Poland	66,81	bronze
104	Vasilije	Pantelic	Serbia	66,21	bronze
105	Ioannis	Karageorgiou	Greece	66,03	bronze
106	Dzonatans Miks	Melgalvis	Latvia	66,01	bronze
107	Nursultan	Soodonbekov	Kyrgyzstan	65,73	bronze
108	Bakdaulet	Seysenkul	Kazakhstan	65,67	bronze
109	Filips	Ecis	Latvia	65,58	bronze
110	Arulanantham	Abbinanthan	Sri Lanka	65,46	bronze
111	Ursa	Konda	Slovenia	65,24	bronze
112	Aleksandar	Trajkovski	North Macedonia	64,75	bronze
113	Jakub	Schimmer	Czech Republic	64,71	bronze

BRONZE MEDAL

Rank	Name	Surname	Country	Total	Medal
114	Povilas	Dapsys	Lithuania	64,61	bronze
115	Anete Patricija	Raiskuma	Latvia	63,57	bronze
116	Ward	Yahya	Israel	63,05	bronze
117	Bulcsu	Fajszi	Hungary	61,77	bronze
118	Rifqi Naufal	Abdjul	Indonesia	61,76	bronze
119	Tom Erik	Steinkopf	Germany	61,40	bronze
120	Mohammad	Bilal	Syria	61,33	bronze
121	Kibriyanur	Abdugafarova	Kazakhstan	61,18	bronze
122	Artyom	Petrosyan	Armenia	61,10	bronze
123	Karam	Khaddour	Syria	60,81	bronze
124	Maciej Krzysztof	Swiatek	Austria	60,75	bronze
125	Gerardo Manuel	Ramirez Valladares	El Salvador	60,47	bronze
126	Andrei Mihai	Banica	Canada	60,21	bronze
127	Abdulaziz	Aljuaid	Saudi Arabia	59,77	bronze
128	Edvards Mikelis	Mezciems	Latvia	59,66	bronze
129	Ghayrat	Samiev	Tajikistan	58,66	bronze
130	Eyad	Alsalhi	Saudi Arabia	58,17	bronze
131	Jasmin Maria	Frei	Switzerland	58,08	bronze
132	Justin Qi Hua	Cheng	Canada	57,49	bronze
133	Ravindu Sanwara	Rathnayake	Sri Lanka	57,43	bronze
134	Mohammad	Alhudaithi	Saudi Arabia	57,24	bronze
135	Sariena	Ye	Australia	57,19	bronze
136	Laurens	Smulders	Netherlands	56,90	bronze
137	Nicholas Jiawei	Wu	Australia	56,82	bronze
138	Georgi Neliyanov	Nedyalkov	Bulgaria	56,51	bronze
139	Matus	Tomco	Slovakia	56,28	bronze
140	Abraham	Antonio Pineda	Mexico	56,17	bronze
141	Firdavs	Sobirov	Uzbekistan	56,16	bronze
142	Istvan Attila	Garamvolgyi	Hungary	56,08	bronze
143	Humberto	Tovar Salazar	Mexico	55,79	bronze
144	Lukas	Rost	Austria	55,54	bronze
145	Valentas	Olikauskas	Lithuania	55,29	bronze
146	Adam	Modic	Slovenia	54,54	bronze
147	Patrik	Znidarsic	Slovenia	54,33	bronze
148	Aleksandr	Beditski	Estonia	54,31	bronze
149	Ron Angelo Atienza	Gelacio	Philippines	53,64	bronze

HONORABLE MENTION

Rank	Name	Surname	Country	Total	Medal
150	Akobir Azamat Ogli	Narzullaev	Uzbekistan	52,36	honorable mention
151	Lennart Eneas	Horn	Switzerland	52,01	honorable mention
152	Konstantinos	Karakaras	Greece	51,83	honorable mention
153	Jorge	Garcia Ponce	Mexico	51,53	honorable mention
154	Axel	Dian	France	51,24	honorable mention
155	Nikolaos	Tsakiris	Greece	51,18	honorable mention
156	Mathieu	Salzburg	France	50,13	honorable mention
157	Thomas	Arkwright	France	48,49	honorable mention
158	Hasan	Abdul Rahman	Syria	48,12	honorable mention
159	Marcelo Josue	Escalante Barrera	El Salvador	47,58	honorable mention
160	Emile Norbert	Eeckhoudt	Belgium	47,17	honorable mention
161	Darko	Stojchev	North Macedonia	46,81	honorable mention
162	Tadas	Danilevicius	Lithuania	46,12	honorable mention
163	Tomas	Kvietkauskas	Lithuania	45,91	honorable mention
164	Shakindi Vihangana	Mahanaida Badalgei	Sri Lanka	44,60	honorable mention

Rank	Name	Surname	Country	Total
165	Sajjan	Raja	Pakistan	44,14
166	Edward	Chen	Canada	43,91
167	Ali	Alhasan	Syria	43,70
168	Nino	Abesadze	Georgia	42,50
169	Altti Olavi Juhanpoika	Makela	Finland	42,23
170	Alfredo Alessandro	Martinez Jimenez	El Salvador	42,14
171	Jens Peter	Nielsen	Denmark	41,63
172	Anne-Sophie Denise	Tilleman	Belgium	41,58
173	loane	Kapanadze	Georgia	41,14
174	Michael Ciaran	Gadaloff	Ireland	38,28
175	Samuel Joonatan	Klaver	Finland	38,06
176	Pascal Damain	Ojochide	Nigeria	37,67
177	Augusto	Palotti Amado	Uruguay	37,27
178	Ceri Jean	Arnott	Ireland	37,02
179	Wamiq Ali	Shaikh	Pakistan	36,97
180	Dimitrios-Polykarpos	Karakostas	Greece	36,20
181	Daniel Alexander	Isler	Switzerland	35,73
182	Ivana Sofia	Espinoza Bojorquez	Mexico	35,01
183	Said	Gasimov	Azerbaijan	34,60
184	Muhammad Hazim Bin	Saleem	Pakistan	34,54
185	Joao Pedro	Bonito Caldeira	Portugal	34,29
186	Jesus Alejandro	Colmenares	Venezuela	33,92
187	Ravshanoy	Mu	Tajikistan	33,86
188	Joseph Michael	Martyn	Ireland	33,59
189	Leonid	Sajkov	North Macedonia	33,56
190	Auriel	Guarino	Ireland	32,38
191	Dante	Breitwiller	France	32,29
192	Örn Steinar	Sigurbjörnsson	Iceland	31,26
193	Simon	Pitte	Belgium	31,13
194	Pascal	Otjens	Netherlands	30,05

Minutes of IChO Steering Committee Meeting

27.07.2020 12:00-13:30 (Ist Time) Over video conference

Agenda points

1. Discussions with observer countries

Representatives of the observer countries have informed the Steering Committee about their preparations, national olympiads and supporting institutions in their respective countries during three separate video conferences organized in July. Representatives also had access to a demo server of the oly-exam tool at the olympiad.

All observing countries have a national olympiad already established or under organization with open access. They have respectable institutions behind their olympiad efforts. The SC is foreseeing no obstacles to their invitation to the upcoming olympiad. Final decisions will be made in the January meeting of the SC.

Second-time observers were Bangladesh, Oman, Trinidad and Tobago. These countries expect to send students to IChO 2021. First time observer countries were: Afghanistan, Albania, Ecuador, Nepal and Paraguay. They can get invited as observers in 2021. Mali has registered as an observer but did not reply to requests for the videoconference. Their observation in 2020 is not accepted.

2. Participation at the 52nd IChO

The SC had a videoconference on July 27, 2020 about the 52nd and the upcoming olympiads.

Nurayet Alimli gave key data for the 2020 olympiad: 60 countries registered with 235 students. One country was ordered to stop exam writing for their students at the last minute. 231 students wrote the exam. The expected participation fees were well received.

Abdullah Aydogan, Turkey's coordinator with the oly-exam team gave a short report about the experiences with the new software. They were generally very contented, only the problem entry was unexpectedly labor intensive. The Swiss author/support team was very helpful generally and especially agile in solving unexpected problems. Members of the SC also found the system very useful and recommended its use in future olympiads. Further minor adaptations to the workflow of the IChO might be requested, but generally the software worked very well.

3. Future Olympiads

- **2021:** Organizers of the Japan olympiad foresee risks concerning the organization of a live olympiad next year if the travel limitations caused by the pandemic will not be removed by then. Their preparations are underway in full force, and they prepare for both possible scenarios: a normal and a remote olympiad. Final decision is expected to happen after the Japanese government made a decision about the delayed Olympic Games (in April of 2021). The Steering Committee meeting in January is planned to be held remotely. Web-site: https://www.icho2021.org/
- **2022:** Nankai University from Tianjin, China is preparing for a regular olympiad in 2022. The olympiad has strong financial and professional support. The relevant Science and Organizing Committees are forming and will start work soon. The website of the event will launch soon. The SC has recommended that former IChO mentors are very helpful in the problem setting committee. Nankai University has two campuses 20 km away from each other: students and mentors will be separated in the two locations.
- **2023:** Switzerland will host the olympiad in Zürich in mid-July. The host institution is ETH, preparations are at the required phase.
- 2024: Saudi Arabia is still considering two locations: Riyadh and Neom City. Decision is expected very soon.

Members of the Steering Committee for the 52nd IChO

Elected:

- I-Jy Chang, Taiwan (2016, 2018)
- Alexander Gladilin, Russia (2018)
- JL Kiappes, USA (2016, 2018)
- Gábor Magyarfalvi, Hungary (2017, 2019), chair
- Petra Ménová, Czech Republic (2018)
- Martin Putala, Slovakia (2019)

Ex officio:

- Anne Szymczak, France (2019)
- Yunus Emre Turkmen, Turkey (2020)
- Nobuhiro Kihara, Japan (2021)
- Dong-Sheng Gao, China (2022)
- Patrik Willi, Switzerland (2023)
- Badr El-Majrathi, Saudi Arabia (2024)
- Abdallah Elmarhoune, UAE (2025) absent

Co-opted:

- Elizbar Elizbarashvili (Georgia)
- Igrar Nazarov (Azerbaijan)

List of Participants

Country	Role	Title	First Name	Last Name
Armenia	Head mentor	Mr.	Andranik	Davinyan
	Mentor	Mr.	Movses	Aghekyan
	Mentor	Mr.	Armen	Galstyan
	Student	Mr.	Levon	Kharatyan
	Student	Mr.	Artyom	Petrosyan
	Student	Mr.	Aren	Hakobyan
	Student	Mr.	Gagok	Tadevosyan
Australia	Head mentor	Mr.	Samuel Jacob	Alsop
	Mentor	Mr.	Mackenzie Hooper	Shaw
	Student	Mr.	Nicholas Jiawei	Wu
	Student	Mr.	Caleb Hsien-Yen	Hsiung
	Student	Ms.	Sariena	Ye
	Student	Mr.	Richard Yanzhou	Huang
Austria	Head mentor	Mr.	Georg	Schellander
	Mentor	Dr.	Liesbeth	Berner
	Mentor	Dr.	Mathias	Scherl
	Student	Mrs.	Magdalena	Lederbauer
	Student	Mr.	Maximilian	Spitaler
	Student	Mr.	Maciej Krzysztof	Swiatek
	Student	Mr.	Lukas	Rost
Azerbaijan	Head mentor	Dr.	Igrar	Nazarov
	Mentor	Mrs.	Fidan	Mammadova
	Mentor	Mrs.	Milana	Agayeva
	Mentor	Mr.	Ali	Aliyev
	Student	Mr.	Azhdar	Farzullazade
	Student	Mr.	Said	Gasimov
	Student	Mrs.	Khanim	Yagublu
	Student	Mr.	Salman	Huseynov
Belgium	Head mentor	Mr.	Stéphane Charles André	Caubergh
	Mentor	Mr.	Hans	Vanhoe
	Mentor	Mr.	Dieter	Plessers
	Student	Ms.	Anne-Sophie Denise	Tilleman
	Student	Mr.	Jérôme	Mayolet
	Student	Mr.	Simon	Pitte
	Student	Mr.	Emile Norbert	Eeckhoudt
Brazil	Head mentor	Dr.	Lucas Carvalho Veloso	Rodrigues
	Mentor	Dr.	Samuel Anderson Alves de	Sousa
	Mentor	Dr.	Joao Paulo	Ataide Martins
	Mentor	Dr.	Nagila Maria P. Silva	Ricardo
	Student	Mr.	Davi Medeiros Fortunato	Catanhede
	Student	Mr.	Ygor de Santana	Moura
	Student	Mr.	Pedro Yudi	Honda
	Student	Mr.	Thiago Jose Veloso	de Souza

Country	Role	Title	First Name	Last Name
Bulgaria	Head mentor	Dr.	Donka Nikolova	Tasheva
	Mentor	Dr.	Penka Vasileva	Tsanova
	Student	Mr.	Damyan Stoyanov	Frantzov
	Student	Mr.	Georgi Neliyanov	Nedyalkov
	Student	Mr.	Teodor Svilenov	Maslyankov
	Student	Mr.	Pavel Atanasov	Nikolov
Canada	Head mentor	Ms.	Jennifer	Pitt
	Mentor	Mr.	Guillaume	Bussiere
	Student	Mr.	Andrei Mihai	Banica
	Student	Mr.	Edward	Chen
	Student	Mr.	Justin Qi Hua	Cheng
	Student	Mr.	Hung	Nguyen
China	Head mentor	Mr.	Jian	Pei
	Mentor	Mrs.	Yingxia	Wang
	Mentor	Mr.	Kai	Li
	Mentor	Mr.	Chuanjun	Song
	Student	Mr.	YUNTIAN	GU
	Student	Mr.	Letian	Li
	Student	Mr.	Haonan	Sun
	Student	Mr.	Zhuo Yang	Zhang
Chinese Taipei	Head mentor	Prof.	Ming-Kang	Tsai
	Mentor	Prof.	WANN-YIN	LIN
	Mentor	Prof.	Ling-Hsien	Tu
	Mentor	Ms.	Mei-Ling	Chen
	Student	Mr.	Heng-Jui	Chang
	Student	Mr.	Meng-Fu	Chen
	Student	Mr.	Chien-Yi	Wu
	Student	Mr.	Shih Peng	Huang
Czech Republic	Head mentor	Mrs.	Petra	Ménová
	Mentor	Mr.	Petr	Holzhauser
	Mentor	Mr.	Jiří	Ledvinka
	Mentor	Mr.	Lukáš	Tomaník
	Student	Mr.	Jan	Vavřín
	Student	Mr.	Jan	Obořil
	Student	Mr.	Filip	Hůlek
	Student	Mr.	Jakub	Schimmer
Denmark	Head mentor	Mr.	Kurt Bjønager	Nielsen
	Mentor	Dr.	Pia	Nielsen
	Student	Mr.	Emil Andsbjerg	Holm
	Student	Mr.	Jens Peter	Nielsen
	Student	Mr.	Thomas Svava	Mortensen
	Student	Mr.	Mathias Abildgaard	Alminde
El Salvador	Head mentor	Mr.	Rene Alexander	Arevalo
	Mentor	Mr.	Johnny Jose	Marquez Castro
	Student	Mr.	Marcelo Josue	Escalante Barrera
	Student	Mr.	Alfredo Alessandro	Martinez Jimenez
	Student	Mr.	Kevin Arturo	Urrutia Alvarez
	Student	Mr.	Gerardo Manuel	Ramirez Valladares

Country	Role	Title	First Name	Last Name
Estonia	Head mentor	Mr.	Vladislav	Ivaništšev
	Mentor	Ms.	Ida	Rahu
	Student	Mr.	Nikita	Žoglo
	Student	Mr.	Filipp	Petuhhov
	Student	Mr.	Aleksandr	Beditski
Finland	Head mentor	Dr.	Kiell Johan Patrik	Knapas
	Mentor	Dr.	Mija Johanna	Mäntymäki
	Mentor	Ms.	Essi *Juulia	Talvitie
	Mentor	Mr.	Jussi Hermanni	Tahvanainen
	Student	Mr.	Samu Matias	Huovinen
	Student	Mr.	Samuel Joonatan	Klaver
	Student	Mr	Altti Olavi Juhanpoika	Mäkelä
	Student	Ms	Netta Karoliina	Karialainen
France	Head mentor	Mrs	Anne-Sophie	Debled
	Mentor	Mr	Clément	Guibert
	Mentor	Mrs	Marie-Blanche	Maubourat
	Student	Mr	Thomas	Arkwright
	Student	Mr	Mathieu	Salzburg
	Student	Mr	Dante	Breitwiller
	Student	Mr		Dien
Georgia	Hood montor	Drof		Elizbarachvili
Ocorgia	Montor	Mrc		Butkhuzi
	Montor	IVIIS. Mr	Vakhtang	Kurtekhalia
	Mentor	IVII.	Conhike	Ruitskilalla
	Nienioi	Mo	Sopriiko	Palsalsia
	Student	IVIS.		Knelidze
	Student	IVIF.	Ioane	Abaaadaa
	Student	IVIS.	NINO Autor dil	
Cormony	Student	IVII.	Avtandi	Giorgadze
Germany	Head mentor	IVITS.	Sonja	Fallest
	Mentor	ivir.	Maximilian	Fellert
	Mentor	Dr.		Purgann Otriath Kalthaff
	Mentor	IVIr.		Strietn-Kalthoff
	Student	ivir.		Steinkopt
	Student	ivir.		vvalter
	Student	ivir.	Maximilian	MITTI
0	Student	Mr.	Linus Albert	Schwarz
Greece	Head mentor	Dr.	Nikolas	Psaroudakis
	Student	Mr.	Ioannis	Karageorgiou
	Student	Mr.	Konstantinos	Karakaras
	Student	Mr.	Dimitrios-Polykarpos	Karakostas
	Student	Mr.	Nikolaos	Tsakıris
Hungary	Head mentor	Dr.	Gabor	Magyarfalvi
	Mentor	Dr.	Szilard	Varga
	Mentor	Mrs.	Katalin	Zih-Perényi
	Student	Mr.	István Dávid	Ficsór
	Student	Mr.	István Attila	Garamvölgyi
	Student	Mr.	Dávid	Benkő
	Student	Mr.	Bulcsú	Fajszi

Country	Role	Title	First Name	Last Name
Iceland	Head mentor	Ms.	Katrín Lilja	Sigurðardóttir
	Mentor	Dr.	Már	Björgvinsson
	Student	Ms.	Birta Rakel	Óskarsdóttir
	Student	Mr.	Örn Steinar	Sigurbjörnsson
	Student	Ms.	Kristín Sif	Daðadóttir
	Student	Mr.	Baldur	Daðason
Indonesia	Head mentor	Prof.	Diulia	Onggo
	Mentor	Dr.	Deana	Wahyuningrum
	Mentor	Dr.	I Nyoman	Marsih
	Mentor	Dr.	Fainan	Failamani
	Student	Mr.	Ivan Candra	Gunawan
	Student	Mr.	Steven	William
	Student	Mr.	Mark	Soesanto
	Student	Mr.	Rifgi Naufal	Abdiul
Iran	Head mentor	Prof.	Seifollah	Jalili
	Mentor	Mr.	Ebrahim	Kianmehr
	Mentor	Dr.	Moideh	Akhavan
	Student	Mr.	Amir	Mahboubi
	Student	Mr	Ramin	Assempour
	Student	Mr	MohammadArvan	TaghyaeeArabi
	Student	Mr	Mohammad Shahabaddin	Daneshvar
Ireland	Head mentor	Dr	Brian Martin	Murphy
	Mentor	Dr.	Carl	Poree
	Student	Ms.	Ceri lean	Arnott
	Student	Mr	Auriel	Guarino
	Student	Mr	Joseph Michael	Martyn
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	Student	IVIL.		Ngwan
	Student	IVIr.	Jovan Olashas kasli	
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