# The 53rd Remote IChO 2021 Japan

July 25 ~ August 2, 2021



### Report

The 53rd International Chemistry Olympiad (IChO) 2021 Japan Organizing Committee

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### Report

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## The 53rd IChO 2021 Japan

### Report

### **Table of Contents**

Message1
President of IChO 2021 Japan Committee Chair of the 53rd IChO 2021 Japan Organizing Committee <b>Kohei Tamao</b>
Overview
Member of the Steering Committee Member of the 53rd IChO 2021 Japan Organizing Committee Vice Chair of Science Committee Vice Chair of Executive Committee Kanagawa University, Professor Nobuhiro Kihara
National Team of Countries11
Results
Certificate and Medals71
Memento and Gifts75
IChO 2021 Japan Photo Collection
Examination
Examination Guideline
Problem English Version with Solution
Reference : Practical Tasks
Catalyzer
IChO 2021 Japan Pre-event
Committee
Acknowledgments to Donations271
Special Thanks to Various Contributions



## Message

#### Kohei Tamao



President of IChO 2021 Japan Committee Chair of the 53rd IChO 2021 Japan Organizing Committee

The 53rd International Chemistry Olympiad, IChO 2021 Japan, was held remotely from July 25 to August 2, 2021, under the slogan "Chemistry! It's Cool!".

Originally, we had been preparing to hold IChO 2021 Japan at Kindai University, one of the biggest private universities in Japan, located in the lively and modern commercial city of Osaka in mid-west Japan, also known as the historically important birthplace of chemical research in this country.

However, in light of the ongoing COVID-19 pandemic, we had no choice but to hold IChO 2021 remotely, following the lead of IChO 2020 Turkey last year.

This was the result of giving top priority to the safety of our young talented students and all participants, even at the expense of practical examinations and opportunities for in-person international exchange. I would like to thank all the International Steering Committee members led by Dr. Gábor Magyarfalvi for their enthusiastic discussion and acceptance of our decision.

The purpose of the IChO is not only to provide a venue for a test of students' chemistry skills, but also to foster communication among students through chemistry and to gain familiarity with the culture of the host country. Despite being a remote competition held under the difficult conditions presented by the COVID-19 pandemic, the question of how to effectively implement these three elements was our biggest challenge.

The key dates were as follows:

July 25 (Sunday): Opening Ceremony

July 28 (Wednesday): Theory Examination

August 2 (Monday): Closing Ceremony

On other days, we offered various initiatives for students to create international friendships and become familiar with Japanese culture, in addition to the challenges of the scientific competition. We also provided a demonstration video of the practical tasks to compensate for the fact that the practical examinations could not be held. Virtual reality avatars for all students were prepared to facilitate remote networking and to give greater realism to virtual participation in the realistic Opening and Closing Ceremonies and virtual visits to sensitive areas such as SPring-8, the world largest synchrotron radiation facility, and the restoration site of an ancient Buddha statue to which access is normally prohibited. The IChO newsletter *Catalyzer*, including these all items, was published every day for a total of 11 editions.

The good news was that we accepted 312 talented students registered from the highest-ever 85 countries and regions of the 89 to which we sent invitations. I would like to express my sincere gratitude and respect for the wonderful efforts of mentors, teachers, and all concerned in each country (in total, 520) to select talented students and set up the examination sites in their own countries.

The theoretical examinations were held on July 28th in each country: the first started at 12:00 JST in New Zealand, the easternmost country, and the last started at 24:00 JST in the USA and Costa Rica, the westernmost countries. The 5-hour examinations ended at 5:00 am JST on July 29. All examination sites were monitored and recorded throughout the examination via Zoom through 100 PC monitors. It is my great pleasure to report that all theoretical examinations were carried out in an atmosphere of justice, fairness, and trust, maintaining the spirit of IChO, and I thank all the invigilators (in total, 183) for their earnest efforts.

In the Closing Ceremony on August 2, a list of medalists was announced: 33 Gold (top 10%), 67 Silver (next 20%), 94 Bronze (next 30%) and 24 honorable mention awardees (top 10% of non-medalists). I would like to congratulate all the awardees on their very best efforts, showcasing the talents and skills they demonstrate every day.

Now I would like to ask all the participating students to keep the following three things in mind as they reflect on this once-in-a-lifetime valuable experience.

First, they were given hope and courage to overcome difficulties through participation in IChO 2021 Japan.

Second, the unprecedented difficulties we are still facing can only be overcome by international friendships and trust.

Third, I want them to remember that chemistry, the central science, is all around us. Chemistry must therefore play a key role in finding solutions for many global challenges, including the energy, environmental, and resource-related challenges that humanity is now facing.

I hope that IChO 2021 Japan helps to foster many talented young people who will go on to play roles as future world leaders. While these talented students did not have the opportunity to meet each other in person this time, I am convinced that one day they may meet each other somewhere in the world when they go to university or graduate school. I sincerely hope that they take the opportunities given to them as participants in IChO 2021 to create strong networks of international friendship, with the slogan "Chemistry! It's Cool!" as their watchword.

Finally, I would like to thank IUPAC, the Ministry of Education, Sports, Science and Technology (MEXT Japan) and the Japan Science and Technology Agency (JST) for their meaningful support, and the more than 180 chemical companies and trading companies in Japan as our sponsors for their substantial financial assistance, as well as numerous personal donations.

My special thanks are also due to all the members of the Japan Committee and Organizing Committee for IChO 2021 Japan, as well as our secretariat and KNT Corporate Business Co., Ltd. Without their remarkable support and endeavors, this remote IChO 2021 Japan would not be possible.



# Overview

The IChO program is intended to stimulate students' interest in chemistry through solving creative chemical problems that are both practical and theoretical. In a usual IChO, the participating students are tested on their chemistry knowledge and skills in a five-hour laboratory practical examination and a five-hour written theoretical examination. It also aims to promote international contacts in chemistry, friendships between young chemists of different nationalities, cooperation among pupils, and exchange of scientific experiences in chemistry.

At 47th IChO 2015 in Baku, Azerbaijan, Japan was invited to hold the 53rd IChO in 2021. It was originally planned to follow the 2020 Olympic and Paralympic Games in Tokyo. We anticipated that popular interest in chemistry would be enhanced by a scientific Olympiad being held after the excitement of a sporting Olympiad.

When we heard the first reports of COVID-19 early in 2020, it appeared to be a minor concern. Despite the virus being thought of as causing a new kind of cold, we knew that the common cold is inactive in summer when the IChO was to be held. However, shortly after the pandemic spread across the globe, it became evident that COVID-19 was active in summer, too. The 2020 Olympics and Paralympics were postponed for one year, and the 52nd IChO 2020 in Turkey was held remotely, because the university venue could not be used for an in-person event during the period scheduled for the IChO.

The IChO is composed of three key elements:

#### (1) Examination

Chemistry is an experiment-based science, with every theory coming out of the laboratory. Therefore, both theoretical and practical examinations play important roles in the IChO.

#### (2) Communication

Talented students from all over the world come together to take part in the IChO. Conversation, cooperation, and communication with each other provide a great opportunity for promising youngsters to enjoy international experiences and to make friends with other participants via their common interest, chemistry.

#### (3) Culture

The venue chosen for the 53rd IChO 2021 Japan, the Kansai area, is 500 km from Tokyo and was the ancient capital where the first government of Japan was established 2681 years ago (according to Japanese legend). Several places were to be visited, including not only very old temples but also state-of-the-art scientific institutes.

In the middle of January 2021, the Organizing Committee (OC) of the 53rd IChO 2021 Japan met with the Steering Committee (SC) of the IChO via Zoom. We discussed two proposals: for an in-person IChO and a remote IChO. Unfortunately, it was already clear that all the elements of the IChO described above could not be included in an in-person IChO during the COVID-19 pandemic, due to difficulties in immigration control and the need for social distancing.

The first priority of any IChO is, of course, the safety of all participants. After the meeting with the SC, the OC finally decided to hold the 53rd IChO 2021 Japan as a remote event. At the end of February, when we had our second meeting with the SC, the holding of a remote IChO was approved.

In this remote IChO, the competition only involved theoretical problems, and the students attended the examination from their own countries. Most of the elements essential to the IChO would be lost in the remote IChO, which was very disappointing.

Even in a remote format, however, the important features of IChO must be maintained as much as possible. The participating students must have extraordinary experiences. Therefore, the OC incorporated several activities and communication tools into the 53rd IChO 2021 Japan to cover these important features:

#### (1) Examination

In order to reinforce the importance of laboratory work, the practical tasks prepared for the 53rd IChO 2021 Japan were made open, despite not being officially approved by the International Jury meeting for the 53rd IChO 2021 Japan. The OC prepared videos in which all tasks were demonstrated with explanations and published the videos as one of the activities during the 53rd IChO 2021 Japan.

The OC will be delighted if those who are inspired by the demonstrations prepare and submit their original videos in which they attempt the practical tasks and discussions. Reports on the tasks will also be highly welcome.

#### (2) Communication

OC prepared a virtual reality (VR) space for communication. When participants accessed the VR space, their avatars were created. Everyone could participate in events and activities via their avatars. In the VR space, there were venues in which avatars could enjoy close conversations, cooperation, and communication with others.

#### (3) Culture

IChO participants were offered virtual visits to several locations. Some of these had been planned for the in-person IChO: Nara City, Osaka City, Kyoto City, and Himeji Castle. However, the OC added some that are very interesting to experience but not suitable for inperson visits due to hazards, sensitivity, space limitations, or language difficulties. SPring-8, a large synchrotron radiation facility that delivers the most powerful synchrotron radiation currently available, is one of the most interesting places in the Kansai area for the participating students of the IChO in particular. However, it is very difficult to visit SPring-8 as an activity in the IChO due to space limitations inside SPring-8 and the sensitivity of its advanced instruments. A workshop for preserving cultural assets, for example, repairing an image of Buddha, is another interesting place where modern chemistry is applied to very old subjects, although it is again very difficult to physically visit such a workshop because of the sensitive work, space limitations, and language difficulties. In the 53rd remote IChO, the participants virtually visited these highly restricted locations to experience more interesting cultural tours than would otherwise be possible.

The preparation of the problems started at April 24, 2018 in the first meeting of Science Committee of OC. After several intensive discussions and meetings, nine theoretical problems and three practical tasks were selected, and were brushed up to high quality problems. To complement these problems, thirty-one theoretical problems and seven practical tasks were prepared to be issued as the Preparatory Problems at February 1, 2021.

The opening ceremony started at 15:00 JST on July 25, 2021. The participants of the 53rd IChO 2021 Japan could access the ceremony via either the VR space or the usual video streaming. Over 200 participants entered the VR space to enjoy the realistic ceremony.

The first version of the theoretical problems was published at 21:00 JST on July 25. It should be noted that 21:00 JST is the almost the only time window to permit cooperation on that day all over the world: 21:00 JST is 24:00 for the easternmost country, New Zealand, and 9:00 for the westernmost country, Costa Rica. Therefore, most of the programs were scheduled at 21:00 JST during the 53rd IChO 2021 Japan.

The Science Committee of OC sought comments on the problems from mentors, revised the problems according to the comments, then proposed a second version of the problems for finalization to the international Jury meeting, the body that decides matters regarding the IChO that bind both participants and organizers. The Jury meeting started at 21:00 JST on July 26 and finished around 2:00 JST on July 27. The Science Committee of OC revised the problems according to the decisions of the Jury meeting and published the official final version at 9:00 JST on July 27. Next, the mentors started to translate the official English version into the individual local languages for their students. All delegations finished their translations by 9:00 JST on July 28.

It should be noted that 60 hours elapsed from the publication of the first version of the problems to the deadline for translation. Of course, contact between mentors and students after the publication of the problems was clearly prohibited in the competition guidelines. If a mentor wanted to cheat, for example, passing on the problems and solutions to his or her

students, we could not prevent it. However, the OC trusted in the professionalism and the pride of mentors. If a mentor had said to their students, "Hey, I'll tell you the problems and solutions, then you'll all get gold medals," they would lose the respect of their students. As expected, there were no suspicious results in the scores obtained by participating students, confirming that the IChO community is strong and ethically healthy.

The translated versions of the problems were made available to the invigilators at 9:00 JST on July 28. The invigilators downloaded and printed out the problems for students by the starting time of the examination. The invigilators are a crucial component of the remote examination. The OC asked country delegations to appoint invigilators who are independent of the mentors, have no relationship with students and have no other activity in the 53rd IChO 2021 Japan. Invigilators were to be socially well-established persons such as school principals and should not be a parent or a relative of a student. For the same reason, the examination location should be a public place such as a school, and the OC requested that each country choose a single location per a country.

Unfortunately, restrictions on movement were very severe in some countries during the period for the 53rd IChO 2021 Japan. Further, some students had to quarantine because their close relatives were infected by COVID-19. In such urgent circumstances, the OC allowed these students to take the examination in their homes, invigilated by their parents. The relevant delegations were asked to guarantee the fairness of the examination, and all delegations worked hard to make the students' homes suitable as examination locations.

A total of 309 students took the examination, while three students were absent. All examination locations were inspected beforehand via Zoom and were monitored and recorded throughout the examination via Zoom.

The earliest examination started at 12:00 JST on July 28 in New Zealand, the easternmost country, and the last examination started at 24:00 JST in USA and Costa Rica, the westernmost country. The examination time was 5 hours. Participating students were not allowed to use any communication devices or computers during the period 19:00 to 24:00 JST to avoid any ill-intentioned communication via the Internet or social media. All these requirements were controlled by the invigilators.

After the examination, the invigilators sorted the answer sheets by page numbers, scanned them to prepare PDF files for each student, and submitted them to the OC. After all answer sheets were received, the Science Committee of OC started marking at 9:00 JST on July 29. In the same time, a pdf file with the answer and the marking scheme was published to all mentors, and mentors also started marking in their own countries. At 23:00 JST on July 29, we published our marking, and started receiving the request of arbitration from mentors till 20:00 JST on July 30.

The arbitration was carried out from 9:00 JST for easternmost countries to 24:00 JST for westernmost countries on July 31. The final results after reflection of all results of arbitration were sent to each country at 6:00 JST on August 1. It was announced to the mentors that any query for the final results should be sent to the Science Committee of OC within 6 hours, although no argument came to OC. Thus, the scores of all students were fixed and finalized at 12:00 JST on August 1, and the medals were allocated according to the regulation of IChO.

The students were awarded in the closing ceremony at 21:00 JST, on August 2, which was held also in the VR space and later published as a streaming video. Even after the closing ceremony, the participants could still enjoy virtual tours in the VR space.

The 53rd IChO 2021 Japan was financially supported by IUPAC, the American Chemical Society and Chinese Chemical Society in Taipei. Theses supports were used to subsidize participation fees for some countries that were facing economic difficulties. This year, there were several countries experiencing economic difficulties due to the COVID-19 pandemic.

The 53rd IChO 2021 Japan was totally managed by Zoom and Oly-Exam softwares. Zoom was used for the international discussion, e.g., Jury meeting and arbitration, and monitoring the examination. Oly-Exam was used for the preparation and translation of the examination problems and grading. On-time communication with mentors was carried out with mail and Telegram software.

After several events over the period of 11 days, the 53rd IChO 2021 Japan was successfully completed. We wish to congratulate all participating students. Some received medals, and some did not. However, they all tried their best to tackle the same chemical problems. When these youngsters meet again as the leaders in the field of chemistry, they will talk about the days of the 53rd IChO 2021 Japan. We will be deeply honored if the 53rd IChO 2021 Japan becomes one of the career milestones marked by the excellent chemists of the future.



#### Nobuhiro Kihara

Member of the Steering Committee Member of the 53rd IChO 2021 Japan Organizing Committee Vice Chair of Science Committee Vice Chair of Executive Committee Kanagawa University, Professor

### The 53rd IChO 2021 Japan

Event Period July 25 ~ August 2, 2021

#### Main host

The 53rd International Chemistry Olympiad (IChO) 2021 Japan Organizing Committee

**Co-host** 

Japan Science and Technology Agency (JST)

#### **Endorsing Institution**

Ministry of Education, Culture, Sports, Science and Technology (MEXT) Ministry of Economy, Trade and Industry (METI) Osaka Prefecture Board of Education

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#### Participating countries/regions 79 +5 Observer countries

Number of participants 709 Students 312 (Number of examinees 309) Mentors 160 Observers 51 Guest 1 Invigilators 185

Date	JST Time (UTC+9)	Student	Mentor/Observers	Invigilator	SC	Organizer
Jul 22, Thu	21:00				Mock exam	
Jul 23, Fri	21:00		Training of Oly-Exam (Zoom)			
Jul 24, Sat	0:00			Training of Oly-Exam (Zoom)		
	21:00				Mock discussion	Mock discussion
Jul 25, Sun	15:00	Opening Ceremony	Opening Ceremony	Opening Ceremony	Opening Ceremony	Opening Ceremony
	21:00		Receipt of the problem for review (Oly-Exam)			Publication of the problem (Oly-Exam)
Jul 26, Mon	9:00		Deadline of feedback (Oly-Exam)			
	21:00		Jury meeting (Zoom)		Jury meeting (Zoom)	Jury meeting (Zoom)
Jul 27, Tue	9:00		Receipt of the authorized problem for translation and submission (Oly- Exam)			Publication of the final version of official problem (Oly-Exam) Information of erratum (Zoom)
Jul 28, Wed	9:00		Deadline of translation	Receipt of the problem to print out (Oly-Exam)		
	14:00 ↓ 29:00	Examination (5 h) Asia $\rightarrow$ Europe $\rightarrow$ America		Submission of the solutions (Oly-Exam) within 2 hours after the end of the examination		Observation of every examination (Zoom/ video) Receipt of all solutions (Oly-Exam) and reports (mail)
	21:30				SC meeting (Zoom)	
Jul 29, Thu	9:00		Receipt of the answer with grading scheme (Oly-Exam)			Distribution of the answer with grading scheme (Oly-Exam)
	9:00	SPring-8 virtual tour	SPring-8 virtual tour			
	23:00		Receipt of scores from Organizer (Oly-Exam) Request for arbitration (Oly-Exam)			Publication of scores (Oly-Exam)

#### Schedule

Date	JST Time (UTC+9)	Student	Mentor/Observers	Invigilator	SC	Organizer
Jul 30, Fri	9:00	Video of Practical Task	Video of Practical Task			
	20:00		Deadline of arbitration request			
	21:00		Jury meeting (Zoom)		Jury meeting (Zoom) SC meeting (Zoom)	Jury meeting (Zoom)
Jul 31, Sat	9:00	Video of preserving cultural assets	Arbitration (Zoom) Asia $\rightarrow$ Europe $\rightarrow$ America			Arbitration (Zoom)
Aug 1, Sun	6:00		Receipt of final results (mail)			Report of final points (mail)
	9:00	Virtual visit for Himeji Catle, Osaka, Kyoto	Virtual visit for Himeji Catle, Osaka, Kyoto			
	12:00		Deadline of argument			
Aug 2, Mon	21:00	Closing Ceremony	Closing Ceremony	Closing Ceremony	Closing Ceremony	Closing Ceremony

#### Profit and loss statement 2019.4~2022.3

income	$1 \text{ USD} \rightarrow 114 \text{ Yen}$
Account	Dollar
Donation income	1,941,560
Subsidies from the country	1,604,986
Participation fee income	85,865
Interest income	168
Miscellaneous income	414
Total amount	3,632,993

detail		
Donation income	Dollar	
Dona	ations from ACS,IUPAC,CSLT	6,217
Dona	ations from companies	1,915,877
Dona	ations from individuals	19,465
Total amount		1,941,560

ACS(American Chemical Society) IUPAC(International Union of Pure and Applied Chemistry) CSLT(Chemical Society Located in Taipei)

#### cost

Account	Dollar
labor cost	494,258
Payroll taxes expense	3,786
Welfare expenses	344
Outsourcing cost	2,075,278
Conference expenses	9,548
Traveling expense	88,955
Postage expense	12,163
Supplies expenses	172,710
Office maintenance and management fees	88,272
Member dues	114
Commission paid	2,370
Lease expenses	31,449
Taxes and dues	932
Compensation paid	4,075
Donations expense	3,881
administrative expenses	193,431
Participation fee	17,222
Printing costs	792
Miscellaneous expenses	114
Relocation fee	309
Total amount	3,200,003

detail		
Expenses directly related to the 53rd IChO	Dollar	
VR-AVATER produ	ction cost	666,349
Video production co	ost	511,650
labor cost		90,788
Ceremony production	on cost	53,070
accommodation cha	rge	68,068
Meeting room renta	l fee	527,904
cost of a meal		9,491
Courier fee and othe	ers	4,439
PC rental fee for mo	onitoring, etc.	31,546
Medals and other so	ouvenirs	95,750
shipping charges		81,013
part-time job offer		12,934
Total amount		2,153,002

# National Team of Countries

### Armenia



Hayk Aghekyan







Tigran Harutyunyan



Sevada Nersisyan

Head Mentor Andranik Davinyan

**Student** 

Mentor Armen Galstyan

Invigilator Artyom Petrosyan

### Australia



Oscar Dong



Austin Lin

Student



Vincent Ng



**Keith Wong** 

Head Mentor Mackenzie Shaw

> Mentor Amy Zhou

Invigilator Samuel Alsop / Yao-Hua Helen Chang / Chris Choon Ng / Carol Zhang

### Austria



**Paul Johann Dorfer** 





**Michael Schembera** 

Head Mentor Georg Schellander

> Mentor Mathias Scherl

Maciej Swiatek

Observer Felix Eder / Florian Kluibenschedl

Invigilator Wolfgang Faber / Paul Glanzer

Student

### Azerbaijan



Salman Huseynov



Lukas Rost

Mahsati Piriyeva



Nariman Shirinli



Khanim Yagublu

Head Mentor Igrar Nazarov

Mentor Milana Agayeva

Invigilator Ali Aliyev / Bezlepkina Veronika

### Bangladesh



**Tawhid Muhammad Mubashwir** 



Safwan Sakib



Mahin Kamal Sawdager



Khalid Hasan Tuhin

#### **Head Mentor** Md Wahab Khan

Mentor

Mohammad Shoeb

#### Observer

Md. Abdul Jabbar / Md. Nurnabi

#### Invigilator

Md. Aminul Haque / N. K. M Akber Hossain / Md. Iqbal Rouf Mamun / Chanchal Kumar Roy

**Student** 

### **Belarus**



Uladzislau Hlatankou



**Kiryl Maroz** 

**Angelina Rogatch** 



Alina Tumashyk

**Head Mentor** Viktar N. Khvalyuk

Mentor Denis G. Shklyaruck

Invigilator Natallia Babaryka / Ekaterina Pavlyuchkova

### Belgium





Louis Pecheur



Lukas Schieble



Jef H. K. Van Eester



Daan Roger Stan Vanhaecke

Head Mentor Hans Vanhoe

Mentor

Sylvestre Dammicco

#### Invigilator

Gilliard Laurane / Cedric Malherbe

Student

### Brazil



Cassia Caroline Aguiar da Ponte



Vinicius da Silveira Lanza Avelar



Marina Malta Nogueira



Hana Gabriela Albuquerque Sousa

Head Mentor Lucas Carvalho Veloso Rodrigues

> Mentor Joao Paulo Ataide Martins

Observer Samuel Anderson Alves Sousa

#### Invigilator

Sergio Maia Melo / Nagila Maria Ponte Silva Ricardo

### Bulgaria



Teodor Svilenov Maslyankov



Georgi Neliyanov Nedyalkov



Pavel Atanasov Nikolov



Samuil Vladimirov Petkov

#### Head Mentor Donka Nikolova Tasheva

Mentor

Penka Vasileva Tsanova

#### Invigilator

Nikola Tomov Burdzhiev / Plamen Danchev Kolev

### Canada



Andrei Banica



Andy Cai

Student



Michael Li



**Terry Wang** 

Head Mentor Guillaume Bussiere

Mentor Jennifer Pitt-Lainsbury

#### Invigilator

Yi (Louise) Lu / Yaoguang Luo / Aleksandra Milicevic / Lisa Stepaniants

### China

#### Student



Xinyu Cai







Bangsen Zhao

Zhangyi Huang

Shu Yang

Head Mentor Yingxia Wang

Mentor

Ping Lyu

#### Observer

Qiaohong He / Zhengjie He / Kai Li / Huaping Xu

Invigilator Qi Chen / Yinxia Yuan

Student

### **Chinese Taipei**



Bo-An Chen



Hsuan-Ting Lin



Chun-Cheng Ting



Rui-Xi Wang

Head Mentor Way-Zen Lee

Mentor Cheng-Huang Lin

**Observer** Yu-Tzu Li / Hsiao-Hua Yu

Invigilator I-Ren Lee / Ming-Kang Tsai

### Costa Rica



Olivia Sojourner Dixon

#### Student



Ignacio Herrera Gamboa

#### Head Mentor José Roberto Vega-Baudrit

Mentor Wendy Villalobos González

Invigilator Mario Villalobos Forbes / Andrea Rivera



Fanny Mariana Solís González

### Croatia



Jasmin Jasarevic



Olga Jerkovic Peric

Student



Fran Miletic



Marko Preocanin

Head Mentor Branka Zorc

Mentor Branimir Bertoša

Invigilator Tin Klacic / Darko Vušak

### Cyprus



Christiana Kosta

#### Student



Giorgos Papachristodoulou



**Stylianos Tamasios** 



Jessica Thackeray

Head Mentor Stella Ioannou Loucaidou

> Mentor Georgios Miliotis

#### Invigilator

Marios Christodoulou / Georgia Ioannou

**Student** 

### **Czech Republic**



Tomáš Heger



Filip Hůlek



**Marek Pavlica** 



**Jakub Sochor** 

#### Head Mentor Petr Holzhauser

Mentor Jiri Ledvinka / Petra Ménová / Lukas Tomanik

> Invigilator Josef Tomeček

### Denmark



Lin Bigom-Eriksen



**Michael Estes** 



**Melanie Muntz** 



Theodor Malte Novrup Redvall

#### Head Mentor Kurt Bjoenager Nielsen

Mentor

Pia Nielsen

#### Invigilator

Susanne Lis Mossin / Michael Munck

### **El Salvador**



Fredi Manuel Barraza Hernandez



Luis Ronaldo Chavez Escamilla

### Student



Emily Alejandra Crespin Guerra



Brenda Nicole Juarez Marroquín

#### **Head Mentor**

Johnny Jose Marquez

Mentor

Marvin Alberto Ramirez Alas

#### Invigilator

Edwin Bladimir Bonilla Ascencio / Rodrigo Ernesto Robles Burgos / Bryan Manuel Salguero Cardoza Alejandro Adrián Ayala Escamilla

#### National Team of Countries 21

### Estonia

#### Student



Aleksandr Beditski



Andrei Kornijenko



Liis Siigur



Siim Tiivel

Head Mentor Ida Rahu

> Mentor Siim Kaukver

Invigilator

Jörgen Metsik

### Finland



Aku Hertell



Henri Kärpijoki

## 1

**Student** 



Otto Keronen



**Samuel Klaver** 

Head Mentor Kjell Knapas

> Mentor Miia Mäntymäki

#### **Observer** Juulia Talvitie

#### Invigilator Mikko Kaipio / Leevi Pesonen

22 The 53rd IChO 2021 Japan

### France



Alexandre Bloquel



**Théodore Halley** 



Théo Mignen



Ruben Tapia

#### Head Mentor Clément Guibert

Mentor

Alix Lenormand

#### Invigilator

Aurélien Moncomble

**Student** 

### Georgia



Nino Abesadze



Lizi Darchia

Ioane Kapanadze



Ketevan Peranidze

Head Mentor Elizbar Elizbarashvili

Mentor Vakhtang Kurtskhalia

Observer Tinatin Buthkhuzi / Sophiko Phatsatsia

### Invigilator

Tamar Bokuchava / Mariam Ghachava / Gia Khatisashvili / Ekaterine Mikautadze

### Germany



Johann Sora Blakytny

### Student



**Tim Bastian Enders** 



Fynn Lasse Noah Kessels



**Linus Albert Schwarz** 

#### Head Mentor Frank Witte

Mentor

Felix Strieth-Kalthoff

Observer

**Maximilian Fellert** 

### Invigilator

Jan Hendrik Frenzel / Philipp Gremler / Uta Purgahn

**Student** 

### Greece



Athanasios Feidakis



Ioannis Karageorgiou



Vasileios Papastamopoulos



**Dimitrios Stylianakis** 

Head Mentor Nikolas Psaroudakis

Mentor Georgios Melidoneas

Invigilator Alexandros Terzopoulos

### Hungary



István Babcsányi



Dávid Benkő



Benedek Sajósi



Lucio Saracco

Head Mentor Gábor Magyarfalvi

Mentor

Szilárd Varga

#### Observer

Katalin Zih-Perenyi

Invigilator Gyorgy Koczan

Student

### Iceland



Dagur Bjorn Benediktsson



Telma Jeanne Bonthonneau



Isak Hugi Einarsson



**Daniel Heidar Jack** 

Head Mentor Katrin Lilja Sigurdardottir

> Mentor Mar Bjorgvinsson

Invigilator Rafn Rafnsson

### India



Mahit Rajesh Gadhiwala





Adarsh Reddy Madur



Dhananjay Raman



**Rishit Singla** 

#### **Head Mentor**

Ankush Gupta

Mentor

Nandita Madhavan

Observer

**Dimple Dutta** 

### Invigilator

Rajesh Chandrakant Gadhiwala / Rupa Reddy Madur / Swapna Mahesh Narvekar / Praveen Pathak / Shirish Rajan Pathare / Lalitha Raman / Harita Pankajkumar Raval / Indrani Das Sen / Dinesh Kumar Singla

**Student** 

### Indonesia



Kevin Lius Bong



Faatih Regind Qashash Roman



Nathanael Reza Putra Widjaja



Hanif Muhammad Zhafran

Head Mentor Deana Wahyuningrum

> Mentor Fainan Failamani

Observer Irma Mulyani

#### Invigilator

Azis Adharis / Damar Nurwahyu Bima / Arie Hardian / Fatiha Khairunnisa

### Iran



Mahyar Afshinmehr



Mahbod Alian Fini



Seyed Mohammad Hossein Barakati



Ehsan Naderi Donig

#### Head Mentor Seifollah Jalili

**Mentor** 

Ebrahim Kianmehr

#### Invigilator

Bahram Madadi / Shahram Seidi

**Student** 

### Ireland



Oscar Eric Moran Despard



**Aoife Mary Morris** 

Oisín Colm Ó Feinneadha



Tong Wu

Head Mentor Carl Poree

Mentor Brian Martin Murphy

Observer

Elizabeth Sarah Gilchrist / John Daniel O'Donoghue

#### Invigilator

Adrian Sanz Arjona / Susannah Calvert / Aine Coogan / Annie Regan

#### National Team of Countries 27

### Israel

#### Student



Nir Cohen



Neta Eiger



Tal Sason



Itamar Steinitz

Head Mentor Izana Nigel

> Mentor Assaf Mauda

Observer

Zeev Groos

Invigilator Maria Lavi

Student

### Japan



Haruhi Isse



Yuya Koike



Kohei Nishiura



Takahiro Takemoto

#### Head Mentor Akira Nagasawa

Mentor

Tsuyoshi Yamaguchi

#### Observer

Asao Nakamura / Toru Shimada

#### Guest

Takuji Hirose

#### Invigilator

Tomohiro Iwai / Hiroyuki Okura / Noriyuki Yonezawa

### Kazakhstan



Sanzhar Bissenali



Khaidar Kairbek



Madiyar Kassymaly



Aigerim Turuspekova

### Head Mentor

Yernur Tolep

Mentor

Anton Morgunov

#### Invigilator

Yerbolat Ablemetov / Zharlagapova Zere

Student

### Korea



Seung Jae Kang



Seoyeon Kim

Myeongjin Shin



Hee Seong Yoon

Head Mentor Bongjin Moon

> Mentor Sung Ik Yang

Observer

Hyuk Kang / Myung Hwan Park

#### Invigilator Myeong-Sook Kim / Yelim Kim

### Kyrgyzstan

### Student



**Kamil Mambetov** 



Nadezhda Ondrina



Ivan Reshetnikov



**Azamat Salamatov** 

#### Head Mentor Bakut Borkoev

Mentor

Kalipa Salieva

#### Invigilator

Dooronbek Mametov / Sharshenali Saitkulov

Student

### Latvia



**Daniils Kargins** 



Džonatans Miks Melgalvis



Vladislavs Tiščenko



Edvards Jānis Treijs

Head Mentor Nauris Narvaišs

> Mentor Ritums Cepītis

Invigilator Kristine Zadvinska

### Lithuania



Tadas Danilevicius



**Povilas Dapsys** 



Laimis Jurkenas



Simonas Melaika

#### Head Mentor Rimantas Raudonis

kimantas kauaonis

Mentor

Lukas Steinys

#### Invigilator

Vytautas Kavaliauskas / Agne Kizalaite

Student

### Luxembourg



Laurent Bommertz



Rafael Dux

Jean-Marc Furlano



Raphaël Menasce

Head Mentor Sam Hoffmann Mentor Sven Linster Invigilator

Claude Kiefer
### Malaysia



Bernie Lim Wei Yuan

### Student



Shawn Vernon Wong Siang Ray



Lim Xu Yao



Wong Yi Yang

Head Mentor Noorsaadah Abd Rahman

> Mentor Sharifuddin Md Zain

#### Invigilator

Jahari Jainal / Lee Lay Peng / Goh Boon Swee / Mary Wong

Student

### Mexico



Jorge García-Ponce



Gerardo Emiliano Gutierrez-Alvarez



Emmanuel Sotomea-Renova



Emilio Alonso Venegas-Hernandez

### Head Mentor

Carlos M Castro-Acuna

Mentor David Octavio Corona-Martinez

#### Invigilator

Hector García-Ortega / Gabriel Palacios-Huerta

### Moldova



Adelina Andrei



Maxim Cojocari-Goncear



Valerian Mocreac



Tatiana Sviriniuc

### **Head Mentor**

Ion Bulimestru

#### **Mentor**

Vasile Graur

#### Invigilator

Stanislav Ciubotaru / Diana Cojocaru

### Mongolia



Irmuun Altankhuyag



Gerel Bayarmagnai

Bumchin Dolgormaa



Temujin Orkhon

Head Mentor Otgondemberel Galaaraidii

Mentor Nyamgerel Choijilsuren

### Observer

Munkhjargal Burenjargal / Battugs Davaasambuu

### Invigilator

Altanzul Altangerel / Saruul Idesh

33

National Team of Countries

### Student

### Montenegro

### Student



**Danijel Aleksic** 







Ksenija Tadic



Milica Zizic

Head Mentor Miljan Bigovic

> Mentor Bojana Ostojic

### Invigilator

#### Momir Radulovic / Ivana Vukcevic

**Student** 

### **Netherlands**



Sebastian Jacob Krikke



Mitchell Rikken



Jochem van den Broek



Max Rudolf Antonius Karel van Hest

#### Head Mentor Emiel de Kleijn

Mentor Kees Beers

#### Invigilator

Martin Groeneveld / Dick Hennink / Marijn Jonker

### **New Zealand**



Abhinav Chawla



Daniel Jiyoun Jang



Mason Minghan Liu



Sam Wuji Zhuang

#### Head Mentor Duncan J McGillivray

Mentor

Sheila Woodgate

#### Invigilator

Jan Giffney / Stephen McCracken / Andrew Rogers

### Nigeria



Joseph Eghenevwegba Ikuru

#### Student



Winston Ukpong

Head Mentor Chinenye Nna Orji

Mentor Aishat Yetunde Abdulkareem

Invigilator Ugochukwu David Uche



lfeanyichukwu Valentine Umeanyika

### North Macedonia



Anja Spasovska



Jan Stojanovski



Darko Stojchev



Mihail Trajkov

Head Mentor Miha Bukleski

Mentor Natasha Ristovska

Invigilator Leon Stojanov

Student

### Norway



Abdur-Raheem Idowu



Tina Kalleson



Joachim Julian Klaussen



Simen Mannsåker

Head Mentor Hans-Petter Hersleth

> Mentor Kristian Vestli

Invigilator

Bjørn Dalhus / Henrik Hovde Sønsteby

### Oman



Lujaina Al Badi



Arwa Al Hashimi



Abdullah Al-Azri



Maryam Al-Hatmi

### **Head Mentor**

**Mohamed Alnaabi** 

Mentor

Said Al Ghawi

#### Invigilator

Fatma Al Badi / Nasser Al Mushaifri / Sultan Al Rahbi / Mohsin Al Riyami

**Student** 

### Pakistan



**Muhammad Ismail** 



Ayesha Junaid

**Rameesha Khursheed** 



Muhammad Yahya

**Head Mentor** Khan M. Khalid

Mentor Muhammad Raza Shah

#### Invigilator

Arslan Ali / Muhammad Imran Malik / Syed Muhammad Saad

### **Philippines**



Nathan Wayne F. Ariston



Ron Angelo A. Gelacio



Aames Juriel B. Morales



Kristoff John F. Padilla

### Head Mentor

Jose M. Andaya

Mentor

Faith Marie Goli Lagua

### Invigilator

Aimee Fontanilla Ariston / Kenneth Arnyl Diaz / Maria Ana Atienza Gelacio / Merlyn Beladas Morales / Raymond Rosalejos Padilla

**Student** 

### Poland



Jakub Krzysztof Kwiatkowski



**Michal Piotr Lipiec** 



Bruno Andrzej Skoczen



Adam Szymon Sukiennik

Head Mentor Marek Orlik

Mentor Aleksandra Misicka-Kesik

#### **Observer** Piotr Kwiatkowski

Invigilator Ewa Pobozy

### Portugal



João Pedro Bonito Caldeira



Mariana Vilela Marta Rio Costa



Tiago Miguel Gomes de Sousa



Beatriz Crisóstomo Valério Figueiredo

### Head Mentor

Vasco Figueiredo Batista

Mentor

João Miguel Pimenta Pereira

#### Invigilator

Diana Cláudia Gouveia Alves Pinto / Carlos Fábio Magalhães da Silva

### Qatar



Nihit Agarwal

### Student



Asmahan Abdulaziz Al-Kuwari



Sushanthi Anandaraja

### Head Mentor

Sara Fahed Al ali

Alahmad

Lamyah Yousef Al-Hayki

Mentor Rabab Farouk Awad

#### Observer

Emad Abdel Rehem Alsaifi / Sherif Abdel Hamid Elhefnawi

#### Invigilator

Sahar Mohammed Omar / Wafaa Gafer Othman

### Romania



Mircea Raul Bodrogean

### Student



Alexandru Catalin Dianu



Stefan Dimitriu



**Tudor Lile** 

Head Mentor Marius Andruh

Mentor Mihaela Matache

#### Invigilator

Adrian Apostol / Anca Paun / Codruta Popescu

**Student** 

### **Russian Federation**



Timofey A. Charkin



Aleksandr E. Trofimov



Andrei S. Tyrin



Georgii M. Zhomin

#### Head Mentor Vadim V. Eremin

Mentor Alexander S. Belov

Observer Alexander K. Gladilin / Leonid V. Romashov

#### Invigilator Sergey I. Kargov

### Saudi Arabia



Mohammad Solaiman AlHadlaq



Mohammad Rashed AlHudaithi



Abdulaziz Abdulrahman AlJuaid



Saeed Sultan Baghdadi

#### Head Mentor Reem Sadeq AlMohammed

Mentor

Abdullah Jassim AlAbdulghani

#### Observer

Waed Zouhir AlKayali / Bader Mohammed AlMajrathi

### Invigilator

**Student** 

Nasser Abdullah AlObaid

### Serbia



Dimitrije Gligorovski



Jovan Marković

Lazar Savić



Nevena Stojković

Head Mentor Dušan Sladić

> Mentor Niko Radulović

Invigilator Irena Novaković / Vidak Raičević

### Singapore



Cheng Jun, Nicholas Goh





Alphonsus Yu Xiang Neo



Chen Yizhou

Head Mentor Wee Boon Tan

Mentor

Hoang Truong Giang

Observer Kailun You

Invigilator Stephanie Jee / Yih Check Wong

**Student** 

### Slovakia



Patrik Fábrik



Samuel Kolesár



Ján Plachý



Matúš Tomčo

Head Mentor Martin Putala

> Mentor Jela Nociarová

Invigilator Samuel Andrejčák

### Slovenia



Jernej Birk



Simon Bukovšek



Vid Kavčič



Patrik Žnidaršič

#### Head Mentor Andrej Godec

Mentor

Berta Košmrlj

#### Invigilator

Miha Lukšič / Aljoša Seljak

**Student** 

### South Africa



Mohammed Tanweer Alli



Erkam Cihan Caglak

Muhammad Mahdi da Costa



Abdul-Baasit Salie

Head Mentor Ajay Bissessur

> Mentor Bice Martincigh

Invigilator Dalaal Abrahams / Ugur Hulusi Patli

### Sri Lanka



Achira Hansindu Kelambi Arachchige





Nadun Naveendra Rajapaksha



Manujaya Praveen Wijesinghe

Head Mentor Chinthaka Nadun Ratnaweera

#### Mentor

Ireshika Chathurani de Silva

#### Invigilator

Hasantha Abayrathna / Sameera Ranmal Gunatilaka / Dulshani Kandambi / Upeksha Welikala

**Student** 

### Sweden



Elsa Bitzén



Dinithi Shalika

Madhubhashini

Erik Bryland



Leopold Kall



Yangyi Qi

Head Mentor Johanna Rogvall

> Mentor Erik Sundén

#### Observer

Cecilia Stenberg

#### Invigilator

Mona Koder Hamid / Mikael Landgren / Tobias Sparrman

### Switzerland

#### Student



Antoine Robin Chèvre



Jessica Rebekka Kurmann



Sandro Pfammatter



Anastasia Aleksandrovna Sandamirskaya

Head Mentor Mario Michele Oreste De Capitani

Mentor

**Maurice Cosandey** 

#### Observer

Linda Katharina Sonderegger / Silena Wegmann / Patrik Oliver Willi

### Invigilator

Gunnar Jeschke / Richard Walter

**Student** 

### Syria



Anas Abbas



Maha Ali

Ahmad Thaer Ater



Ali Marouf

Head Mentor Yomen Sayedsoleman Atassi

Mentor Mohamad Khaled Al Joumaa

Invigilator Tamam Hawa / Dima Khalil / Lara Shabea

#### National Team of Countries 45

### Tajikistan

### Student



**Muhammad Barotov** 



**Shahzod Nazirov** 



Muhammadzhon Otakhonov



Nuriddin Valizoda

#### Head Mentor Khushang Sobirov

Mentor

Daler Salimov

#### Invigilator Ramazon Ziyoev

**Student** 

### Thailand



Sathira Jantarakulchai



Nichawadee Kanjanakosit



Jirapat Rujirayuk



Lita Tantipraphat

#### Head Mentor Torsak Luanphaisarnnont

Mentor Chaiya Prasittichai

Observer

Nattapong Paiboonvorachat / Nisalak Trongsiriwat

### Invigilator

Charoensak Mueangkaew / Oratai Rueangsombat / Sakol Warintaraporn

### **Trinidad and Tobago**



Vineeta Bujhawan



**Jaasiel Edwards** 



Alayna Ragbar



Aiden Ramgoolam

#### **Head Mentor** Nigel Kevin Jalsa

**Mentor** 

Terry Mohammed

### Invigilator

April Koon-Jagassar / Anton Manoo

Student

### Turkey



Sebnem Gul



**Goktug Gulsoy** 

**Deniz Guner** 



Berkan Tarak

#### **Head Mentor** Arif Dastan

Mentor

Yunus Emre Turkmen

#### Invigilator

Dilgam Ahmedli / Nurullah Saraçoğlu / Baturalp Yalçın

### Turkmenistan

### Student





Yusup Dovletmyradov

Gozel Dovranova



Davut Muhammetgulyyev



Berdigylych Rejepbayev

#### Head Mentor Nazar Mammedov

Mentor Serdar Begenjov

#### Invigilator Amangeldi Meretglychov

**Student** 

### Ukraine



**Ihor Kholomieiev** 



Daria Klymenko



Yurii Okis



**Oleksandr Zaporozhets** 

#### Head Mentor Kostiantyn Gavrylenko

Mentor Dmytro Volochnyuk

#### Invigilator

Alexander Lyapunov / Makhankova Valeriya

### **United Arab Emirates**



Ahmed Abdulaziz Alsabbagh



Vaidik Rajesh Hurkat



Yasmin Mahmood Abdulla Mohammad Ali



**Devavrat Verma** 

Head Mentor Abdallah El Marhoune

Student

Mentor Manish Vijay Chhatre

Invigilator Pooja Badal Debath

**Student** 

### **United Kingdom**



Harry John List



Zachary John McGuire



**Rtvik Patel** 



**Alexander Ramsay** Thow

**Head Mentor Ben Pilgrim** 

> **Mentor Alex Thom**

Observer JI Kiappes / Andrew Taylor

> Invigilator **Charlotte Turner**

### **United States of America**



**Kien Phuong** 



Nikhil Seshadri



Qiyang Zhou



Yitian Zhu

Head Mentor Joseph Daniel Houck

Student

Mentor

Esther Hines

#### Observer

Lily Lambert Raines / Laura Serbulea

### Invigilator

Alvin Collins / David Horwitz / Kelly Love / Malgorzata Thatcher

**Student** 

### Uruguay



Agustín Almeida Ahlers



Agustín Corbo Borche



Mariano Díaz Borges



Candela S. Gómez

Head Mentor Santiago Rostán Talasimov

> Mentor Agustina Vila

Invigilator Guillermo Bragunde / Laura Posada

### Uzbekistan



Sobirjon Amanov



lkromiddin Boymahammadov



Durdona Muxtarxujayeva



**Firdavs Sobirov** 

#### Head Mentor Davron Tukhtaev

Mentor

Ortikboy Eshankulov

Invigilator Aziz Khasanov

### Venezuela



Alberto Josué Alava Cedeño

### Student



Verónica Landaeta Hernández

Head Mentor Alessandro D. Trigilio

Mentor Amalia J. Torrealba

#### Invigilator

Laury Bravo / María P. Hurtado / Carmelina M. Kurilo / Nayleth Yépez

### Vietnam

### Student



Anh Duy Nguyen









Phuong Duc Nam Pham

Head Mentor Ha Ngoc Nguyen

Mentor

Phong Van Pham

Observer

Ngan Thi Bich Nguyen

### Invigilator

Hai Thi Hong Le / Thuy Thi Thu Luong / Mo Thi Nguyen / Ha Thi Thu Nguyen

### Observer

### Afghanistan

Rahmkhuda Karimi

Ecuador Andrea Fernanda Barcia

Kuwait Essa Menhal Alqallaf

> Nepal Surgeon Bc

Paraguay

Juan Marcos Serafini Careaga

Country	Student	Mentor	Observer	Guest	Invigilator	Total
Armenia	4	2			1	7
Australia	4	2			4	10
Austria	4	2	2		2	10
Azerbaijan	4	2			2	8
Bangladesh	4	2	2		4	12
Belarus	4	2			2	8
Belgium	4	2			2	8
Brazil	4	2	1		2	9
Bulgaria	4	2			4	10
Canada	4	2			4	10
China	4	2	4		2	12
Chinese Taipei	4	2	2		2	10
Costa Rica	3	2			2	7
Croatia	4	2			2	8
Cyprus	4	2			2	8
Czech Republic	4	4			1	9
Denmark	4	2			2	8
El Salvador	4	2			4	10
Estonia	4	2			1	7
Finland	4	2	1		2	9
France	4	2			1	7
Georgia	4	2	2		4	12
Germany	4	2	1		3	10
Greece	4	2			1	7
Hungary	4	2	1		1	8
Iceland	4	2			1	7
India	4	2	1		9	16
Indonesia	4	2	1		4	11
Iran	4	2			2	8
Ireland	4	2	2		4	12
Israel	4	2	1		1	8
Japan	4	2	2	1	3	12
Kazakhstan	4	2			2	8
Korea	4	2	2		2	10
Kyrgyzstan	4	2			2	8
Latvia	4	2			1	7
Lithuania	4	2			2	8
Luxembourg	4	2			1	7
Malaysia	4	2			4	10
Mexico	4	2			2	8
Moldova	4	2			2	8
Mongolia	4	2	2		2	10
Montenegro	4	2			2	8
Netherlands	4	2			3	9

Country	Student	Mentor	Observer	Guest	Invigilator	Total
New Zealand	4	2			3	9
Nigeria	3	2			1	6
North Macedonia	4	2			1	7
Norway	4	2			2	8
Oman	4	2			4	10
Pakistan	4	2			3	9
Philippines	4	2			5	11
Poland	4	2	1		1	8
Portugal	4	2			2	8
Qatar	4	2	2		2	10
Romania	4	2			3	9
<b>Russian Federation</b>	4	2	2		1	9
Saudi Arabia	4	2	2		1	9
Serbia	4	2			2	8
Singapore	4	2	1		2	9
Slovakia	4	2			1	7
Slovenia	4	2			2	8
South Africa	4	2			2	8
Sri Lanka	4	2			4	10
Sweden	4	2	1		3	10
Switzerland	4	2	3		2	11
Syria	4	2			3	9
Tajikistan	4	2			1	7
Thailand	4	2	2		3	11
Trinidad and Tobago	4	2			2	8
Turkey	4	2			3	9
Turkmenistan	4	2			1	7
Ukraine	4	2			2	8
United Arab Emirates	4	2			1	7
United Kingdom	4	2	2		1	9
United States of America	4	2	2		4	12
Uruguay	4	2			2	8
Uzbekistan	4	2			1	7
Venezuela	2	2			4	8
Vietnam	4	2	1		4	11
Afghanistan			1			1
Ecuador			1			1
Kuwait			1			1
Nepal			1			1
Paraguay			1			1
total	312	160	51	1	185	709





## **Gold Medal**

Rank	Name	Country	Medal	Total
1	Shu Yang	China	Gold	97.57
2	Zhangyi Huang	China	Gold	97.08
3	Xinyu Cai	China	Gold	95.61
4	Bangsen Zhao	China	Gold	94.39
5	Sobirjon Amanov	Uzbekistan	Gold	92.14
6	Mircea Raul Bodrogean	Romania	Gold	90.54
7	Aleksandr E. Trofimov	Russian Federation	Gold	88.67
8	Anh Duy Nguyen	Vietnam	Gold	88.43
9	Bo-An Chen	Chinese Taipei	Gold	88.33
10	Georgii M. Zhomin	Russian Federation	Gold	88.13
11	Chun-Cheng Ting	Chinese Taipei	Gold	87.96
12	Phuong Duc Nam Pham	Vietnam	Gold	86.86
13	Qiyang Zhou	United States of America	Gold	86.83
14	Berkan Tarak	Turkey	Gold	86.20
15	Chen Yizhou	Singapore	Gold	85.35
16	Alexander Ramsay Thow	United Kingdom	Gold	84.33
17	Rui-Xi Wang	Chinese Taipei	Gold	84.05
18	Cheng Jun, Nicholas Goh	Singapore	Gold	83.99
19	Nir Cohen	Israel	Gold	83.71
20	Timofey A. Charkin	Russian Federation	Gold	83.59
21	Tudor Lile	Romania	Gold	82.69
22	Adarsh Reddy Madur	India	Gold	81.99
23	Mahbod Alian Fini	Iran	Gold	81.76
24	Deniz Guner	Turkey	Gold	81.34
25	Andrei S. Tyrin	<b>Russian Federation</b>	Gold	81.31
26	Dhananjay Raman	India	Gold	81.30

Rank	Name	Country	Medal	Total
27	Yitian Zhu	United States of America	Gold	81.03
28	Filip Hůlek	Czech Republic	Gold	80.95
29	Harry John List	United Kingdom	Gold	80.90
30	Anh Le Thao Nguyen	Vietnam	Gold	80.33
31	Mahyar Afshinmehr	Iran	Gold	80.17
32	Myeongjin Shin	Korea	Gold	80.14
33	Alexandru Catalin Dianu	Romania	Gold	79.82



## Silver Medal

Rank	Name	Country	Medal	Total
34	Duong Hoang Nguyen	Vietnam	Silver	79.05
35	Stefan Dimitriu	Romania	Silver	78.81
36	Sebnem Gul	Turkey	Silver	78.81
37	Uladzislav Hlatankov	Belarus	Silver	78.74
38	Alphonsus Yu Xiang Neo	Singapore	Silver	77.76
39	Michal Piotr Lipiec	Poland	Silver	77.48
40	Oscar Dong	Australia	Silver	77.22
41	Seung Jae Kang	Korea	Silver	76.88
42	Nikhil Seshadri	United States of America	Silver	76.11
43	Faatih Regind Qashash Roman	Indonesia	Silver	76.06
44	Bernard Tze Wei Kwee	Singapore	Silver	75.83
45	Hsuan-Ting Lin	Chinese Taipei	Silver	74.87
46	Mahit Rajesh Gadhiwala	India	Silver	74.29
47	Seyed Mohammad Hossein Barakati	Iran	Silver	72.82
48	Oisín Colm Ó Feinneadha	Ireland	Silver	72.75
49	Oleksandr Zaporozhets	Ukraine	Silver	71.96
50	Goktug Gulsoy	Turkey	Silver	70.76

Rank	Name	Country	Medal	Total
51	Shahzod Nazirov	Tajikistan	Silver	70.49
52	Hee Seong Yoon	Korea	Silver	69.93
53	Jirapat Rujirayuk	Thailand	Silver	69.79
54	Jovan Marković	Serbia	Silver	69.42
55	Linus Albert Schwarz	Germany	Silver	69.32
56	Muhammad Barotov	Tajikistan	Silver	68.80
57	Vinicius da Silveira Lanza Avelar	Brazil	Silver	68.34
58	Lucio Saracco	Hungary	Silver	67.68
59	Ioannis Karageorgiou	Greece	Silver	67.17
60	Nichawadee Kanjanakosit	Thailand	Silver	67.03
61	Davut Muhammetgulyyev	Turkmenistan	Silver	66.40
62	Takahiro Takemoto	Japan	Silver	65.92
63	Kohei Nishiura	Japan	Silver	65.65
64	Bruno Andrzej Skoczen	Poland	Silver	65.63
65	Khaidar Kairbek	Kazakhstan	Silver	65.20
66	Mohammad Solaiman AlHadlaq	Saudi Arabia	Silver	64.93
67	Marek Pavlica	Czech Republic	Silver	64.38
68	Ehsan Naderi Donig	Iran	Silver	64.21
69	Patrik Žnidaršič	Slovenia	Silver	64.00
70	Seoyeon Kim	Korea	Silver	63.13
71	Gerel Bayarmagnai	Mongolia	Silver	62.88
72	Temujin Orkhon	Mongolia	Silver	62.78
73	Kien Phuong	United States of America	Silver	62.56
74	Tong Wu	Ireland	Silver	61.87
75	Zachary John McGuire	United Kingdom	Silver	61.69
76	Rishit Singla	India	Silver	61.60
77	Andy Cai	Canada	Silver	61.36
78	Lita Tantipraphat	Thailand	Silver	60.66
79	Džonatans Miks Melgalvis	Latvia	Silver	60.60
80	Yuya Koike	Japan	Silver	60.54
81	Mohammad Rashed AlHudaithi	Saudi Arabia	Silver	60.11

Rank	Name	Country	Medal	Total
82	Abdulaziz Abdulrahman AlJuaid	Saudi Arabia	Silver	59.89
83	Matúš Tomčo	Slovakia	Silver	59.85
84	Itamar Steinitz	Israel	Silver	59.60
85	Gozel Dovranova	Turkmenistan	Silver	59.56
86	Ron Angelo A. Gelacio	Philippines	Silver	58.34
87	Simon Bukovšek	Slovenia	Silver	57.50
88	Michael Schembera	Austria	Silver	57.20
89	Sanzhar Bissenali	Kazakhstan	Silver	57.17
90	Tim Bastian Enders	Germany	Silver	57.12
91	Pavel Atanasov Nikolov	Bulgaria	Silver	56.83
92	Berdigylych Rejepbayev	Turkmenistan	Silver	56.72
93	Dávid Benkő	Hungary	Silver	56.28
94	Yusup Dovletmyradov	Turkmenistan	Silver	56.10
95	Madiyar Kassymaly	Kazakhstan	Silver	55.62
96	Povilas Dapsys	Lithuania	Silver	55.52
97	Nathan Wayne F. Ariston	Philippines	Silver	55.36
98	Daniils Kargins	Latvia	Silver	55.21
99	Jakub Krzysztof Kwiatkowski	Poland	Silver	54.81
100	Ihor Kholomieiev	Ukraine	Silver	54.71



## **Bronze Medal**

Rank	Name	Country	Medal	Total
101	Kevin Lius Bong	Indonesia	Bronze	53.77
102	Tadas Danilevicius	Lithuania	Bronze	53.71
103	Khanim Yagublu	Azerbaijan	Bronze	53.59
104	Sathira Jantarakulchai	Thailand	Bronze	53.30
105	Irmuun Altankhuyag	Mongolia	Bronze	53.07

Rank	Name	Country	Medal	Total
106	Kamil Mambetov	Kyrgyzstan	Bronze	52.79
107	Neta Eiger	Israel	Bronze	52.75
108	lstván Babcsányi	Hungary	Bronze	52.51
109	Samuil Vladimirov Petkov	Bulgaria	Bronze	52.42
110	Durdona Muxtarxujayeva	Uzbekistan	Bronze	52.18
111	Lazar Savić	Serbia	Bronze	52.12
112	Hanif Muhammad Zhafran	Indonesia	Bronze	51.97
113	Darko Stojchev	North Macedonia	Bronze	51.86
114	Vladislavs Tiščenko	Latvia	Bronze	51.06
115	Maciej Swiatek	Austria	Bronze	50.96
116	Keith Wong	Australia	Bronze	50.89
117	Johann Sora Blakytny	Germany	Bronze	50.81
118	Andrei Banica	Canada	Bronze	50.65
119	Firdavs Sobirov	Uzbekistan	Bronze	50.47
120	Ketevan Peranidze	Georgia	Bronze	50.47
121	Abdur-Raheem Idowu	Norway	Bronze	50.24
122	Ruben Tapia	France	Bronze	49.63
123	Austin Lin	Australia	Bronze	49.56
124	Patrik Fábrik	Slovakia	Bronze	49.56
125	Aigerim Turuspekova	Kazakhstan	Bronze	49.45
126	Nathanael Reza Putra Widjaja	Indonesia	Bronze	49.42
127	Edvards Jānis Treijs	Latvia	Bronze	49.41
128	Georgi Neliyanov Nedyalkov	Bulgaria	Bronze	49.28
129	Salman Huseynov	Azerbaijan	Bronze	48.49
130	Cassia Caroline Aguiar da Ponte	Brazil	Bronze	48.22
131	Angelina Rogatch	Belarus	Bronze	48.04
132	Benedek Sajósi	Hungary	Bronze	47.96
133	Alina Tumashyk	Belarus	Bronze	47.73
134	Nariman Shirinli	Azerbaijan	Bronze	47.44
135	Saeed Sultan Baghdadi	Saudi Arabia	Bronze	47.39
136	Ahmad Thaer Ater	Syria	Bronze	47.36

Rank	Name	Country	Medal	Total
137	Maha Ali	Syria	Bronze	47.32
138	Jorge García-Ponce	Mexico	Bronze	46.82
139	Michael Li	Canada	Bronze	46.71
140	Lukas Rost	Austria	Bronze	46.48
141	Teodor Svilenov Maslyankov	Bulgaria	Bronze	46.40
142	Nadun Naveendra Rajapaksha	Sri Lanka	Bronze	46.15
143	Yurii Okis	Ukraine	Bronze	46.09
144	Dimitrije Gligorovski	Serbia	Bronze	45.98
145	Achira Hansindu Kelambi Arachchige	Sri Lanka	Bronze	45.71
146	Marina Malta Nogueira	Brazil	Bronze	45.55
147	Fran Miletic	Croatia	Bronze	45.31
148	Haruhi Isse	Japan	Bronze	45.22
149	Jernej Birk	Slovenia	Bronze	45.05
150	Yangyi Qi	Sweden	Bronze	45.03
151	Aleksandr Beditski	Estonia	Bronze	44.70
152	Vincent Ng	Australia	Bronze	44.41
153	Anas Abbas	Syria	Bronze	44.28
154	Adam Szymon Sukiennik	Poland	Bronze	44.24
155	Tomáš Heger	Czech Republic	Bronze	44.08
156	Ikromiddin Boymahammadov	Uzbekistan	Bronze	43.17
157	Fynn Lasse Noah Kessels	Germany	Bronze	43.07
158	Jakub Sochor	Czech Republic	Bronze	43.03
159	Emilio Alonso Venegas-Hernandez	Mexico	Bronze	42.97
160	Michael Estes	Denmark	Bronze	42.57
161	Liis Siigur	Estonia	Bronze	42.57
162	Jochem van den Broek	Netherlands	Bronze	42.53
163	Nino Abesadze	Georgia	Bronze	42.01
164	Hayk Aghekyan	Armenia	Bronze	41.82
165	Aames Juriel B. Morales	Philippines	Bronze	41.19
166	Théodore Halley	France	Bronze	40.99
167	Valerian Mocreac	Moldova	Bronze	40.56

Rank	Name	Country	Medal	Total
168	Alexandre Bloquel	France	Bronze	40.41
169	Laimis Jurkenas	Lithuania	Bronze	40.39
170	Mahsati Piriyeva	Azerbaijan	Bronze	40.28
171	Daan Roger Stan Vanhaecke	Belgium	Bronze	40.26
172	Simonas Melaika	Lithuania	Bronze	40.10
173	Sandro Pfammatter	Switzerland	Bronze	39.92
174	loane Kapanadze	Georgia	Bronze	39.86
175	Fredi Manuel Barraza Hernandez	El Salvador	Bronze	39.45
176	Tatiana Sviriniuc	Moldova	Bronze	39.35
177	Mason Minghan Liu	New Zealand	Bronze	39.27
178	Ján Plachý	Slovakia	Bronze	39.06
179	Oscar Eric Moran Despard	Ireland	Bronze	38.93
180	Leonid Asatryan	Armenia	Bronze	38.91
181	Terry Wang	Canada	Bronze	38.77
182	Hana Gabriela Albuquerque Sousa	Brazil	Bronze	38.75
183	Tal Sason	Israel	Bronze	38.69
184	Tigran Harutyunyan	Armenia	Bronze	38.53
185	Andrei Kornijenko	Estonia	Bronze	38.41
186	Nevena Stojković	Serbia	Bronze	38.31
187	Adelina Andrei	Moldova	Bronze	38.16
188	Samuel Kolesár	Slovakia	Bronze	37.99
189	Sebastian Jacob Krikke	Netherlands	Bronze	37.50
190	Paul Johann Dorfer	Austria	Bronze	37.47
191	Lin Bigom-Eriksen	Denmark	Bronze	37.19
192	Manujaya Praveen Wijesinghe	Sri Lanka	Bronze	36.84
193	Kiryl Maroz	Belarus	Bronze	36.57
194	Maxim Cojocari-Goncear	Moldova	Bronze	36.06



# Honorable mention

Rank	Name	Country	Medal	Total
195	Bumchin Dolgormaa	Mongolia	Honorable Mention	35.43
196	Abhinav Chawla	New Zealand	Honorable Mention	35.00
197	Aku Hertell	Finland	Honorable Mention	34.86
198	Daria Klymenko	Ukraine	Honorable Mention	34.83
199	João Pedro Bonito Caldeira	Portugal	Honorable Mention	34.66
200	Théo Mignen	France	Honorable Mention	34.60
201	Ali Marouf	Syria	Honorable Mention	34.56
202	Olga Jerkovic Peric	Croatia	Honorable Mention	34.45
203	Sam Wuji Zhuang	New Zealand	Honorable Mention	34.40
204	Samuel Klaver	Finland	Honorable Mention	34.27
205	Vid Kavčič	Slovenia	Honorable Mention	33.37
206	Jessica Rebekka Kurmann	Switzerland	Honorable Mention	33.21
207	Safwan Sakib	Bangladesh	Honorable Mention	32.87
208	Gerardo Emiliano Gutierrez-Alvarez	Mexico	Honorable Mention	31.69
209	Rafael Dux	Luxembourg	Honorable Mention	31.43
210	Aoife Mary Morris	Ireland	Honorable Mention	31.06
211	Henri Kärpijoki	Finland	Honorable Mention	30.82
212	Dinithi Shalika Madhubhashini	Sri Lanka	Honorable Mention	30.61
213	Daniel Jiyoun Jang	New Zealand	Honorable Mention	30.57
214	Athanasios Feidakis	Greece	Honorable Mention	30.17
215	Jean-Marc Furlano	Luxembourg	Honorable Mention	29.88
216	Vaidik Rajesh Hurkat	United Arab Emirates	Honorable Mention	28.98
217	Mahin Kamal Sawdager	Bangladesh	Honorable Mention	28.76
218	Khalid Hasan Tuhin	Bangladesh	Honorable Mention	28.62



Rank	Name	Country	Total
219	Emmanuel Sotomea-Renova	Mexico	28.20
220	Simen Mannsåker	Norway	28.15
221	Lizi Darchia	Georgia	27.62
222	Joachim Julian Klaussen	Norway	25.84
223	Dimitrios Stylianakis	Greece	25.71
224	Anastasia Aleksandrovna Sandamirskaya	Switzerland	25.41
225	Theodor Malte Novrup Redvall	Denmark	25.37
226	Nadezhda Ondrina	Kyrgyzstan	25.37
227	Nihit Agarwal	Qatar	25.34
228	Anja Spasovska	North Macedonia	25.09
229	Marko Preocanin	Croatia	24.75
230	Joseph Eghenevwegba Ikuru	Nigeria	24.57
231	Mariana Vilela Marta Rio Costa	Portugal	24.45
232	Sevada Nersisyan	Armenia	24.03
233	Jan Stojanovski	North Macedonia	23.86
234	Danijel Aleksic	Montenegro	23.62
235	Devavrat Verma	United Arab Emirates	22.86
236	Azamat Salamatov	Kyrgyzstan	22.58
237	Emily Alejandra Crespin Guerra	El Salvador	22.31
238	Melanie Muntz	Denmark	22.25
239	Ivan Reshetnikov	Kyrgyzstan	21.95
240	Vasileios Papastamopoulos	Greece	21.39
241	Tina Kalleson	Norway	21.12
242	Beatriz Crisóstomo Valério Figueiredo	Portugal	20.68
243	Leopold Kall	Sweden	20.48
244	Tawhid Muhammad Mubashwir	Bangladesh	20.47
245	Mihail Trajkov	North Macedonia	20.42
246	Kristoff John F. Padilla	Philippines	20.34

Rank	Name	Country	Total
247	Jef H. K. Van Eester	Belgium	19.77
248	Lim Xu Yao	Malaysia	19.77
249	Yasmin Mahmood Abdulla Mohammad Ali	United Arab Emirates	19.52
250	Jasmin Jasarevic	Croatia	19.20
251	Agustín Corbo Borche	Uruguay	19.02
252	Ayesha Junaid	Pakistan	18.60
253	Erik Bryland	Sweden	18.22
254	Mitchell Rikken	Netherlands	17.95
255	Nuriddin Valizoda	Tajikistan	16.99
256	Giorgos Papachristodoulou	Cyprus	15.63
257	Tiago Miguel Gomes de Sousa	Portugal	15.53
258	Dagur Bjorn Benediktsson	Iceland	14.71
259	Otto Keronen	Finland	14.59
260	Raphaël Menasce	Luxembourg	14.43
261	Mariano Díaz Borges	Uruguay	14.36
262	Luis Ronaldo Chavez Escamilla	El Salvador	13.81
263	Muhammad Mahdi da Costa	South Africa	13.57
264	Verónica Landaeta Hernández	Venezuela	13.42
265	Agustín Almeida Ahlers	Uruguay	13.25
266	Alberto Josué Alava Cedeño	Venezuela	12.91
267	Antoine Robin Chèvre	Switzerland	12.84
268	Louis Pecheur	Belgium	12.83
269	Lukas Schieble	Belgium	12.69
270	Christiana Kosta	Cyprus	12.62
271	Max Rudolf Antonius Karel van Hest	Netherlands	12.62
272	Arwa Al Hashimi	Oman	12.53
273	Wong Yi Yang	Malaysia	12.49
274	Elsa Bitzén	Sweden	12.38
275	Telma Jeanne Bonthonneau	Iceland	12.34
276	Jessica Thackeray	Cyprus	12.09
277	Bernie Lim Wei Yuan	Malaysia	12.03
278	Muhammad Yahya	Pakistan	11.58
279	Laurent Bommertz	Luxembourg	11.48

Rank	Name	Country	Total
280	Sushanthi Anandaraja	Qatar	10.75
281	Sara Fahed Al ali Alahmad	Qatar	9.07
282	Muhammad Ismail	Pakistan	8.71
283	Iva Djurickovic	Montenegro	8.42
284	Ahmed Abdulaziz Alsabbagh	United Arab Emirates	8.36
285	Stylianos Tamasios	Cyprus	8.05
286	Daniel Heidar Jack	Iceland	7.88
287	Rameesha Khursheed	Pakistan	7.77
288	Shawn Vernon Wong Siang Ray	Malaysia	7.72
289	Fanny Mariana Solís González	Costa Rica	7.33
290	Olivia Sojourner Dixon	Costa Rica	7.29
291	Maryam Al-Hatmi	Oman	7.25
292	Candela S. Gómez	Uruguay	7.08
293	Muhammadzhon Otakhonov	Tajikistan	7.06
294	Abdullah Al-Azri	Oman	6.99
295	Alayna Ragbar	Trinidad and Tobago	6.89
296	Aiden Ramgoolam	Trinidad and Tobago	6.21
297	Vineeta Bujhawan	Trinidad and Tobago	6.12
298	Lujaina Al Badi	Oman	5.61
299	Isak Hugi Einarsson	Iceland	5.58
300	Ignacio Herrera Gamboa	Costa Rica	5.19
301	Mohammed TanweerAlli	South Africa	5.02
302	Jaasiel Edwards	Trinidad and Tobago	4.55
303	Asmahan Abdulaziz Al-Kuwari	Qatar	4.54
304	Erkam Cihan Caglak	South Africa	4.33
305	Brenda Nicole Juarez Marroquín	El Salvador	4.01
306	lfeanyichukwu Valentine Umeanyika	Nigeria	2.99
307	Ksenija Tadic	Montenegro	2.79
308	Abdul-Baasit Salie	South Africa	1.92
309	Milica Zizic	Montenegro	1.41
unfortunate absence	Siim Tiivel	Estonia	_
unfortunate absence	Rtvik Patel	United Kingdom	_
unfortunate absence	Winston Ukpong	Nigeria	-
	Total Score		
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Maximum	97.566		
Minimum	1.415		
Average	43.913		
Standard Deviation	24.259		

Problem No.	Q1 (11)	Q2 (11)	Q3 (8)	Q4 (11)	Q5 (12)	Q6 (13)	Q7 (13)	Q8 (11)	Q9 (10)
Maximum	11	11	8	11	12	13	13	11	10
Minimum	0	0	0	0	0	0	0	0	0
Average	5.395	3.942	3.422	5.448	5.140	4.743	5.917	4.906	5.001
Standard Deviation	3.289	3.239	2.725	3.781	3.400	3.573	4.308	3.454	3.464



## **Histogram of Points**















# **Certificate and Medals**



Certificate

#### Medal Design Concept: "The Chemical Vortex Leading to the Future" Designer: Sakiko Matsumoto

F rom the center to the edge, the entire medal forms the shape of a vortex, giving the impression of a whirling motion. This movement represents the global impact and upcoming success of young students, originating at ICh02021 Japan. Through the designs found on both sides of the medal, ICh02021 supports the bright future of the contestants. The obverse side features three kinds of popular auspicious patterns to express aspects of Japanese culture.

The reverse side contains the logo, which is represented in a simple and emphatic way through an image that spreads across the world.



Seigaiha (青海波) translates to blue ocean waves. The endlessly calm waves are a prayer for long-lasting happiness and a peaceful life.

 $Shipp\bar{o}$  Tsunagi ( $t: \le \sim \lambda \le$ ) is a pattern of connecting circles, expressing a wish for happiness, harmony, and connection. This connection is as valuable as the Seven Treasures of Buddhism: gold, silver, lapis lazuli, agate, seashell, amber, and coral.

Asanoha (麻の葉) is a pattern representing hemp leaves. Because hemp is resilient, grows vigorously, and requires little care, it is often used as a pattern in the *kimono* of young children in the hope that they grow up big and strong. It is also meant to ward off evil.

The ribbon represents the image of a whirlpool flowing from the medal in indigo, black, and vermillion, which is the color of Japan. The design also expresses the impact that the students will have in the world.



Obverse side



**Reverse side** 

# Chemistry! It's Cool!



# **Memento and Gifts**

## **Memento and Gifts**

Our memento and gifts, presented to all students, mentors and observers, consist of a tin water pot (pewter ware), an "azuma bukuro" and a tote bag with our catch-phrase and characters printed. Some explanations are given below.

### [Tin water pot]

A tin water pot has been selected as memento because tin ware is known as one of traditional crafts famous for Osaka, where the 53rd IChO 2021 Japan was originally planned to be held.

Tin has been used since very early in the human history, due to its easy-to-scouring nature and its relatively low melting point (231.9  $^{\circ}$ C). Tin water pot made around 1500 B.C. has been discovered in Egypt. Pewter ware, made of 97% tin, was brought to Japan for the first time about 1300 years ago; it seems to have travelled along the Silk Road and arrived via China. Since then in Japan tin had only been used as table ware for ruling class and as tools for Buddist temples and shrines, until a huge tin mine was discovered in the 17th century, after when pewter ware began to be used commonly as utensils for serving and drinking sake and tea.

It is known that a tin processing factory existed in Osaka at the latest in 1679. The production of tin and pewter ware established itself as a major industry in Osaka thanks to its position as a distribution hub. The tin ware made in Osaka was designated Traditional Craft as "Osaka Naniwa Pewterware" in 1983.

#### [Azuma bukuro]

"Azuma bukuro", meaning "east bag", is a traditional Japanese ecofriendly carry and shopping bag made of light and soft cloth. This type of bag was originally made in Edo (old name of Tokyo) during the Edo era (1603~1868), where is located from east (azuma) from Kyoto, old capital of Japan. Kyoto people used it conveniently by calling "Azuma bukuro". The "Azuma bukuro" should be useful in our modern life.

### [Tote bag]

The tote bag has our catch phrase "Chemistry! It's Cool!", as well as five cards of element symbols O, Mo, Te, Na, Si, carried by our characters: "OMOTENASI" in total means warm hospitality in Japanese. We hope that this will be used for a long time as a commemorative item of the 53rd IChO 2021 Japan.



Memento and Gifts

# Ceremony

## IChO 2021 Japan Photo Collection



## IChO 2021 Japan Photo Collection

# Examination



# Meeting

### IChO 2021 Japan Photo Collection



### IChO 2021 Japan Photo Collection

# Activity

Explainers videos for the practical tasks @Kindai Univ.



Virtual Visit to SPring-8



## Secretariat

## IChO 2021 Japan Photo Collection



# Examination

# **Examination Guideline**







## IChO 2021 Japan Examination Guideline

10 June, 2021 Version 2.2 Organizing Committee of IChO2021 Japan

#### 1. General

1-1. Purpose of This Guideline

Due to the COVID-19 pandemic, IChO2021 Japan will be held remotely. This guideline is published to ensure that the theoretical examination for this remote IChO is conducted appropriately.

This document institutes the rules to be followed. It also provides countries with recommended operational methods to protect their delegations from potential (or false) accusations of cheating. Please read this document carefully.

#### 1-2. Time Zone

All dates and times on this document are based on Japan Standard Time (JST), which is Coordinated Universal Time (UTC) +9 hours. Japan does not use daylight saving time during the summer.

#### 1-3. Future Updates of This Document

This document may be updated in the future. When a modification is made to this document, the IChO2021 Organizing Committee will announce the modification immediately, and send the updated version of the guideline to all country coordinators.

- 2. Examination Date and Timetable
- 2-1. Examination Date

The theoretical examination will take place on 28 July, 2021.

#### 2-2. Examination Time

- The duration of the examination is 5 hours.

- The details of the examination (printing time, starting time, ending time, scanning time, times and length of bathroom breaks, and calculator model) must be reported by invigilators. The report form to be completed by invigilators will be provided with the student examination papers.

#### 2-3. Examination Timetable

- The official examination period is 7:00 pm to 12:00 pm JST. If that period is not convenient in the time zone of the participating country, the examination may start up to 5 hours earlier or later. However, in this case, the participating students must observe a total communication ban (blackout) that includes the official examination period. For example, if they start earlier, they must remain secluded until 12:00 pm JST, and if they start later, they must be in isolation from 7:00 pm JST. If the participating country wishes to further change their examination time (for example, further earlier start), they may consult with the Organizer.

- All competitors in each country must have the same examination timetable to avoid illintentioned communication among competitors. Countries with multiple time zones must set their timetable on the basis of one specific time zone and conduct the examination accordingly.

- All countries must submit their choices for starting time, location and recording method via the registration site by 30 June.

#### 2-4. Management of the Examination

- The preparation of the examination (discussions, voting, translation, printing) will be conducted using Oly-Exam software. Mentors will read, comment and vote on, and translate the examination text using the Oly-Exam software. Only a browser and internet access are necessary.

- Manuals for the Oly-Exam software can be found at https://demo.oly-exams.org/docs/ In the event of any difficulties, mentors and invigilators should refer to the manual. The Organizing Committee will also provide technical support during IChO2021.

- The mentor and the invigilator for each country will receive individual accounts to access Oly-Exam.

- Online training for Oly-Exam will be held at 9:00 pm JST on 23 July via Zoom. The details of the Zoom meeting will be announced separately. All mentors and invigilators are expected to attend the training. Observer countries are also invited. The training session will be recorded, and the link to the recorded file will be available during IChO2021.

#### 3. Examination Conditions

#### 3-1. Location of Examination

- The examination location must be a calm and quiet room with electricity, PC or smartphone, web camera, microphone, high quality printer, scanner with PDF- conversion software, and stable internet connection. Each location will be checked via Zoom before the examination.

- It is the responsibility of the country to maintain the location in a state suitable for the

examination. No additional time will be given, even if the examination is interrupted as a result of local problems.

- The examination location should not be the home of a student or a student's relative.

- A single location for the full number of 4 students is highly preferred. If legal travel restrictions in the country forbid a single location, multiple locations for one country are acceptable. In this case, all locations must follow the same examination timetable, and must meet all the requirements. All locations must be notified to the IChO2021 Organizer with the names of the invigilators.

- The students in each location are to be supervised by 1 or 2 invigilators during the examination.

- The students must maintain an appropriate distance from each other in the examination room.

#### 3-2. Invigilators

- Invigilators must be independent of the mentors, must have no relationship with students and must have no other activity in IChO2021. Invigilators should be socially well-established persons such as school principals. The names, positions, and affiliations of the invigilators will be open, as well as those of the mentors.

- Invigilators should not be a parent or a relative of a student.

- Each delegation must register all invigilators at the registration site.

- The invigilators need a good command of English.

- Invigilators will receive an individual account to access Oly-Exam. This account only allows them to access the PDF files of the official English version and final translated version of the problems, and to upload the scanned answers.

- Invigilators must complete the downloading and the printing of the English version and the final translated version of the problems for each student before starting the examination. The problems and answer sheets must be printed clearly. The Organizing Committee will not take any responsibility if an unclear print-out results in incorrect answers given by a student.

- Invigilators should clearly announce the examination timetable to the students before the examination.

- Students are not allowed to use any electronic communication devices (e.g., smartphone, computers, smartwatches) during the examination and between 7:00 pm and 12:00 pm JST. Taking account of different examination starting and ending times, the total blackout periods are as follows:

Exam start	Exam end	Total blackout period
2:00 pm JST	7:00 pm JST	2:00 pm - 12:00 pm JST
3:00 pm JST	8:00 pm JST	3:00 pm - 12:00 pm JST
4:00 pm JST	9:00 pm JST	4:00 pm - 12:00 pm JST

5:00 pm JST	10:00 pm JST	5:00 pm - 12:00 pm JST
6:00 pm JST	11:00 pm JST	6:00 pm - 12:00 pm JST
7:00 pm JST	12:00 pm JST	7:00 pm - 12:00 pm JST
8:00 pm JST	1:00 am* JST	7:00 pm - 1:00 am* JST
9:00 pm JST	2:00 am* JST	7:00 pm - 2:00 am* JST
10:00 pm JST	3:00 am* JST	7:00 pm - 3:00 am* JST
11:00 pm JST	4:00 am* JST	7:00 pm - 4:00 am* JST
12:00 pm JST	5:00 am* JST	7:00 pm - 5:00 am* JST
*. 00 1.1.		

<sup>\*: 29</sup> July

Students are to give their devices to the invigilators before the blackout period shown above. The invigilators will store them for the total blackout period. If the total blackout period includes mid-night or early morning, the invigilators may store them until the next day or from a day before the examination day. The invigilators must ensure that the students do not use any computers installed in the examination location over the relevant total blackout period.

- Invigilators must not allow the students to open the booklet of problems before the examination starts.

- After the examination, invigilators should scan all answer sheets to prepare one PDF file per student, sorting the sheets in the order of the page numbers. All PDF files should be submitted to the IChO2021 Organizer using Oly-Exam within 2 hour after the end of the examination. The answer sheets must be scanned clearly and properly. The Organizing Committee will not take any responsibility if grading is impossible due to unreadable scanning. Only a PDF format file is acceptable.

- Students are not supposed to ask questions during the exam. Invigilators are not to speak with students other than to issue the instructions to begin and end the examination. Students may view the official English version of the examination only when they request clarification of a problem.

- Invigilators may prepare water and snacks or refreshments for the students outside the examination room.

- It is strongly recommended that recording, printing, scanning and uploading files are tested before the examination.

#### 3-3. Equipment

- Only a non-programmable calculator, good writing pen and a ruler can be used during the examination.

- The calculator should be a scientific electronic calculator by which logarithmic function, using both base 10 and e, exponential function, and root can be calculated. Students must be familiar with how to use the calculator, and can use their own calculator. The brand and the model name or number of the calculator must be notified

from the registration site.

- Students should write their answers only using a pen with dark ink. The invigilators may test the printing and scanning process in advance for readability.

#### 3-4. Recording

Videos of the students must be recorded from the beginning to the end of the examination.

All students (whole body) and their activities need to be visible. The IChO2021 Organizer will send the individual Zoom meeting links to invigilators. Invigilators should click on the link at a reasonable time before the examination to directly enter the Zoom meeting hosted by the IChO2021 Organizer. The recording in the cloud will start automatically. Invigilators should place their PC or web camera at a location where the whole room (four students together) can be seen. All devices must have a stable internet connection and the data-transfer rate must be greater than 2 Mbps. If a country faces a technical problem regarding a stable internet connection because of local factors, it must report the situation to the IChO2021 Organizer before the examination. In this situation, offline recording of the examination will be approved, and the invigilators must upload the recorded video data after the examination. If recording offline, the video-camera or recording device must be able to record at least 5 hours in an easily shared format (e.g. MP4) with a reasonable file size and quality. The recording can be made in parts without any perceivable time-gaps (e.g. two devices are used alternatively). The recording file must have time-stamps. Students or their parents must give their written consent for the recording and its sharing with the IChO2021 Organizer.

4. Important Dates

9:00 pm JST, 23 July

Online training for Oly-Exam will be held via Zoom.

#### 9:00 am JST, 25 July

The online opening ceremony will start. The access point for the ceremony will be announced separately. After the opening ceremony, the mentors are not allowed to contact the students.

#### 9:00 pm JST, 25 July

Oly-Exam will be open for access. The first versions of the problems will be provided to mentors, who can submit questions, suggestions, corrections and comments via Oly-Exam. Online discussion will end at 9:00 am JST, 26 July. The Organizing Committee expects mentors to post all discussions on Oly-Exam to keep the Jury meeting short.

9:00 pm JST, 26 July

The first International Jury meeting will be held via Zoom to finalize the problems. The Zoom meeting link and password will be sent to mentors.

The attendees' display names should be their Country Code (three letters) followed by their name (e.g., JPN\_Aaa Bbb). The display name can be changed after entering the Zoom meeting.

Only the head mentor can vote in the Jury meeting. When the Jury meeting is split into two parallel sessions, and the head mentor and mentor attend each session separately, mentor can also vote.

Observers can attend the Jury meeting, but guests are not allowed. If the display name does not match the registered name, the host will dismiss this attendee from the Zoom meeting after taking care to ensure that only the appropriate people attend the Jury meeting.

#### 9:00 am JST, 27 July

Translation via Oly-Exam will begin. The official English versions of the problems will be provided to mentors via Oly-Exam. If any revisions have been made, Oly-Exam will show the revised version of the problems along with the previous version. The changes can therefore be readily reflected in the translations by the mentors.

After the translations are completed, the mentors should approve the translated versions of the problems. Once the mentors approve a translation, no more changes are allowed. Therefore, approvals must be done carefully. The translations must be completed by 9:00 am JST, 28 July.

#### 11:00 am JST, 28 July

Invigilators can access Oly-Exam to print out the translated versions of the problems along with the official English version.

#### 2:00 pm to 12:00 pm JST, 28 July

Invigilators instruct the students to start the examination according to the time schedule in each country.

#### 7:00 pm JST, 28 July to 5:00 am JST, 29 July

Invigilators instruct the students to stop the examination at 5 hours after the start time (i.e. from 2:00 pm to 7:00 pm JST in the earliest timetable and from 12:00 pm to 5:00 am JST in the latest timetable). The invigilators collect all answer sheets, sort and scan them, and convert them to PDF files. The PDF files for each student are submitted to Oly-Exam.

#### 9:00 am JST, 29 July

The student answers, solutions, and marking scheme are provided to mentors via Oly-Exam. The Organizer and the mentors begin marking.

#### 9:00 am JST, 30 July

Grading of the students will be announced by the Organizer. The mentors decide the arbitration list and report it via Oly-Exam. The deadline for requests will be 9:00 pm JST, 30 July.

#### 9:00 pm JST, 30 July

The second International Jury meeting will be held via Zoom. This meeting is intended mainly for IChO business. The time slots for arbitration will be also announced. The attendees are requested to follow the Zoom meeting rules noted above.

#### 9:00 am JST, 31 July to 12:00 am JST, 1 August

Arbitration will be conducted via Zoom. The mentors should enter the Zoom meeting for every problem. Mentors are requested to follow the Zoom meeting rules noted above. Arbitration time slots will be arranged according to the local time zones of participating countries.

9:00 am JST, 1 August The final points scores will be provided to mentors via Oly-Exam.

#### 9:00 pm JST, 2 August

The online closing ceremony will start. Students may attend the ceremony with their avatars. The access point for the ceremony will be announced via email and the website. Medals and certificates will be sent to the participants via surface mail. Certificates can also be sent via email.

#### 5. Contact Us

5-1. Technical Support

During the Olympiad period, technical issues should be reported to support@icho2021.org. The support team will get back to you as soon as possible.

#### 5-2. Instant Communication

Telegram will be used for text-based and instant announcements. Information on how to access Telegram will be provided separately. All mentors and invigilators are expected to download the Telegram application on their mobile device or computer

before IChO2021 to avoid missing any instant information from the Organizing Committee. Telegram display names should consist of a Country Code (three letters) followed by the person's name (e.g., JPN\_Aaa Bbb).

#### Instruction for Invigilators

1. Training of Oly-Exam

There will be a training session of Oly-Exam for Invigilators via Zoom meeting at 0:00 JST, July 24 (15:00 UTC, July 23): https://zoom.us/j/4189597251?pwd=R3dXQjkremxFNmJaY1BZWFByS0pDdz09 Meeting ID: 418 959 7251 Pass Code: 916970

In this session, following topics will be discussed:

- How to access Oly-Exam
- How to download the examination problems (both the official English version and the translated version) and answer sheets
- How to submit the scanned pdf files after the examination
- 2. Information for the examination

Access accounts for Oly-Exam, Zoom ID for on-line recording, and student codes will be informed after the training session.

The following information should be checked before the examination:

- Names of students in all locations of your country
- Starting time of the examination in the local time
- Brand name and model name of each calculators

#### 3. Communication ban

Students are not allowed to use any electronic communication devices (e.g., smartphone, computers, smartwatches) during the examination and between 7:00 pm and 12:00 pm JST, 28 July. Invigilators have to control the communication ban.

#### 4. Setting of the Location

The examination location should be a calm and quiet room. Please maintain the location in a state suitable for the examination.

The students must maintain an appropriate distance from each other in the examination room.

Invigilators should prepare water and snacks or refreshments for the students. Basically, they should be outside of the examination room not to disturb other students. However, they can be inside of the room or on the desk if invigilators can manage the examination room adequately.

The location should have:

- Electricity
- PC or smartphone with zoom application
- Web camera (PC-built-in camera can be used)
- Microphone (PC-built-in microphone can be used)
- High quality printer

- Scanner with PDF-conversion software
- Stable internet connection.

No additional time will be given, even if the examination is interrupted as a result of local problems. It is strongly recommended that recording, printing, scanning and uploading files are tested before the examination.

#### 5. Equipment

Students can use only:

- A non-programmable scientific electronic calculator
- Good writing pen with dark ink
- A ruler

Students are allowed to put equipment that is necessary for the examination (e.g., medicine and handkerchief) on their desk.

#### 6. Recording

All students (whole body) and their activities during the examination will be recorded via Zoom application.

Invigilators should enter the Zoom meeting hosted by the organizer at a reasonable time before the examination. The recording in the cloud will start. Invigilators should place their PC or web camera at a location where all students in the location can be viewed.

The location will be inspected by the organizer. Please follow the request of the organizer who controls the Zoom meeting.

**Only for the country that registered Off-line recording**: If a country registered the off-line recording because of local factors, invigilators have to record the examination as the same manner of on-line recording. The video-camera or recording device used in off-line recording must be able to record at least 5 hours in an easily shared format (e.g., MP4) with a reasonable file size, quality, and time-stamp. The recording can be made in parts without any perceivable time-gaps (e.g., two devices are used alternatively). The URL for upload will be informed separately.

- 7. Examination
  - Invigilators can access Oly-Exam after 9:00 am JST (0:00 am UTC), 28 July to download the problems and answer sheets (both the translated and the official English version). Invigilators must complete the downloading and the printing of the both materials (A4 format) for each student before starting the examination. The problems and answer sheets must be printed clearly on only one side (the back must be blank). Although some problems include color figures, color-printing is not essential. The print-out can be bound separately for each student. Any binding stationary (clip, stapler, binder etc.) can be used.

Every problem and answer sheets have student codes. If there are more than one examination locations in the country, carefully prepare the only necessary problems and answer sheets for the location.

- Please also download and print out the report form from the download site of Oly-Exam. The report form will be available also from the Web site: https://www.icho2021.org/problems/icho2021/
- Invigilators may activate Zoom link 30-60 min before the examination to connect the organizer. The organizers will inform a Zoom link for a country. If there are more than one examination locations in the country, use the same link in the country.
- After Zoom connection is established, the organizer will inspect the examination room: Name of invigilators and students, the face of students, the position of camera for recording, distance between students, calculator, etc.
- After the inspection, the organizer will be invisible, although the organizer will be always there. Please do not mute. Please do not stop video. To maintain the examination room calm, the volume can be minimized.
- Invigilators should clearly announce the examination timetable to the students before the examination. Invigilators must not allow the students to open the booklet of problems before the examination starts.
- At least 5 min before the starting time, invigilators allow the students to read the General Instruction at the first page.
- At the exact starting time registered, invigilators have to instruct the students to start the examination. All locations in the country must follow the same examination timetable.
- Students are not supposed to ask questions during the exam. Invigilators are not to speak with students other than to issue the instructions to begin and end the examination. Students may request the break for bathroom, water, and snacks, and may view the official English version of the examination only when they clarification of a problem.
- The details of the examination (printing time, starting time, ending time, scanning time, and times and length of bathroom breaks) must be recorded by invigilators.
- Invigilators announce the warning at 30 min before the end time (4 hours and 30 min after the start time).
- Invigilators instruct the students to stop the examination at 5 hours after the start time. All students have to stop working. If students do not stop writing, warn the nullification of the points.
- After the examination, invigilators collect all answer sheets, sort the sheets in the order of the page numbers, and scan them to prepare **one PDF file per problem and per student**. The PDF files for each student are submitted to organizer using Oly-Exam within 2 hours after the end of the examination. The answer sheets must be scanned clearly and properly. **Even blank answer**

#### sheets must be uploaded.

All process must be confidential, and invigilator must keep the students away from the answer sheets after the examination.

# **Problem English Version** with Solution









International Chemistry Olympiad 2021 Japan The 53rd IChO 2021 Japan 25th July - 2nd August, 2021 https://www.icho2021.org







#### **General Instruction**

- You are allowed to use only pen to write the answer.
- Your calculator must be non-programmable.
- This examination has 9 problems.
- You can solve the problems in any order.
- You will have **5 hours** to solve all problems.
- You can **begin** working only after the **START** command is given.
- All results must be written in the appropriate answer boxes with pen on the **answer sheets**. Use the back of the question 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 examination.
- 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 your hand and wait until an invigilator arrives.

#### **GOOD LUCK!**

#### **Problems and Grading Information**

	Title	Total Score	Percentage
1	Hydrogen at a Metal Surface	24	11
2	Isotope Time Capsule	35	11
3	Lambert–Beer Law?	22	8
4	The Redox Chemistry of Zinc	32	11
5	Mysterious Silicon	60	12
6	The Solid-State Chemistry of Transition Metals	45	13
7	Playing with Non-benzenoid Aromaticity	36	13
8	Dynamic Organic Molecules and Their Chirality	26	11
9	Likes and Dislikes of Capsules	23	10
		Total	100





### **Physical Constants and Equations**

#### Constants

Speed of light in vacuum	$c = 2.99792458 \times 10^8 \mathrm{m \ s^{-1}}$
Planck constant	$h = 6.62607015  imes 10^{-34}  { m J \ s}$
Elementary charge	$e = 1.602176634 \times 10^{-19} \mathrm{C}$
Electron mass	$m_{\rm e}=9.10938370\times 10^{-31}{\rm kg}$
Electric constant (permittivity of vacuum)	$\varepsilon_0 = 8.85418781 \times 10^{-12}  \mathrm{F}  \mathrm{m}^{-1}$
Avogadro constant	$N_{\rm A} = 6.02214076 \times 10^{23}{\rm mol^{-1}}$
Boltzmann constant	$k_{\rm B} = 1.380649 \times 10^{-23}  {\rm J}  {\rm K}^{-1}$
Faraday constant	$F = N_{\rm A} \times e = 9.64853321233100184 \times 10^4  {\rm C \ mol^{-1}}$
Gas constant	$R = N_{\rm A}  imes k_{\rm B} = 8.31446261815324~{\rm J~K^{-1}~mol^{-1}}$
	$= 8.2057366081  imes 10^{-2} \mathrm{L} \;\mathrm{atm} \;\mathrm{K}^{-1} \mathrm{mol}^{-1}$
Unified atomic mass unit	$u = 1 \mathrm{Da} = 1.66053907 \times 10^{-27} \mathrm{kg}$
Standard pressure	$p=1bar=10^5Pa$
Atmospheric pressure	$p_{atm} = 1.01325  imes 10^5  Pa$
Zero degree Celsius	$0 ^{\circ}\mathrm{C} = 273.15\mathrm{K}$
Ångstrom	$1 \text{ Å} = 10^{-10} \text{ m}$
Picometer	$1 \mathrm{pm} = 10^{-12} \mathrm{m}$
Electronvolt	$1 \mathrm{eV} = 1.602176634 \times 10^{-19} \mathrm{J}$
Part-per-million	$1 \mathrm{ppm} = 10^{-6}$
Part-per-billion	$1  \mathrm{ppb} = 10^{-9}$
Part-per-trillion	$1  ppt = 10^{-12}$
pi	$\pi = 3.141592653589793$
The base of the natural logarithm (Euler's number)	e = 2.718281828459045




#### Equations

The ideal gas law	PV = nRT , where $P$ is the pressure, $V$ is the volume, $n$ is the amount of substance, T is the absolute temperature of ideal gas.
Coulomb's law	$F = k_{e} \frac{q_1 q_2}{r^2}$
	, where $F$ is the electrostatic force, $k_{\rm e} (\simeq 9.0 \times 10^9 {\rm N}{\rm m}^2{\rm C}^{-2})$ is Coulomb's constant, $q_1$ and $q_2$ are the magnitudes of the charges, and $r$ is the distance between the charges.
The first law of thermo- dynamics	$\Delta U=q+w$ , where $\Delta U$ is the change in the internal energy, $q$ is the heat supplied, $w$ is the work done.
Enthalpy H	H = U + PV
Entropy based on Boltz- mann's principle <i>S</i>	$S = k_{\sf B} \ln W$ , where $W$ is the number of microstates.
The change of entropy	$\Delta S = \frac{q_{\text{rev}}}{T}$
$\Delta S$	, where $q_{\sf rev}$ is the heat for the reversible process.
Gibbs free energy <i>G</i>	G = H - TS $\Delta_r G^\circ = -RT \ln K = -zFE^\circ$ , where $K$ is the equilibrium constant, $z$ is the number of electrons, $E^\circ$ is the standard electrode potential.
Reaction quotient <i>Q</i>	$\begin{split} &\Delta_{\mathbf{r}}G = \Delta_{\mathbf{r}}G^{\circ} + RT \ln Q \\ &\text{For a reaction} \\ &aA + bB \rightleftharpoons cC + dD \\ &Q = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \\ &\text{, where } [A] \text{ is the concentration of } A. \end{split}$





Heat change $\Delta q$	$\Delta q = n c_{\rm m} \Delta T$
	, where $c_{\sf m}$ is the temperature-independent molar heat capacity.
Nernst equation for re- dox reaction	$E = E^{\circ} + \frac{RT}{zF} \ln \frac{C_{\text{ox}}}{C_{\text{red}}}$ , where $C_{\text{ox}}$ is the concentration of oxidized substance, $C_{\text{red}}$ is the concentration of reduced substance.
Arrhenius equation	$k = A \exp\left(-\frac{E_a}{RT}\right)$ , where $k$ is the rate constant, $A$ is the pre-exponential factor, $E_a$ is the activation energy. $\exp(x) = e^x$
Lambert–Beer equation	$A = \varepsilon lc$ , where $A$ is the absorbance, $\varepsilon$ is the molar absorption coefficient, $l$ is the optical path length, $c$ is the concentration of the solution.
Henderson–Hasselbalch equation	For an equilibrium $HA \rightleftharpoons H^+ + A^-$ , where equilibrium constant is $K_a$ , $pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$
Energy of a photon	$E = h\nu = h\frac{c}{\lambda}$
	, where $\nu$ is the frequency, $\lambda$ is the wavelength of the light.
The sum of a geometric	When $x \neq 1$ ,
series	$1 + x + x^{2} + \dots + x^{n} = \sum_{i=0}^{n} x^{i} = \frac{1 - x^{n+1}}{1 - x}$
Approximation equation	When $x \ll 1$ ,
that can be used to solve problems	$\frac{1}{1-x} \simeq 1+x$



**G0-6** English (Official)

#### **Periodic Table**

18	Helum Helum 4.003	<sup>so</sup> Neon	20.180 Ar Agon 39.948	% <b>자</b>	Kerpton 83.798	× se	Xenon 131.293	8 R	Radon [222]	118 Og	[294]						
17	:	e T e	18.998 CI CNorine 35.452	з р	Bromine 79.904	s –	lodine 126.904	At	Astatine [210]	TS TS Terressine	[293]	ŗ	Ξ	174.967	103	۲	[262]
16		<sup>8</sup> O <sup>9</sup>	15.999 16 S 32.068	se "	Selenium 78.971	۲e Te	Tellurium 127.60	<sup>™</sup> 6	Poionium [210]	116 LV Livernorium	[293]	F	² ₽	Yterteum 173.045	102	Ŷ	Notelium [259]
15	2	7 Ntoogen	14.007 15 Phosphorus 30.974	33 As	Arsenic 74.922	sb *	Antimony 121.760	8 iB	Bsmuth 208.98	115 MC Moscovium	[289]	de	μ μ	Thulium 168.934	101	ΡW	Mendelevium [258]
14	:	e Carbon	12.011 Si 28.085	ge ¤	Germanium 72.630	s n	Tin 118.710	<sup>∞</sup> d	Lead 207.2	FIE	[289]	1	° Ш	Entum 167.259	100	Ē	Femium [257]
13	2	s 🛛 🗤	10.814 13 Al Aluminum 26.982	s' Ga	Galtum 69.723	위드	hdum 114.818	۶F	Thellum 204.384	Nhonium Nhonium	[278]	4	ੇ ਸ	<sup>Holmium</sup> 164.930	8	ŝ	Einsteinium [252]
12			_	zn 30	Zme 65.38	å å	Cadmium 112.414	° B	Mercury 200.592	Connection	[285]	20	2	Dysprosium 162.500	96	σ	Calibrium [252]
=	:		ctive element)	° O	Cepper 63.546	٩g	<sup>Shver</sup> 107.868	۸u	00d 196.967	111 Rg Roentsonium	[280]	10	e P	Tethium 158.925	46	凿	Derkolum [247]
10	2		s for the radios	88 <b>IZ</b>	Nchel 58.693	°* ₽d	Paladium 106.42	≈ £	Platnum 195.084	DS Ds	[281]	2	gg	Gedolinium 157.25	8	ę	Curium [247]
a			(in parenthosi	° S	Cotalt 58.933	å fi	Rhodum 102.906	<i>۲۲</i>	hidum 192.217	Meibnerium	[276]	12	Ë	Europium 151.964	35	Am	Americium [243]
ď		atomic number Symbol name	atomic weight	s e	55.845	å B	Ruthenium 101.07	≈ so	Osmium 190.23	108 Hs Hassium	[277]	8	Sa	Samenum 150.36	đ	Ъ	Plutonium [239]
-	, Ray.	113 Nhorium	[278]	۶Å	Manganese 54.938	tc <sup>48</sup>	Technetium [99]	ж Ве	Rhenium 186.207	Bh Bh	[272]	4	, E	Promethium [145]	8	ď	Neptunium [237]
8				ة <sup>ي</sup>	Chromium 51.996	42 Mo	Molybolinum 95.95	× N	Tungsten 183.84	sos Sg Seaborium	[271]	4	PZ	Neodymium 144.242	32	⊃	238.029
4				s >	Vanadum 50.942	÷ ₿	Nicbium 92.906	л Та	Tantatum 180.948	Db Dbb	[268]	52	÷ ۲	Praseodymium 140.908	16	Ра	Protactinum 231.036
4				¤ ⊨	Tanium 47.867	<sup>ده</sup> Zr	Ziconium 91.224	۳ ۲	Hathium 178.49	104 Rf Ruthertordium	[267]	12	° °	Cerium 140.116	8	£	Thorium 232.038
~				sc "	Scandium 44.956	4 ک	Ythium 88.906	5771 La-Lu	Larthanoids	89-103 AC-Lr Actionals		5	Ľa	138.905	60	Ac	Actinum [227]
•	2	4 Be Beryflium	9.012 12 Magnesium 24.306	s eg	Calcium 40.078	در ۳	87.62	8ª 8	Barium 137.327	Bation Bation	[226]	10.00	La-Lu	Lanhanoids	89-103	Ac-Lr	Actinoids
F	Hydregen 1.008	e :- "	6.968 11 Na <sup>sodum</sup> 22.990	: ×	79.098	" ď	Rubidum 85.468	s S	Caesium 132.905	87 Fr	[223]						

106 The 53rd IChO 2021 Japan





#### <sup>1</sup>H NMR Chemical Shifts



 $\Delta \delta$  for one alkyl group-substitution: *ca.* +0.4 ppm





### Hydrogen at a Metal Surface

	11 % of the total									
Question	A.1	A.2	B.1	B.2	B.3	B.4	Total			
Points	6	4	5	3	3	3	24			
Score										



Hydrogen is expected to be a future energy source that does not depend on fossil fuels. Here, we will consider the hydrogen-storage process in a metal, which is related to hydrogen-transport and -storage technology.

#### Part A

As hydrogen is absorbed into the bulk of a metal via its surface, let us first consider the adsorption process of hydrogen at the metal surface,  $H_2(g) \rightarrow 2H(ad)$ , where the gaseous and adsorbed states of hydrogen are represented as (g) and (ad), respectively. Hydrogen molecules (H<sub>2</sub>) that reach the metal surface (M) dissociate at the surface and are adsorbed as H atoms (Fig. 1). Here, the potential energy of H<sub>2</sub> is represented by two variables: the interatomic distance, *d*, and the height relative to the surface metal atom, *z*. It is assumed that the axis along the two H atoms is parallel to the surface and that the center of gravity is always on the vertical dotted line in Fig. 1. Fig. 2 shows the potential energy in units of kJ per mole of H<sub>2</sub>. The solid line spacing is 20 kJ mol<sup>-1</sup>, the dashed line spacing is 100 kJ mol<sup>-1</sup>, and the spacing between solid and dashed lines is 80 kJ mol<sup>-1</sup>. The zero-point vibration energy is ignored.











Fig.2





A.1For each of the following items (i)–(iii), **select** the closest value from A–G.6pt(i) The interatomic distance for a gaseous  $H_2$  molecule(ii) The interatomic distance between metal atoms ( $d_M$  in Fig. 1)(iii) The distance of adsorbed H atoms from the surface ( $h_{ad}$  in Fig. 1)

A. 0.03 nm B. 0.07 nm C. 0.11 nm D. 0.15 nm E. 0.19 nm F. 0.23 nm G. 0.27 nm

#### (i) B (ii) F (iii) A **6 points in total:** 2 point for (i), (ii) and (iii)

A.2 For each of the following items (i)–(ii), <u>select</u> the closest value from A–H. (i) the energy required for the dissociation of gaseous H <sub>2</sub> to gaseous H $[H_2(g) \rightarrow 2H(g)]$ (ii) the energy released during the adsorption of a gaseous H <sub>2</sub> [H <sub>2</sub> (g) $\rightarrow 2H(ad)$ ] A. 20 kJ mol <sup>-1</sup> B. 40 kJ mol <sup>-1</sup> C. 60 kJ mol <sup>-1</sup> D. 100 kJ mol <sup>-1</sup> E. 150 kJ mol <sup>-1</sup> F. 200 kJ mol <sup>-1</sup> G. 300 kJ mol <sup>-1</sup> H. 400 kJ mol <sup>-1</sup>						4pt
		A. 20 kJ mol <sup>-1</sup> E. 150 kJ mol <sup>-1</sup>	B. 40 kJ mol <sup>-1</sup> F. 200 kJ mol <sup>-1</sup>	C. 60 kJ mol <sup>-1</sup> G. 300 kJ mol <sup>-1</sup>	D. 100 kJ mol <sup>-1</sup> H. 400 kJ mol <sup>-1</sup>	

(i) H (ii) D **4 points in total:** 2 points for (i) and (ii)

#### Part B

The adsorbed hydrogen atoms are then either absorbed into the bulk, or recombine and desorb back into the gas phase, as shown in the reactions (1a) and (1b). H(ab) represents a hydrogen atom absorbed in the bulk.

$$H_2(g) \stackrel{k_1}{\underset{k_2}{\longleftrightarrow}} 2H(ad)$$
(1a)

$$H(ad) \xrightarrow{k_3} H(ab)$$
 (1b)

The reaction rates per surface site for adsorption, desorption, and absorption are  $r_1[s^{-1}], r_2[s^{-1}]$  and  $r_3[s^{-1}]$ , respectively. They are expressed as:



Q1-4 English (Official)

$$r_1 = k_1 P_{\mathsf{H}_2} (1 - \theta)^2 \tag{2}$$

$$r_2 = k_2 \theta^2 \tag{3}$$

$$r_3 = k_3 \theta \tag{4}$$

where  $k_1 [s^{-1} Pa^{-1}]$ ,  $k_2 [s^{-1}]$  and  $k_3 [s^{-1}]$  are the reaction rate constants and  $P_{H_2}$  is the pressure of  $H_2$ . Among the sites available on the surface,  $\theta$  ( $0 \le \theta \le 1$ ) is the fraction occupied by H atoms. It is assumed that adsorption and desorption are fast compared to absorption ( $r_1, r_2 \gg r_3$ ) and that  $\theta$  remains constant.

**B.1**  $r_3$  can be expressed as: 5pt  $r_3 = \frac{k_3}{1 + \sqrt{\frac{1}{P_{\text{H}_2}C}}}$  (5)

**Express** C using  $k_1$  and  $k_2$ .

From 
$$r_1, r_2 \gg r_3$$
 and  $r_1 = r_2 + r_3$ ,  
 $r_1 = r_2$ .  
Then  $k_1 P_{H_2}(1-\theta)^2 = k_2 \theta^2$  (1')  
Solve for  $\theta$ :  
 $\theta = \frac{1}{1 + \sqrt{\frac{k_2}{P_{H_2}k_1}}}$  (2')  
 $1 + \sqrt{\frac{k_2}{P_{H_2}k_1}}$   
From  $r_3 = k_3 \theta$ :  
 $r_3 = \frac{k_3}{1 + \sqrt{\frac{k_2}{P_{H_2}k_1}}}$   
Thus,  $C = \frac{k_1}{k_2}$   
**5** points in total:  
5 points for the final correct answer  
partial points:  
(1') and (2'): 2 points each.

A metal sample with a surface area of  $S = 1.0 \times 10^{-3} \text{ m}^2$  was placed in a container (1L =  $1.0 \times 10^{-3} \text{ m}^3$ ) with H<sub>2</sub> ( $P_{\text{H}_2} = 1.0 \times 10^2 \text{ Pa}$ ). The density of hydrogen-atom adsorption sites on the surface was  $N = 1.3 \times 10^{18} \text{ m}^{-2}$ . The surface temperature was kept at T = 400 K. As the reaction (1) proceeded,  $P_{\text{H}_2}$  decreased at a constant rate of  $v = 4.0 \times 10^{-4} \text{ Pa s}^{-1}$ . Assume that H<sub>2</sub> is an ideal gas and that the volume of the metal sample is negligible.





# **B.2** Calculate the amount of H atoms in moles absorbed per unit area of the surface 3pt per unit time, $A \text{ [mol s}^{-1} \text{ m}^{-2} \text{]}$ .

The change in the amount of hydrogen atoms per unit time in the gas phase is  $A \times S$ . Thus,  $A \times S = \frac{2vV}{RT}$  (1')  $= 2 \times 4.0 \times 10^{-4} \times \frac{1.0 \times 10^{-3}}{8.31 \times 400} = 2.4 \times 10^{-10} \text{ mol s}^{-1}$ Therefore,  $A = 2.4 \times 10^{-7} \text{ mol s}^{-1} \text{ m}^{-2}$  **3 points in total:** 2 points for (1'), and 1 point for the final answer. -1 point if  $A \times S = \frac{vV}{RT}$  (missing the factor 2).

**B.3** At T = 400 K, C equals  $1.0 \times 10^2$  Pa<sup>-1</sup>. <u>Calculate</u> the value of  $k_3$  at 400 K. If you 3pt did not obtain the answer to **B.2**, use  $A = 3.6 \times 10^{-7}$  mol s<sup>-1</sup> m<sup>-2</sup>.





The relationship between 
$$r_3$$
 and  $A$  is:  

$$A = r_3 \times \frac{N}{N_A}$$
Thus,  

$$r_3 = A \times \frac{N_A}{N} = 1.1 \times 10^{-1} \text{ s}^{-1} (1')$$

$$\frac{\text{Solution 1}}{r_3 = \frac{k_3}{1 + \sqrt{\frac{k_2}{P_{H_2}k_1}}} = \frac{k_3}{1 + \sqrt{\frac{1}{10000}}} = \frac{k_3}{1.01} (2')$$
Thus,  

$$k_3 = 1.01 \times r_3 = 1.1 \times 10^{-1} \text{ s}^{-1}$$

$$\frac{\text{Solution 2}}{\text{Under the condition } P_{H_2}C \gg 1, \text{ it follows that:}$$

$$r_3 = \frac{k_3}{1 + \sqrt{\frac{k_2}{P_{H_2}k_1}}} \approx \frac{k_3}{1} = k_3 (3')$$
Thus,  

$$\frac{k_3 = r_3 = 1.1 \times 10^{-1} \text{ s}^{-1}}{(1.7 \times 10^{-1} \text{ s}^{-1} \text{ with } A = 3.6 \times 10^{-7} \text{ mol s}^{-1} \text{ m}^{-2})}$$

$$\frac{3 \text{ points in total:}}{2 \text{ points for the correct value (1').}}$$
(if correct formulation (1'), 1 point).  
1 point for the final correct answer.  
It does not affect the score whether the approximation of (3') is used or not.

**B.4** At a different *T*,  $C = 2.5 \times 10^3 \text{ Pa}^{-1}$  and  $k_3 = 4.8 \times 10^{-2} \text{ s}^{-1}$  are given. For  $r_3$  as a 3pt function of  $P_{\text{H}_2}$  at this temperature, **select** the correct plot from (a)–(h).





 $r_{3} = \frac{k_{3}}{1 + \sqrt{\frac{1}{P_{H_{2}}C}}}$ (1')  $\approx \frac{k_{3}}{\sqrt{\frac{1}{P_{H_{2}}C}}} = k_{3}\sqrt{P_{H_{2}}C} = 2.4\sqrt{P_{H_{2}}}$ Thus if The figures show the region in which  $P_{\rm H_2}C\ll 1.$  Therefore,

Thus, (b)

**3 points in total:** 3 points for selecting (b).







## Isotope Time Capsule

11 % of the total									
Question	A.1	A.2	A.3	A.4	Total				
Points	8	8	10	9	35				
Score									



Molecular entities that differ only in isotopic composition, such as  $CH_4$  and  $CH_3D$ , are called isotopologues. Isotopologues are considered to have the same chemical characteristics. In nature, however, there exists a slight difference.

Assume that all of the substances shown in this Question are in a gas phase.

Let us consider the following equilibrium:

The entropy, *S*, increases with increasing the number of possible microscopic states of a system, *W*:

$$S = k_{\mathsf{B}} \ln W \tag{2}$$

W = 1 for  ${}^{12}C^{16}O_2$  and  ${}^{12}C^{18}O_2$ . In contrast, W = 2 for a  ${}^{12}C^{16}O^{18}O$  molecule because the oxygen atoms are distinguishable in this molecule. As the right-hand side of the equilibrium shown in eq. 1 has two  ${}^{12}C^{16}O^{18}O$  molecules,  $W = 2^2 = 4$ .



<b>A.1</b> The enthalpy change, $\Delta H$ , of eq. 3 is positive regardless of the temperature. 8pt	t
$H_2 + DI \rightleftharpoons HD + HI$ (3)	
<b><u>Calculate</u></b> the equilibrium constants, $K$ , for eq. 3 at very low (think of $T \to 0$ ) and very high (think of $T \to +\infty$ ) temperatures. Assume that the reaction remains unchanged at these temperatures and that $\Delta H$ converges to a constant value for high temperatures.	
$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} = -RT \ln K \rightarrow \ln K = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$	
$\left(K = \exp\left[-\frac{\Delta H^{\circ}}{RT}\right] \exp\left[\frac{\Delta S^{\circ}}{R}\right]\right) $	
$T \to 0$ : As $\Delta H^{\circ} > 0$ , ln K converges to $-\infty$ and therefore $K = 0$ .	
$T \to +\infty: \ln K \to \frac{\Delta S^{\circ}}{R}$	
Given that $\Delta S^{\circ}$ per 1 mole is $N_{A}k_{B} \ln W = R \ln 2$ , $K = 2$ .	
8 points in total:	
3 points for the correct answer for $T \rightarrow 0$ ,	
5 points for the correct answer for $T \to +\infty$ .	
Partial points:	41
If neither the correct answer for $T \to 0$ nor that for $T \to +\infty$ is obtained: 2 points for showing $A H^{\circ} = A S^{\circ}$	that
$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}.$	
If the correct answer for $T \to +\infty$ is not obtained: 2 points for showing that $W = 2$ .	

The  $\Delta H$  of the following process can be explained by molecular vibrations.

$$2HD \rightleftharpoons H_2 + D_2$$
  $K = \frac{[H_2][D_2]}{[HD]^2}$  (4)

At T = 0 K, the vibrational energy of a diatomic molecule whose vibration frequency is  $\nu [s^{-1}]$  is expressed as:

$$E = \frac{1}{2}h\nu\tag{5}$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \tag{6}$$

Wherein k is the force constant and  $\mu$  the reduced mass, which is expressed in terms of the mass of the two atoms in the diatomic molecule,  $m_1$  and  $m_2$ , according to:

#### 116 The 53rd IChO 2021 Japan





$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{7}$$

**A.2** The vibration of  $H_2$  is at 4161.0 cm<sup>-1</sup> when reported as a wavenumber. 8pt <u>**Calculate**</u> the  $\Delta H$  of the following equation at T = 0 K in units of J mol<sup>-1</sup>.

 $2HD \rightarrow H_2 + D_2 \tag{8}$ 

Assume that:

- only the vibrational energy contributes to the  $\Delta H$ .
- the k values for H<sub>2</sub>, HD, and D<sub>2</sub> are identical.
- the mass of H to be 1 Da and the mass of D to be 2 Da.

$$\begin{split} \mu_{\rm H_2} &= 1/2\,{\rm Da},\,\mu_{\rm HD} = 2/3\,{\rm Da},\,\mu_{\rm D_2} = 1\,{\rm Da}.\\ {\rm Using}\,\,\nu &= \frac{1}{2\pi}\sqrt{\frac{k}{\mu}},\,\frac{\nu_{\rm HD}}{\nu_{\rm H_2}} = \sqrt{\frac{\mu_{\rm H_2}}{\mu_{\rm HD}}}\,{\rm and}\,\,\frac{\nu_{\rm D_2}}{\nu_{\rm H_2}} = \sqrt{\frac{\mu_{\rm H_2}}{\mu_{\rm D_2}}}\,{\rm are\ obtained}. \end{split}$$
The frequency of the  $H_2$  vibration is 4161.0 cm<sup>-1</sup> in units of wavenumbers. Therefore, the frequencies of the molecular vibration for HD and D<sub>2</sub> are calculated to be 3603.5 cm<sup>-1</sup> and 2942.3 cm<sup>-1</sup>, respectively. The difference of the zero-point energies of eq. 4 is calculated to be  $(4161.0 + 2942.3)/2 - 3603.5 = -51.9 \,\mathrm{cm}^{-1}$ .  $E = N_A h \nu = N_A h c \tilde{\nu}$  ( $\tilde{\nu}$ : frequency in wavenumbers), and therefore  $E = \Delta H^\circ = -621 \, \text{J} \, \text{mol}^{-1}$ . 8 points in total: 2 points for the correct vibrational frequency of HD (1 point for the correct  $\mu$  value of HD, 1 point for the correct formulation  $\left(\frac{\nu_{HD}}{\nu_{H_2}} = \sqrt{\frac{\mu_{H_2}}{\mu_{HD}}}\right)$  to calculate the vibrational frequency of HD), 2 points for the correct vibrational frequency of  $D_2$ (1 point for the correct  $\mu$  value of D<sub>2</sub>,  $\left(\frac{\nu_{D_2}}{\nu_{H_2}} = \sqrt{\frac{\mu_{H_2}}{\mu_{D_2}}}\right)$  to calculate the vibrational frequency of D<sub>2</sub>), 1 point for the correct formulation 2 points for the correct conversion from cm<sup>-1</sup> to J mol<sup>-1</sup> (partial points: 1 point for the correct conversion from  $cm^{-1}$  to J ( $N_A$  is missing)), 2 points for the correct energy difference (partial points: -1 point when the value is not divided by 2, -1 point when the sign is wrong).



Q2-4 English (Official)

The molar ratio of H<sub>2</sub>, HD, and D<sub>2</sub> depends on the temperature in a system in equilibrium. Here,  $\Delta_{D_2}$  is defined as the change of the molar ratio of D<sub>2</sub>.

$$\Delta_{\mathsf{D}_2} = \frac{R_{\mathsf{D}_2}}{R_{\mathsf{D}_2}^*} - 1 \tag{9}$$

Here,  $R_{D_2}$  refers to  $\frac{[D_2]}{[H_2]}$  in the sample and  $R_{D_2}^*$  to  $\frac{[D_2]}{[H_2]}$  at  $T \to +\infty$ . It should be noted here that the distribution of isotopes becomes random at  $T \to +\infty$ .

**A.3** **Calculate** 
$$\Delta_{D_2}$$
 with natural D abundance when the isotopic exchange is in equilibrium at the temperature where  $K$  in eq. 4 is 0.300. Assume that the natural abundance ratios of D and H are  $1.5576 \times 10^{-4}$  and  $1 - 1.5576 \times 10^{-4}$ , respectively.





Let the sum of the concentrations of  $H_2$ , HD, and  $D_2$  be C. Solution 1:  $T \to +\infty \left( K = 1/4 \right) :$ 
$$\begin{split} [\mathsf{H_2}]_{\mathbf{0}} &= (1-1.5576\times 10^{-4})^2 C = 9.9969\times 10^{-1} C \\ [\mathsf{D_2}]_{\mathbf{0}} &= (1.5576\times 10^{-4})^2 C = 2.4261\times 10^{-8} C \end{split}$$
K = 0.300:Let the amount of change in the molar ratio be x.  $\frac{[\mathsf{H}_2][\mathsf{D}_2]}{[\mathsf{H}\mathsf{D}]^2} = \frac{\left(\frac{[\mathsf{H}_2]_0}{C} + x\right)\left(\frac{[\mathsf{D}_2]_0}{C} + x\right)}{\left(\frac{[\mathsf{H}\mathsf{D}]_0}{C} - 2x\right)^2} = K$ Solve the equation for x when K = 0.300:  $(1-4K)x^2 + \left(\frac{[\mathsf{H}_2]_0}{C} + \frac{[\mathsf{D}_2]_0}{C} + 4K\frac{[\mathsf{H}\mathsf{D}]_0}{C}\right)x + \left(\frac{[\mathsf{H}_2]_0[\mathsf{D}_2]_0}{C^2} - K\frac{[\mathsf{H}\mathsf{D}]_0^2}{C^2}\right) = 0,$  $x = 4.8504 \times 10^{-9}$ From this value, we obtain  $[H_2] = 9.9969 \times 10^{-1} C$  and  $[D_2] = 2.9112 \times 10^{-8} C$ .  $\Delta_{D_2} = \frac{R_{D_2}}{R_{D_2}^*} - 1 = \frac{\frac{2.9112 \times 10^{-8}}{9.9969 \times 10^{-1}}}{\frac{2.4261 \times 10^{-8}}{9.9969 \times 10^{-1}}} - 1 = 0.200$ Solution 2: By using an appropriate approximation, we can obtain the answer without calculating the concentration of each species. Let the increase of  $[D_2]$  be  $\delta$ .  $K = \frac{[H_2][D_2]}{[HD]^2} = \frac{([H_2]_0 + \delta)([D_2]_0 + \delta)}{([HD]_0 - 2\delta)^2} \simeq \frac{[H_2]_0([D_2]_0 + \delta)}{[HD]_0^2} = \frac{[H_2]_0[D_2]}{[HD]_0^2}$   $\Delta_{D_2} = \frac{R_{D_2}}{R_{D_2}^*} - 1 = \frac{\frac{[D_2]}{[H_2]_0}}{\frac{[D_2]_0}{[H_2]_0}} - 1 \simeq \frac{[D_2]}{[D_2]_0} - 1 = \frac{\frac{[H_2]_0[D_2]}{[HD]_0^2}}{\frac{[H_2]_0[D_2]_0}{[HD]_0^2}} - 1 \simeq \frac{0.300}{0.250} - 1 = 0.200$ 10 points in total: 1 point for the correct  $[H_2]_0$ , 1 point for the correct  $[D_2]_0$ , 2 points for the correct formulation for either  $[H_2]$  or  $[D_2]$ , 2 points for the correct [H<sub>2</sub>], 2 points for the correct  $[D_2]$ , and 2 points for the correct  $\Delta_{D_2}$ . Full marks when the correct  $\Delta_{D_2}$  is shown using an appropriate approximation (without calculating each concentration). Partial points: 5 points for showing that  $[H_2]_0 \simeq [H_2]$ . No deficiency point when the sum of the concentration, C, is assumed to be 1.





In general, the molar ratio of the doubly substituted isotopologue, which contains two heavy isotope atoms in one molecule, increases with decreasing temperature. Let us consider the molar ratio of CO<sub>2</sub> molecules with molecular weights of 44 and 47, which are described as CO<sub>2</sub>[44] and CO<sub>2</sub>[47] below. The quantity  $\Delta_{47}$  is defined as:

$$\Delta_{47} = \frac{R_{47}}{R_{47}^*} - 1 \tag{10}$$

 $R_{47}$  refers to  $\frac{[CO_2[47]]}{[CO_2[44]]}$  in the sample and  $R_{47}^*$  to  $\frac{[CO_2[47]]}{[CO_2[44]]}$  at  $T \to +\infty$ . The natural abundances of carbon and oxygen atoms are shown below; ignore isotopes that are not shown here.

	<sup>12</sup> C	<sup>13</sup> C
natural abundance	0.988888	0.011112

	<sup>16</sup> O	<sup>17</sup> O	<sup>18</sup> O
natural abundance	0.997621	0.0003790	0.0020000

The temperature dependence of  $\Delta_{47}$  is determined as follows, where T is given as the absolute temperature in units of K:

$$\Delta_{47} = \frac{36.2}{T^2} + 2.920 \times 10^{-4} \tag{11}$$

**A.4** The 
$$R_{47}$$
 of fossil plankton obtained from the Antarctic seabed was  $4.50865 \times 10^{-5}$ . 9pt **Estimate** the temperature using this  $R_{47}$ . This temperature is interpreted as the air temperature during the era in which the plankton lived. Consider only the most common isotopologue of  $CO_2[47]$  for the calculation.





The most common isotopologue of  $CO_2[47]$  is  ${}^{13}C^{16}O^{18}O$ . The molar ratio of  ${}^{13}C^{16}O^{18}O$  in the case where all the isotopes are distributed randomly is:  $0.011112 \times 0.002000 \times 0.997621 \times 2$  [O is distinguishable] =  $4.43423 \times 10^{-5}$ The molar ratio of  ${}^{12}C^{16}O_2$  ( $CO_2[44]$ ) in the case where all the isotopes are distributed randomly is:  $0.988888 \times 0.997621^2 = 9.84188 \times 10^{-1}$   $R_{47}^* = \frac{4.43423 \times 10^{-5}}{9.84188 \times 10^{-1}} = 4.50547 \times 10^{-5}$   $\Delta_{47} = 7.06 \times 10^{-4}$  T = 296 K. **9 points in total:** 2 points by indicating that the most common isotopologue of  $CO_2[47]$  is  ${}^{13}C^{16}O^{18}O$ . 3 points for the correct molar ratio of  ${}^{13}C^{16}O^{18}O$  (1 point when  $\times 2$  is missing), 2 points for the correct T. (1 deficiency point when the calculated T is a negative value.)





## Lambert-Beer Law?

8 % of the total									
Question A.1 B.1 B.2 T									
Points	10	6	6	22					
Score									

In this problem, ignore the absorption of the cell and the solvent. The temperatures of all solutions and gases are kept constant at 25  $^{\circ}$ C.

#### Part A

An aqueous solution **X** was prepared using HA and NaA. The concentrations [A<sup>-</sup>], [HA], and [H<sup>+</sup>] in solution **X** are  $1.00 \times 10^{-2}$  mol L<sup>-1</sup>,  $1.00 \times 10^{-3}$  mol L<sup>-1</sup>, and  $1.00 \times 10^{-4}$  mol L<sup>-1</sup>, respectively, which are correlated via the following acid-base equilibrium:

$$\mathsf{HA} \rightleftharpoons \mathsf{A}^- + \mathsf{H}^+ \qquad \qquad K = \frac{[\mathsf{A}^-][\mathsf{H}^+]}{[\mathsf{HA}]} \tag{1}$$

The optical path length is *l* in Part A. Ignore the density change upon dilution. Assume that no chemical reactions other than eq 1 occur.





**A.1** The absorbance of **X** was  $A_1$  at a wavelength of  $\lambda_1$ . Then, solution **X** was diluted 10pt to twice its initial volume using hydrochloric acid with pH = 2.500. After the dilution, the absorbance was still  $A_1$  at  $\lambda_1$ . **Determine** the ratio  $\varepsilon_{HA}/\varepsilon_{A^-}$ , where  $\varepsilon_{HA}$  and  $\varepsilon_{A^-}$  represent the absorption coefficients of HA and of A<sup>-</sup>, respectively, at  $\lambda_1$ .

$$\begin{split} &K = \frac{[\mathsf{A}^{-}][\mathsf{H}^{+}]}{[\mathsf{H}\mathsf{A}]} = \frac{(1.00 \times 10^{-2})(1.00 \times 10^{-4})}{1.00 \times 10^{-3}} = 1.00 \times 10^{-3} \text{ mol } \mathsf{L}^{-1} \\ &\text{Concentration before the dilution:} \\ &[\mathsf{H}\mathsf{A}] = 1.00 \times 10^{-3} \text{ mol } \mathsf{L}^{-1} \\ &[\mathsf{A}^{-}] = 1.00 \times 10^{-2} \text{ mol } \mathsf{L}^{-1} \\ &[\mathsf{H}^{+}] = 1.00 \times 10^{-4} \text{ mol } \mathsf{L}^{-1} \\ &[\mathsf{H}^{+}] = 1.00 \times 10^{-4} \text{ mol } \mathsf{L}^{-1} \\ &[\mathsf{H}^{+}] = 5.00 \times 10^{-4} \text{ mol } \mathsf{L}^{-1} \\ &[\mathsf{H}^{+}] = 5.00 \times 10^{-3} \text{ mol } \mathsf{L}^{-1} \\ &[\mathsf{H}^{+}] = \frac{1.00 \times 10^{-4} + 3.16 \times 10^{-3}}{2} = 1.63 \times 10^{-3} \text{ mol } \mathsf{L}^{-1} \\ &[\mathsf{H}^{+}] = \frac{1.00 \times 10^{-4} + 3.16 \times 10^{-3}}{2} = 1.63 \times 10^{-3} \text{ mol } \mathsf{L}^{-1} \\ &[\mathsf{P}\mathsf{H} = 2.500 \to [\mathsf{H}^{+}] = 3.16 \times 10^{-3} \text{ mol } \mathsf{L}^{-1} \\ &[\mathsf{P}\mathsf{H}] = \frac{(5.00 \times 10^{-3} - x)(1.63 \times 10^{-3} - x)}{5.00 \times 10^{-4} + x} = 1.00 \times 10^{-3} \text{ mol } \mathsf{L}^{-1} \\ &\mathsf{Solve the equation for } x: x = 1.19 \times 10^{-3} \text{ mol } \mathsf{L}^{-1} \\ &\to [\mathsf{A}^{-}] = 3.81 \times 10^{-3} \text{ mol } \mathsf{L}^{-1}, \\ &\mathsf{H}\mathsf{A}] = .69 \times 10^{-3} \mathsf{c}_{\mathsf{A}^{-}} + 1.00 \times 10^{-3} \varepsilon_{\mathsf{H}\mathsf{A}} \\ &\mathsf{By solving this equation:} \frac{\varepsilon_{\mathsf{H}\mathsf{A}}/\varepsilon_{\mathsf{A}^{-}} = 9.0 \\ \\ &\mathsf{10 points in total:} \\ &\mathsf{2 points for the correct } K \text{ value,} \\ &\mathsf{2 points for the correct } [\mathsf{A}^{-}] \text{ and } [\mathsf{H}\mathsf{A}] \text{ values after dilution}, \\ &\mathsf{2 points for the correct } \mathsf{I}^{-1} \text{ and } [\mathsf{H}\mathsf{A}] \text{ values after dilution}, \\ &\mathsf{2 points for the correct } \mathsf{I}^{-1} \text{ and } [\mathsf{H}\mathsf{A}] \text{ values after dilution}, \\ &\mathsf{2 points for the correct } \mathsf{I}^{-1} \text{ and } [\mathsf{H}\mathsf{A}] \text{ values after dilution}, \\ &\mathsf{2 points for the correct } \mathsf{I}^{-1} \text{ and } [\mathsf{H}\mathsf{A}] \text{ values after dilution}, \\ &\mathsf{2 points for the correct } \mathsf{I}^{-1} \text{ and } [\mathsf{H}\mathsf{A}] \text{ values after dilution}, \\ &\mathsf{2 points for the correct } \mathsf{I}^{-1} \text{ and } [\mathsf{H}\mathsf{A}] \text{ values after dilution}, \\ &\mathsf{2 points for the correct } \mathsf{I}^{-1} \text{ and } [\mathsf{H}\mathsf{A}] \text{ values } \mathsf{I}^{-1} \text{ and } \varepsilon_{\mathsf{H}\mathsf{A}}. \\ \\ &\mathsf{A points for the correct } \mathsf{I}^{-1} \text{ and } [\mathsf{H}\mathsf{A}] \text{ values } \mathsf{I}^{-1} \text{ and } \varepsilon_{\mathsf{A}} \text{ and } \varepsilon_{\mathsf{A}} \text{ and } \varepsilon_{\mathsf$$





#### Part B

Let us consider the following equilibrium in the gas phase.

$$D \rightleftharpoons 2M$$
 (2)

Pure gas D is filled into a cuboid container that has a transparent movable wall with a cross-section of S (see the figure below) at a pressure P, and equilibrium is established while the total pressure is kept at P. The absorbance of the gas is  $A = \varepsilon(n/V)l$ , where  $\varepsilon$ , n, V, and l are the absorption coefficient, amount of the gas in moles, volume of the gas, and optical path length, respectively. Assume that all components of the gas mixture behave as ideal gases.



Use the following definitions if necessary.

	Initia	state	After equilibrium		
	D	М	D	М	
Partial pressure	Р	0	$p_{D}$	$p_{M}$	
Amount in moles	$n_0$	0	$n_{D}$	$n_{M}$	
Volume	V	7 0	V		





**B.1** The absorbance of the gas at  $\lambda_{B1}$  measured from direction x ( $l = l_x$ ) was  $A_{B1}$  6pt both at the initial state and after the equilibrium. <u>Determine</u> the ratio  $\varepsilon_D / \varepsilon_M$  at  $\lambda_{B1}$ , where  $\varepsilon_D$  and  $\varepsilon_M$  represent the absorption coefficients of D and of M, respectively.

Solution 1:

The absorbance at the initial state is:  $A_{\text{B1}} = \frac{\varepsilon_{\text{D}} n_0}{V_0} l_x$ The absorbance after equilibrium is:  $A_{\text{B1}} = \frac{\varepsilon_{\text{D}} n_{\text{D}} + \varepsilon_{\text{M}} n_{\text{M}}}{V} l_x$ 

From the ideal gas law, the following relationship is obtained:

$$\frac{n_0}{V_0} = \frac{P}{RT} = \frac{n_{\rm D} + n_{\rm M}}{V}$$
 (\*1)

From these equations, the following relationship is obtained:

$$\begin{split} A_{\mathsf{B}\mathsf{1}} &= \frac{\varepsilon_\mathsf{D} n_0}{V_0} l_x = \frac{\varepsilon_\mathsf{D} (n_\mathsf{D} + n_\mathsf{M})}{V} l_x = \frac{\varepsilon_\mathsf{D} n_\mathsf{D} + \varepsilon_\mathsf{M} n_\mathsf{M}}{V} l_x \\ &\rightarrow \varepsilon_\mathsf{D} n_\mathsf{M} = \varepsilon_\mathsf{M} n_\mathsf{M} \\ &\rightarrow 0 = (\varepsilon_\mathsf{M} - \varepsilon_\mathsf{D}) n_\mathsf{M} \\ &\text{As } n_\mathsf{M} > 0 \text{ after the equilibrium, } \underline{\varepsilon_\mathsf{D}} = \underline{\varepsilon_\mathsf{M}} \text{ holds at } \lambda_{\mathsf{B}\mathsf{1}}. \end{split}$$

#### Solution 2:

Using the ideal gas law, the absorbance at the initial state is expressed as:  $\sum_{n=1}^{\infty} p_n$ 

$$\begin{split} A_{\mathsf{B1}} &= \frac{\varepsilon_{\mathsf{D}} n_0}{V_0} l_x = \varepsilon_{\mathsf{D}} \frac{1}{RT} l_x \text{ (*2)} \\ \text{The absorbance after equilibrium is:} \\ A_{\mathsf{B1}} &= \frac{\varepsilon_{\mathsf{D}} n_{\mathsf{D}} + \varepsilon_{\mathsf{M}} n_{\mathsf{M}}}{V} l_x = \frac{\varepsilon_{\mathsf{D}} p_{\mathsf{D}} + \varepsilon_{\mathsf{M}} p_{\mathsf{M}}}{RT} l_x \text{ (*3)} \end{split}$$

From these equations, the following relationship is obtained:  $P = (-p_{1} + p_{2} + p_{3})$ 

$$A_{\mathsf{B1}} = \varepsilon_{\mathsf{D}} \frac{P}{RT} l_x = \frac{\varepsilon_{\mathsf{D}} p_{\mathsf{D}} + \varepsilon_{\mathsf{M}} p_{\mathsf{M}}}{RT} l_x$$

Using the fact that  $p_{\rm D} = P - p_{\rm M}$ ,  $\varepsilon_{\rm D}P = \varepsilon_{\rm D}(P - p_{\rm M}) + \varepsilon_{\rm M}p_{\rm M} = \varepsilon_{\rm D}P + (\varepsilon_{\rm M} - \varepsilon_{\rm D})p_{\rm M}$   $\rightarrow 0 = (\varepsilon_{\rm M} - \varepsilon_{\rm D})p_{\rm M}$ As  $p_{\rm M} > 0$  after the equilibrium,  $\underline{\varepsilon_{\rm D}}/\varepsilon_{\rm M} = \underline{1}$  holds at  $\lambda_{\rm B1}$ .

#### 6 points in total:

3 points for showing conversion using ideal gas law (either eq. \*1, \*2, or \*3). Full marks when the correct relationship between  $\varepsilon_D$  and  $\varepsilon_M$  is shown even without any derivation written.





**B.2** The absorbance of the gas at  $\lambda_{B2}$  measured from direction y was  $A_{B2}$  both at the initial state ( $l = l_{y0}$ ) and after the equilibrium ( $l = l_y$ ). **Determine** the ratio  $\varepsilon_D / \varepsilon_M$  at  $\lambda_{B2}$ .

Solution 1:

The absorbance at the initial state is:  $A_{\rm B2} = \frac{\varepsilon_{\rm D} n_0}{V_0} l_{y0}$ The absorbance after equilibrium is:  $A_{\rm B2} = \frac{\varepsilon_{\rm D} n_{\rm D} + \varepsilon_{\rm M} n_{\rm M}}{V} l_y$ Using the fact that:  $l_y = l_{y0} \frac{\mathbf{v}}{V_0}$ The absorbance after equilibrium is expressed as follows:  $A_{\mathrm{B2}} = \frac{\varepsilon_{\mathrm{D}} n_{\mathrm{D}} + \varepsilon_{\mathrm{M}} n_{\mathrm{M}}}{V} l_{y} = \frac{\varepsilon_{\mathrm{D}} n_{\mathrm{D}} + \varepsilon_{\mathrm{M}} n_{\mathrm{M}}}{V_{0}} l_{y0}$ From these equations, the following relationship is obtained:  $A_{B2} = \frac{\varepsilon_{D} n_{0}}{V_{0}} l_{y0} = \frac{\varepsilon_{D} n_{D} + \varepsilon_{M} n_{M}}{V_{0}} l_{y0}$ Using the fact that:  $n_{\rm M} = 2(n_0 - n_{\rm D})$  (\*4) The following relationship is obtained:  $\varepsilon_{\mathsf{D}} n_0 = \varepsilon_{\mathsf{D}} n_{\mathsf{D}} + 2 \varepsilon_{\mathsf{M}} (n_{\mathsf{0}} - n_{\mathsf{D}}) = 2 \varepsilon_{\mathsf{M}} n_0 + (\varepsilon_{\mathsf{D}} - 2 \varepsilon_{\mathsf{M}}) n_{\mathsf{D}}$  $\rightarrow (\varepsilon_{\rm D} - 2\varepsilon_{\rm M})n_0 = (\varepsilon_{\rm D} - 2\varepsilon_{\rm M})n_{\rm D}$ As  $n_0 > n_D$  after the equilibrium,  $\varepsilon_D = 2\varepsilon_M$  holds at  $\lambda_{B2}$ . Solution 2: Using the fact that  $V_0 = l_{y0}S$ , the absorbance at the initial state is expressed as:  $A_{\mathsf{B2}} = \frac{\varepsilon_{\mathsf{D}} n_0}{V_0} l_{y0} = \varepsilon_{\mathsf{D}} \frac{n_0}{S}$ Using the fact that  $V = l_y S$ , the absorbance after equilibrium is expressed as:  $A_{\mathsf{B2}} = \frac{\varepsilon_{\mathsf{D}} n_{\mathsf{D}} + \varepsilon_{\mathsf{M}} n_{\mathsf{M}}}{V} l_{y} = \frac{\varepsilon_{\mathsf{D}} n_{\mathsf{D}} + \varepsilon_{\mathsf{M}} n_{\mathsf{M}}}{S}$ From these equations, the following relationship is obtained:  $A_{\rm B2} = \varepsilon_{\rm D} \frac{n_0}{S} = \frac{\varepsilon_{\rm D} n_{\rm D} + \varepsilon_{\rm M} n_{\rm M}}{S}$ Using the fact that:  $n_{\rm M} = 2(n_0 - n_{\rm D})$  (\*4) The following relationship is obtained:  $\varepsilon_{\mathsf{D}} n_0 = \varepsilon_{\mathsf{D}} n_{\mathsf{D}} + 2 \varepsilon_{\mathsf{M}} (n_{\mathsf{0}} - n_{\mathsf{D}}) = 2 \varepsilon_{\mathsf{M}} n_0 + (\varepsilon_{\mathsf{D}} - 2 \varepsilon_{\mathsf{M}}) n_{\mathsf{D}}$  $\rightarrow (\varepsilon_{\rm D} - 2\varepsilon_{\rm M})n_0 = (\varepsilon_{\rm D} - 2\varepsilon_{\rm M})n_{\rm D}$ As  $n_0 > n_D$  after the equilibrium,  $\varepsilon_D / \varepsilon_M = 2$  holds at  $\lambda_{B2}$ . 6 points in total:

3 points for showing the relationship that  $n_{\rm M}$  is twice of  $n_0 - n_{\rm D}$  as in eq.\*4. Full marks when the correct relationship between  $\varepsilon_{\rm D}$  and  $\varepsilon_{\rm M}$  is shown even without any derivation written.





## **The Redox Chemistry of Zinc**

	11 % of the total									
Question	A.1	A.2	B.1	B.2	B.3	B.4	Total			
Points	6	5	4	3	5	9	32			
Score										



Zinc has long been used as alloys for brass and steel materials. The zinc contained in industrial wastewater is separated by precipitation to detoxify the water, and the obtained precipitate is reduced to recover and reuse it as metallic zinc.

#### Part A

The dissolution equilibrium of zinc hydroxide  $Zn(OH)_2(s)$  at 25 °C and the relevant equilibrium constants are given in eq. 1–4.

$$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^{-}(aq) \qquad K_{sp} = 1.74 \times 10^{-17}$$
(1)

$$\operatorname{Zn}(\operatorname{OH})_2(s) \rightleftharpoons \operatorname{Zn}(\operatorname{OH})_2(\operatorname{aq})$$
  $K_1 = 2.62 \times 10^{-6}$  (2)

$$Zn(OH)_2(s) + 2OH^{-}(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq) \qquad K_2 = 6.47 \times 10^{-2}$$
(3)

$$H_2O(I) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 1.00 \times 10^{-14}$$
(4)





The solubility, *S*, of zinc (concentration of zinc in a saturated aqueous solution) is given in eq. 5.

$$S = [Zn^{2+}(aq)] + [Zn(OH)_2(aq)] + [Zn(OH)_4^{2-}(aq)]$$
(5)

**A.1** When the equilibria in eq. 1-4 are established, <u>calculate</u> the pH range 6pt in which  $[Zn(OH)_2(aq)]$  is the greatest among  $[Zn^{2+}(aq)]$ ,  $[Zn(OH)_2(aq)]$  and  $[Zn(OH)_4^{2-}(aq)]$ .

#### Solution 1:

```
From [Zn(OH)_2(aq)] > [Zn^{2+}]:
  K_{sp}
rac{sp}{[OH^-]^2} < K_1 (1')
Solve this for [OH-]:
pH > 8.4
[Zn(OH)_2(aq)] > [Zn(OH)_4^{2-}]:
K_1 > K_2 [OH^-]^2 (2')
Solve this for [OH<sup>-</sup>]:
pH < 11.8
Thus,
8.4 < pH < 11.8
Solution 2:
From (1):
log[Zn^{2+}][OH^{-}]^{2} = log K_{sp}
\log[Zn^{2+}] = \log K_{sp} - 2\log[OH^{-}]
From (2'):
\log[Zn(OH)_2(aq)] = \log K_1
[Zn(OH)_2(aq)] > [Zn^{2+}]:
\begin{array}{l} \log {\rm K_{sp}}-2\log [{\rm OH^{-}}] < \log {\rm K_{1}} \ (1') \\ \log {\rm K_{sp}}-2 \ ({\rm pH}-14) < \log {\rm K_{1}} \end{array}
From (3'):
\log([Zn(OH)_4^{2-}]/[OH^{-}]^2) = \log K_2
\log[Zn(OH)_{4}^{2-}] = 2\log[OH^{-}] + \log K_{2}
[Zn(OH)_2(aq)] > [Zn(OH)_4^2]:
\log K_1 > 2 \log[OH^-] + \log K_2 (2')
\log K_1 > 2 (pH - 14) + \log K_2
Thus,
8.4 < pH < 11.8
```

#### 6 points in total: 3 points for 8.4 < pH 3 points for pH < 11.8. Partial point: If correct answers are not obtained; (1') and (2'): 2 points each.





**A.2** A saturated aqueous solution of  $Zn(OH)_2(s)$  with pH = 7.00 was prepared and 5pt filtered. NaOH was added to this filtrate to increase its pH to 12.00. <u>Calculate</u> the molar percentage of zinc that precipitates when increasing the pH from 7.00 to 12.00. Ignore the volume and temperature changes.

For pH=12.00:  $\log[Zn(OH)_{4}^{2-}] = -29.19 + 2 pH = -5.19$  $\log[Zn(OH)_{2}(aq)] = -5.58$  $\log[Zn^{2+}] = 11.24 - 2\,\mathrm{pH} = -12.76$ Thus,  $S = 9.0865 \times 10^{-6} \text{ mol } \text{L}^{-1}$  (1') For pH=7.00:  $\log[Zn(OH)_{4}^{2-}] = -29.19 + 2 pH = -15.19$  $\log[Zn(OH)_2(aq)] = -5.58$  $\log[Zn^{2+}] = 11.24 - 2 \,\mathrm{pH} = -2.76$ Thus,  $S = 1.7404 \times 10^{-3} \,\mathrm{mol}\,\mathrm{L}^{-1}$  (2') The percentage of zinc precipitated is:  $1.7404 \times 10^{-3} - 9.0865 \times 10^{-6}$ - = 0.9948 = 99.5% $1.7404 \times 10^{-3}$ **5** points in total: 2 points for the correct value of (1'). 2 points for the correct value of (2').

1 point for the final correct answer. The calculation for the negligible component is not required.

#### Part B

Next, the recovered zinc hydroxide is heated to obtain zinc oxide according to the reaction below:

$$Zn(OH)_2(s) \rightarrow ZnO(s) + H_2O(I)$$
(6)

The zinc oxide is then reduced to metallic zinc by reaction with hydrogen:

$$ZnO(s) + H_2(g) \rightarrow Zn(s) + H_2O(g)$$
(7)

**B.1** In order for reaction (7) to proceed at a hydrogen pressure kept at 1 bar, it is necessary to reduce the partial pressure of the generated water vapor. <u>Calculate</u> the upper limit for the partial pressure of water vapor to allow reaction (7) to proceed at 300 °C. Here, the Gibbs formation energies of zinc oxide and water vapor at 300 °C and 1 bar for all gaseous species are  $\Delta G_{ZnO}(300^{\circ}C) = -2.90 \times 10^2 \text{ kJ mol}^{-1}$  and  $\Delta G_{H_2O}(300^{\circ}C) = -2.20 \times 10^2 \text{ kJ mol}^{-1}$ , respectively.





 $\begin{aligned} &\text{Zn} + \frac{1}{2}\text{O}_2 \to \text{ZnO}, \ \Delta G_{\text{ZnO}}(300^\circ\text{C}) = -2.90 \times 10^2 \text{ kJ mol}^{-1} \\ &\text{H}_2 + \frac{1}{2}\text{O}_2 \to \text{H}_2\text{O}, \ \Delta G_{\text{H}_2\text{O}}(300^\circ\text{C}) = -2.20 \times 10^2 \text{ kJ mol}^{-1} \\ &\text{Thus,} \\ &\text{ZnO} + \text{H}_2 \to \text{Zn} + \text{H}_2\text{O}, \ \Delta G = \Delta G_{\text{H}_2\text{O}}(300^\circ\text{C}) - \Delta G_{\text{ZnO}}(300^\circ\text{C}) \text{ (1')} \\ &= 7.0 \times 10^1 \text{ kJ mol}^{-1} \\ &\text{In}K = \ln \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} = -\frac{\Delta G}{RT} \text{ (2')} \\ &\text{From } T = 573.15 \text{ K}, \\ &p_{\text{H}_2\text{O}} = 4.14 \times 10^{-7} \text{ bar} = 4.1 \times 10^{-7} \text{ bar} \end{aligned}$ 

2 point for the correct formulation of (2'). 1 point for the correct final answer.

Metallic zinc is used as a negative electrode (anode) material for metal-air batteries. The electrode consists of Zn and ZnO. It uses the following redox reaction to generate electricity with the electromotive force (e.m.f.) at 25 °C and pressure of 1 bar,  $E^{\circ}$ .

$$\operatorname{Zn}(s) + \frac{1}{2}O_2(g) \to \operatorname{ZnO}(s)$$
  $E^\circ = 1.65 \,\mathrm{V}$  (8)

**B.2** A zinc–air battery was discharged at 20 mA for 24 hours. <u>Calculate</u> the change 3pt in mass of the negative electrode (anode) of the battery.

The reaction  $\text{Zn} \to \text{ZnO}$  occurs at the negative electrode and consumes 2 mol electrons per mol Zn oxidized.

Thus, the weight change is:  $W = \frac{0.02 \times 24 \times 60 \times 60 \times 16}{2F}$  (1') = 0.14 g

**3 points in total;**2 points for the correct formulation (1').1 point for the correct final answer.







Mt. Fuji

**B.3** Consider the change of e.m.f. of a zinc–air battery depending on the environment. **Calculate** the e.m.f. at the summit of Mt. Fuji, where the temperature and altitude are -38 °C (February) and 3776 m, respectively. The atmospheric pressure is represented by

$$P\left[\mathsf{bar}\right] = 1.013 \times \left(1 - \frac{0.0065h}{T + 0.0065h + 273.15}\right)^{5.257} \tag{9}$$

at altitude h [m] and temperature T [°C]. The molar ratio of oxygen in the atmosphere is 21%. The Gibbs energy change of reaction (8) is  $\Delta G_{ZnO}(-38^{\circ}C) = -3.26 \times 10^2 \text{ kJ mol}^{-1}$  at  $-38^{\circ}C$  and 1 bar.





#### Solution 1:

From (9), the air pressure at 3776 m and  $T = -38 \,^{\circ}\text{C}$  is  $P = 0.6011 \,\text{bar}$  (1') From the oxygen content of 21%, the partial pressure of oxygen is:  $P_{O_2} = 0.126 \,\text{bar}$ From the Nernst equation ( $T = -38 \,^{\circ}\text{C}$ ) :  $E(-38 \,^{\circ}\text{C}) - E^{\circ}(-38 \,^{\circ}\text{C}) = -\frac{RT}{2F} \ln \frac{1}{\sqrt{P_{O_2}}} = -0.01048 \,\text{V} = -0.01 \,\text{V}$  (2')  $E^{\circ}(-38 \,^{\circ}\text{C}) = -\frac{\Delta G^{\circ}(-38 \,^{\circ}\text{C})}{2F} = \frac{326000}{2F} = 1.6894 \,\text{V} = 1.69 \,\text{V}$  (3') From (2') and (3'):  $E(-38 \,^{\circ}\text{C}) = 1.68 \,\text{V}$ 

#### Solution 2:

From (9), the air pressure at 3776 m and  $T = -38 \degree \text{C}$  is P = 0.6011 bar (1')From the oxygen content of 21%, the partial pressure of oxygen is:  $P_{O_2} = 0.126 \text{ bar}$   $\Delta G(-38\degree \text{C}) = \Delta G\degree (-38\degree \text{C}) - \frac{1}{2}RT \ln P_{O_2}$  (2')  $= -3.24 \times 10^2 \text{ kJ mol}^{-1}$   $E(-38\degree \text{C}) = -\frac{\Delta G(-38\degree \text{C})}{2F}$  (3') = 1.68 V(° is used for 1 bar)

#### 5 points in total:

1 point for the correct value of (1').

- 2 points for the correct formulation of (2').
- 1 point for the correct formulation of (3')
- 1 point for the correct final answer.

B.4	<u><b>Calculate</b></u> the Gibbs energy change for reaction (6) at $25$ °C. Note that the standard reduction potentials, $E^{\circ}(Zn^{2+}/Zn)$ and $E^{\circ}(O_2/H_2O)$ at $25$ °C and 1 bar are given as (10) and (11), respectively.					
	$Zn^{2+} + 2e^- \rightarrow Zn$	$E^\circ(Zn^{2+}/Zn) = -0.77V$	(10)			
	$\mathrm{O_2} + 4\mathrm{H^+} + 4\mathrm{e^-} \rightarrow 2\mathrm{H_2O}$	$E^\circ(\mathrm{O_2/H_2O}) = 1.23\mathrm{V}$	(11)			





From (10):  $\operatorname{Zn}^{2+} + 2e^- \rightarrow \operatorname{Zn}, E^\circ = -0.77 \,\mathrm{V}$  $\Delta G^{\circ} = -2F \times -0.77$  (1')  $= 148.59 \, \mathrm{kJ} \, \mathrm{mol}^{-1}$ From (8):  $\operatorname{Zn} + \frac{1}{2}\operatorname{O}_2 \to \operatorname{ZnO}, E^\circ = 1.65 \,\mathrm{V}$  $\Delta G^{\circ} = -2F \times 1.65 \text{ (2')}$  $= -318.40\,{\rm kJ\,mol^{-1}}$ From (11):  $\mathrm{O_2} + 4\mathrm{H^+} + 4\mathrm{e^-} \rightarrow 2\mathrm{H_2O}, E^\circ = 1.23\,\mathrm{V}$  $\Delta G^{\circ} = -4F \times 1.23$  (3')  $= -474.71 \, \text{k} \, \text{mol}^{-1}$ From (1):  $Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2(s), K_{sp} = 1.74 \times 10^{-17}$  $\Delta G^{\circ} = -RT \ln K_{\rm sp}^{-1} \, \text{(4')}$  $= -95.662 \, \text{kJ} \, \text{mol}^{-1}$ From (4):  $\mathrm{H^{+}+OH^{-}\rightarrow H_{2}O}, K_{\mathrm{W}}=1\times10^{-14}$  $\Delta G^{\circ} = -RT \ln K_{w}^{-1} (5')$ = -79.912 kJ mol<sup>-1</sup> From  $\frac{(1')\times 2+(2')\times 2-(3')-(4')\times 2+(5')\times 4}{2}$  $\text{Zn}(\text{OH})_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}, \Delta G^{\circ} = 3.0 \sim 3.4 \times 10^3 \,\text{J}\,\text{mol}^{-1}$ (distributed depending on the handling of figures) 9 points in total: 1 points for correct formulation (1'). 1 points for correct formulation (2'). 1 points for correct formulation (3'). 2 points for correct formulation (4'). 2 points for correct formulation (5'). 2 point for the correct final answer.





## **Mysterious Silicon**

12 % of the total								
Question	A.1	A.2	A.3	A.4	B.1	B.2	B.3	Total
Points	9	7	6	10	5	15	8	60
Score								



Although silicon is also a group 14 element like carbon, their properties differ significantly.

#### Part A

Unlike the carbon–carbon triple bond, the silicon–silicon triple bond in a compound formulated as  $R^1-Si \equiv Si-R^1$  (R: organic substituent) is extremely reactive. For example, it reacts with ethylene to form a cyclic product that contains a four-membered ring.



When  $R^1-Si \equiv Si-R^1$  is treated with an alkyne ( $R^2-C \equiv C-R^2$ ), the four-membered-ring compound **A** is formed as an initial intermediate. Further reaction of another molecule of  $R^2-C \equiv C-R^2$  with **A** affords isomers **B** and **C**, both of which have benzene-like cyclic conjugated structures, so-called 'disilabenzenes' that contain a six-membered ring and can be formulated as  $(R^1-Si)_2(R^2-C)_4$ .



## $R^1-Si\equiv Si-R^1 + R^2-C\equiv C-R^2 \longrightarrow A \xrightarrow{R^2-C\equiv C-R^2} B + C$

The <sup>13</sup>C NMR analysis of the corresponding six-membered ring skeletons  $Si_2C_4$  shows two signals for **B** and one signal for **C**.

**A.1 Draw** the structural formulae of **A**, **B**, and **C** using R<sup>1</sup>, R<sup>2</sup>, Si, and C, with one of 9pt the possible resonance structures.



membered ring skeleton is drawn correctly. **D** S points. (2 points when the SI-SI-C-C-C-C sixmembered ring skeleton is drawn correctly. 1 point when 1,4- or 1,3-disilabenzene is depicted. 0 points when only the 1,4- or 1,3-disilabenzene is shown and  $R^1$  and  $R^2$  are drawn incorrectly.)**C**: 3 points: (2 points when the SI-C-C-SI-C-C six-membered ring skeleton is drawn correctly. 1 point when 1,2- or 1,3-disilabenzene is depicted. 0 points when only the 1,2- or 1,3-disilabenzene is shown and  $R^1$  and  $R^2$  are drawn incorrectly.)

**A.2** Calculate the aromatic stabilization energy (ASE) for benzene and **C** (in the case of  $R^1 = R^2 = H$ ) as positive values, considering the enthalpy change in some hydrogenation reactions of unsaturated systems shown below (Fig. 1).







The aromatic stabilization energy (ASE) can be calculated as the difference of the sum of the heat of hydrogenation of each double bond and the heat of hydrogenation of the aromatic compound. ASE for benzene:  $135 \times 3 - 173 = 232 \text{ kJ mol}^{-1}$ ASE for 1,4-disilabenzene (C=C + 2 Si=C):  $(135 + 213 \times 2) - 389 = 172 \text{ kJ mol}^{-1}$ 

# **7 points in total:** 3 points for ASE for benzene and 4 points for compound **C**. 3 points for the correct ASE value for benzene (2 points when the values have the correct magnitude but are negative.). 4 points for the correct ASE value for compound **C**, 1,4-disilabenzene. (3 points when the values have the correct magnitude but are negative.) (4 points for the ASE value for 1,2-disilabenzene $(206 + 135 \times 2) - 326 = 150 \text{ kJ mol}^{-1}$ or $(213 \times 2 + 135) - 326 = 235 \text{ kJ mol}^{-1}$ when the 1,2-disilabenzene is written as a structure of **C**. 4 points for the ASE value for 1,3-disilabenzene $(135 + 213 \times 2) - 368 = 193 \text{ kJ mol}^{-1}$ when the 1,3-disilabenzene is written as a structure of **C**.)

When a xylene solution of **C** is heated, it undergoes isomerization to give an equilibrium mixture of compounds **D** and **E**. The molar ratio is **D** : **E** = 1 : 40.0 at 50.0 °C and **D** : **E** = 1 : 20.0 at 120.0 °C.







$$\begin{aligned} \mathsf{T} &= \mathsf{50} \ ^\circ \mathsf{C} = \mathsf{323.15} \ \mathsf{K} \left( \frac{1}{RT} = 0.3722 \right) \colon K_{\mathsf{DE}} = 40 \\ \mathsf{T} &= \mathsf{120} \ ^\circ \mathsf{C} = \mathsf{393.15} \ \mathsf{K} \left( \frac{1}{RT} = 0.3095 \right) \colon K_{\mathsf{DE}} = 20 \\ \mathsf{According to } \ln \ K_{\mathsf{DE}} &= -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \\ \Delta H &= -\frac{\ln(K_{\mathsf{DE50}}) - \ln(K_{\mathsf{DE120}})}{\frac{1}{RT_{50}} - \frac{1}{RT_{120}}} = -\frac{\ln 40 - \ln 20}{0.3722 - 0.3059} = -10.5 \ \mathsf{kJ \, mol^{-1}} \\ \hline \mathbf{6} \ \mathsf{points:} \ (\mathsf{+4 \, points for the correct equation. -2 points for the positive value.}) \end{aligned}$$

The isomerization from **C** to **D** and to **E** proceeds via transformations of  $\pi$ -bonds into  $\sigma$ -bonds without breaking any  $\sigma$ -bonds. A <sup>13</sup>C NMR analysis revealed one signal for the Si<sub>2</sub>C<sub>4</sub> skeleton of **D** and two signals for that of **E**. The skeleton of **D** does not contain any three-membered rings, while **E** has two three-membered rings that share an edge.

**A.4 Draw** the structural formulae of **D** and **E** using R<sup>1</sup>, R<sup>2</sup>, Si, and C.

10pt





Based on the signals observed in the  $^{13}$ C NMR spectra, the following structures could be suggested for **D** and **E**:



In addition, considering that **D** has no three-membered ring in its skeleton while **E** has two threemembered rings that share an edge, the structures of **D** and **E** can be determined to be those shown below:



**10 points in total:** 5 points for each correct structure. (4 points for incorrect substituents R<sup>1</sup> or R<sup>2</sup>. 3 points for other candidates based on the information from the <sup>13</sup>C NMR spectra; 2 points for Si-regioisomers that would satisfy the <sup>13</sup>C NMR spectral information; 1 point for Si-regioisomers that would not satisfy the <sup>13</sup>C NMR spectral information.) For **D**: 2 points for other Dewer-benzene structure (because "not contain any three-membered rings"). For **E**: 2 points for other benzvalene structure (because "two three-membered rings that share an edge.").

#### Part B

Silicon is able to form highly coordinated compounds (> four substituents) with electronegative elements such as fluorine. As metal fluorides are often used as fluorination reagents, highly coordinated silicon fluorides also act as fluorination reagents.

The fluorination reaction of  $CCl_4$  using  $Na_2SiF_6$  was carried out as follows.

#### • Standardization of Na<sub>2</sub>SiF<sub>6</sub> solution :

 $\cdot$  Preparation

Aqueous solution **F**: 0.855 g of  $Na_2SiF_6$  (188.053 g mol<sup>-1</sup>) dissolved in water (total volume: 200 mL).

Aqueous solution **G**: 6.86 g of  $Ce_2(SO_4)_3$  (568.424 g mol<sup>-1</sup>) dissolved in water (total volume: 200 mL).

 $\cdot \ {\rm Procedure}$ 





Precipitation titration of a solution **F** (50.0 mL) by dropwise adding solution **G** in the presence of xylenol orange, which coordinates to  $Ce^{3+}$ , as an indicator. After adding 18.8 mL of solution **G**, the color of the solution changes from yellow to magenta. The generated precipitate is a binary compound that contains  $Ce^{3+}$ , and the only resulting silicon compound is  $Si(OH)_4$ .

D 1	Write the balanced equation	p for the reaction of N	No SiE with $Co(SO)$	Ent
D. I	write the balanced equality		$va_2 Sir_6 viii Ce_2(SO_4)$	3. JPL

 $\begin{aligned} \mathsf{Na}_2\mathsf{SiF}_6 &= 188.053 \text{ g mol}^{-1}. \text{ The concentration of } \mathsf{Na}_2\mathsf{SiF}_6 \text{ in solution } \mathbf{F} \text{ is} \\ \frac{0.855 \text{ g}}{200 \text{ mL}} &= \frac{4.548 \times 10^{-3} \text{ mol}}{0.2 \text{ L}} &= 2.274 \times 10^{-2} \text{ mol } \text{L}^{-1} (\mathbf{F}) \\ \mathsf{Ce}_2(\mathsf{SO}_4)_3 &= 568.424 \text{ g mol}^{-1}. \text{ The concentration of } \mathsf{Ce}_2(\mathsf{SO}_4)_3 \text{ in solution } \mathbf{G} \text{ is} \\ \frac{6.860 \text{ g}}{200 \text{ mL}} &= \frac{1.207 \times 10^{-2} \text{ mol}}{0.2 \text{ L}} &= 6.034 \times 10^{-2} \text{ mol } \text{L}^{-1} (\mathbf{G}) \\ \text{The concentration of } \mathsf{Ce}^{3+} \text{ ions in } \mathbf{G} \text{ is } 6.034 \times 10^{-2} \times 2 &= 1.207 \times 10^{-2} \text{ mol } \text{L}^{-1}. \\ \text{In 50.0 mL of solution } \mathbf{F}: 2.274 \times 10^{-2} \times \frac{50.0}{1000} &= 1.137 \times 10^{-3} \text{ mol of } \mathsf{Na}_2\mathsf{SiF}_6 \text{ was included}. \\ \text{In 18.8 mL of solution } \mathbf{G}: 6.034 \times 10^{-2} \times \frac{18.8}{1000} &= 1.134 \times 10^{-3} \text{ mol of } \mathsf{Ce}_2(\mathsf{SO}_4)_3 \text{ was included}. \\ \mathsf{Ars. Na}_2\mathsf{SiF}_6 \text{ should react with } \mathsf{Ce}_2(\mathsf{SO}_4)_3 \text{ in a 1:1 ratio.} \\ \mathsf{Ans. Na}_2\mathsf{SiF}_6 + \mathsf{Ce}_2(\mathsf{SO}_4)_3 + 4 \text{ H}_2\mathsf{O} &\to 2 \text{ CeF}_3 + \mathsf{Si}(\mathsf{OH})_4 + \mathsf{Na}_2\mathsf{SO}_4 + 2 \text{ H}_2\mathsf{SO}_4 \\ \end{array} \end{aligned}$ 

is written on the right side of the equation; +1 points when "Si(OH)<sub>4</sub>" is written on the right side of the equation.) Full mark for showing ionic compounds, which soluble in water as ions/ion pairs such as NaHSO<sub>4</sub>, Na<sup>+</sup>, H<sup>+</sup>, and etc. (The calculation procedure is not necessary.)

#### • Reaction of CCl<sub>4</sub>with Na<sub>2</sub>SiF<sub>6</sub>:

(Substance losses by *e.g.* evaporation are negligible during the following operations.)

Na<sub>2</sub>SiF<sub>6</sub>(*x* [g]) was added to CCl<sub>4</sub> (500.0 g) and heated to 300 °C in a sealed pressure-resistant reaction vessel. The unreacted Na<sub>2</sub>SiF<sub>6</sub> and generated NaCl were removed by filtration. The filtrate was diluted to a total volume of 1.00 L with CCl<sub>4</sub> (solution **H**). The <sup>29</sup>Si and <sup>19</sup>F NMR spectra of solution **H** showed SiF<sub>4</sub> as the only silicon compound. In the <sup>19</sup>F NMR spectrum, in addition to SiF<sub>4</sub>, signals corresponding to CFCl<sub>3</sub>, CF<sub>2</sub>Cl<sub>2</sub>, CF<sub>3</sub>Cl, and CF<sub>4</sub> were observed (*cf.* Table 1). The integration ratios in the <sup>19</sup>F NMR spectrum are proportional to the number of fluorine nuclei.

Table 1					
<sup>19</sup> F NMR data	CFCl <sub>3</sub>	CF <sub>2</sub> Cl <sub>2</sub>	CF <sub>3</sub> Cl	CF <sub>4</sub>	
Integration ratio	45.0	65.0	18.0	2.0	

 $SiF_4$  is hydrolyzed to form  $H_2SiF_6$  according to the following eq. 8:

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6 \tag{8}$$

Solution **H** (10 mL) was added to an excess amount of water, which resulted in the complete hydrolysis of SiF<sub>4</sub>. After separation, the  $H_2SiF_6$  generated from the hydrolysis in the aqueous solution was neutralized and completely converted to  $Na_2SiF_6$  (aqueous solution **J**).




The precipitate of unreacted Na<sub>2</sub>SiF<sub>6</sub> and NaCl, which was removed by filtration in the initial step (underlined), was completely dissolved in water to give an aqueous solution (solution K; 10.0 L).

Then, additional precipitation titrations using solution **G** were carried out, and the endpoints of the titrations with **G** were as follows:

·For solution J (entire amount): 61.6 mL.

·For 100 mL of solution K: 44.4 mL.

It should be noted here that the coexistence of NaCl or  $SiO_2$  has no effect on the precipitation titration.

**B.2 Calculate** the mass of the NaCl produced in the reaction vessel (information 15pt underlined), and <u>calculate</u> the mass (x [g]) of the Na<sub>2</sub>SiF<sub>6</sub> used as a starting material.

 $\underline{3}$  SiF<sub>4</sub> + 2 H<sub>2</sub>O  $\rightarrow$  SiO<sub>2</sub> +  $\underline{2}$  H<sub>2</sub>SiF<sub>6</sub>

The ratio of the consumed SiF<sub>4</sub> and the generated  $H_2SiF_6$  should be 3:2.

As Na<sub>2</sub>SiF<sub>6</sub> reacts with Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in a 1:1 ratio, the amount of SiF<sub>6</sub><sup>2-</sup> in the aqueous solution **J** is  $(6.034 \times 10^{-2} \text{ mol L}^{-1}) \times (61.6 \times 10^{-3} \text{ L}) = 3.717 \times 10^{-3} \text{ mol.}$  Considering the equation shown above,

10 mL of the diluted solution **H** contains  $3.717 \times 10^{-3}$  mol  $\times \frac{3}{2} = 5.576 \times 10^{-3}$  mol of SiF<sub>4</sub>. Thus, 1.00

L of diluted solution **H** contains  $5.576 \times 10^{-3}$  mol  $\times \frac{1000}{10} = 5.576 \times 10^{-1}$  mol of SiF<sub>4</sub>.

The amount of fluorine atoms that replace the chlorine atoms of CCl<sub>4</sub> should be twice the amount of SiF<sub>4</sub> formed during the reaction. Thus,  $2 \times 0.5576 = 1.115$  mol of F<sup>-</sup> should replace Cl<sup>-</sup> to result in the formation of NaCl. 1.115 mol  $\times$  58.44 g mol<sup>-1</sup> = 65.17 g of NaCl was formed. Ans.: 65.2 g (NaCl)

As Na<sub>2</sub>SiF<sub>6</sub> reacts with Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in a 1:1 ratio, the amount of SiF<sub>6</sub><sup>2-</sup> in 100 mL of aqueous solution K is  $44.4 \times 10^{-3}$  L  $\times (6.034 \times 10^{-2} \text{ mol L}^{-1}) = 2.679 \times 10^{-3}$  mol. Accordingly, the residual amount of Na<sub>2</sub>SiF<sub>6</sub> in 10.0 L of aqueous solution **K** is  $2.679 \times 10^{-3}$  mol  $\times \frac{10.0 \text{ L}}{100 \text{ mL}} = 0.2679$  mol. In total, the amount of Na<sub>2</sub>SiF<sub>6</sub> used as a starting material is  $(0.2679 \text{ mol} + 0.5576 \text{ mol}) \times 188.0 \text{ g mol}^{-1} = 155.2 \text{ g}$ Ans.: 155 g (Na<sub>2</sub>SiF<sub>6</sub>)

#### 15 points in total:

·10 points for the correct amount of NaCl:

- +3 points for the amount of SiF<sub>6</sub><sup>2-</sup> in solution J ( $3.717 \times 10^{-3}$  mol)
- +2 point for the amount of SiF<sub>4</sub> in 10 mL of the diluted solution **H** (5.576  $\times$  10<sup>-3</sup> mol)
- +2 point for the amount of SiF<sub>4</sub> in 1.00 L of the solution **H** (5.576  $\times$  10<sup>-1</sup> mol)
- +2 points for the amount of NaCl in mol (1.115mol)
- +1 point when the amount of NaCl is shown in gram.
- •5 points for the correct amount of Na<sub>2</sub>SiF<sub>6</sub>:
- +2 points for the amount of SiF<sub>6</sub><sup>2-</sup> in solution **K** (2.68 × 10<sup>-3</sup>mol) +1 point for the amount of SiF<sub>6</sub><sup>2-</sup> before dilution to prepare solution **K** (2.68 × 10<sup>-1</sup>mol)
- +1 point for the addition of the amount of SiF<sub>4</sub> in solution H (8.26  $\times$  10<sup>-1</sup>mol)
- +1 for answering the initial amount of  $Na_2SiF_6$  in [g].
  - **B.3** 77.8% of the CCl<sub>4</sub> used as a starting material was unreacted. Calculate the mass 8pt of CF<sub>3</sub>Cl generated.





500.0 g = 3.250 mol of CCl<sub>4</sub> was initially used as a starting material. Thus, the amount of the products that contain at least one F atom is 3.250 mol  $\times$  0.222 = 0.721 mol.

The ratio of integrals in the <sup>19</sup>F NMR spectrum is  $CFCl_3 : CF_2Cl_2 : CF_3Cl : CF_4 = 45.0 : 65.0 : 18.0 : 2.0. Thus, the mole ratio of these compounds should be <math>CFCl_3 : CF_2Cl_2 : CF_3Cl : CF_4 = 45.0 : 32.5 : 6.0 : 0.5 = 90 : 65 : 12 : 1. Accordingly, the amount of <math>CF_3Cl (104.46 \text{ g mol}^{-1})$  is  $0.721 \text{ mol} \times \frac{12}{90 + 65 + 12 + 1} = 0.0515 \text{ mol} = 0.0515 \times 104.46 \text{ g} = 5.38 \text{ g}$ Ans.: 5.38 g

**8 points:** (6 points for the answer in [mol]; 4 points for the correct molar ratio of substances  $CFCI_3 : CF_2CI_2 : CF_3CI : CF_4 = 90 : 65 : 12 : 1$ ).





## The Solid-State Chemistry of Transition Metals

				13	3 % of th	e total					
Question	A.1	A.2	A.3	B.1	B.2	B.3	B.4	C.1	C.2	C.3	Total
Points	6	3	3	6	4	4	4	5	5	5	45
Score											



Volcano at Sakurajima island

#### Part A

Japan is one of the countries with the highest numbers of volcanos worldwide. When silicate minerals crystallize from magma, a part of the transition-metal ions ( $M^{n+}$ ) in the magma is incorporated into the silicate minerals. The  $M^{n+}$  studied in the problem are coordinated by oxide ions ( $O^{2-}$ ) and adopt a four-coordinate tetrahedral ( $T_d$ ) geometry in the magma and six-coordinate octahedral ( $O_h$ ) geometry in the silicate minerals, both of which exhibit a high-spin electron configuration. The distribution coefficient of  $M^{n+}$  between the silicate minerals and magma, D, can be expressed by:

$$D = \frac{[M]_{s}}{[M]_{l}}$$

where  $[M]_s$  and  $[M]_l$  are the concentrations of  $M^{n+}$  in the silicate minerals and the magma, respectively. The table below shows the D values of  $Cr^{2+}$  and  $Mn^{2+}$  as examples.

	Cr2+	Mn <sup>2+</sup>
D	7.2	1.1





Let  $\Delta_0$  and CFSE<sup>O</sup> be the energy separation of the d-orbitals of M<sup>n+</sup> and the crystal-field stabilization energy in a  $O_h$  field, respectively. Let  $\Delta_T$  and CFSE<sup>T</sup> be those in a  $T_d$  field.

**A.1** <u>**Calculate**</u>  $|CFSE^O - CFSE^T| = \Delta CFSE$  in terms of  $\Delta_O$  for  $Cr^{2+}$ ,  $Mn^{2+}$ , and  $Co^{2+}$ ; 6pt assume  $\Delta_T = 4/9\Delta_O$ .

The d-orbitals of a six-coordinate octahedral complex split into two groups  $e_g (d_{x^2-y^2}, d_{z^2})$ , and  $t_{2g} (d_{xy}, d_{yz}, d_{zx})$  with an energy separation of  $\Delta_0$ . The energies of the  $e_g$  and  $t_{2g}$  orbitals relative to the barycenter are +0.60 $\Delta_0$  and -0.40 $\Delta_0$ , respectively. Likewise, the d-orbitals of a four-coordinate tetrahedral complex split into two groups  $t_2 (d_{xy}, d_{yz}, d_{zx})$  and  $e (d_{x^2-y^2}, d_{z^2})$  with an energy separation of  $\Delta_T$ . The energies of the  $t_2$  and e orbitals relative to the barycenter are +0.40 $\Delta_T$  and -0.60 $\Delta_T$ , respectively. Therefore, in the case of a high-spin electron configuration, CFSE<sup>O</sup> and CFSE<sup>T</sup> for Cr<sup>2+</sup> (3d<sup>4</sup> :  $t_{2g}^{3}e_{g}^{1}$  or  $e^{2}t_{2}^{2}$ ) are -0.60 $\Delta_0$  and -0.40 $\Delta_T$  (= -0.18 $\Delta_0$ ), respectively. CFSE<sup>O</sup> and CFSE<sup>T</sup> for Mn<sup>2+</sup> (3d<sup>5</sup> :  $t_{2g}^{3}e_{g}^{2}$  or  $e^{2}t_{2}^{3}$ ) are both zero. CFSE<sup>O</sup> and CFSE<sup>T</sup> for Co<sup>2+</sup> (3d<sup>7</sup> :  $t_{2g}^{4}e_{g}^{3}$  or  $e^{4}t_{2}^{3}$ ) are -0.80 $\Delta_0$  and -1.2 $\Delta_T$  (= -0.53 $\Delta_0$ ), respectively. Accordingly, |CFSE<sup>O</sup>-CFSE<sup>T</sup>| =  $\Delta$ CFSE values for each metal ion are,  $Cr^{2+}$ :  $|-0.60\Delta_0 - (-0.18\Delta_0)| = 0.42\Delta_0$ , Mn<sup>2+</sup>: <u>0</u>, Co<sup>2+</sup>:  $|-0.80\Delta_0 - (-0.53\Delta_0)| = 0.27\Delta_0$ 

**6 points in total:** 2 points each for ΔCFSE of the three divalent metal ions.

**A.2** A linear relationship is observed by plotting  $\ln D$  against  $\Delta CFSE / \Delta_0$  in the Carte- 3pt sian coordinate system shown below. **Estimate** D for  $Co^{2+}$ .







The coordinates of Mn<sup>2+</sup> and Cr<sup>2+</sup> are (0, 0.095) and (0.42, 1.97), respectively. The linear regression line calculated from these coordinates would be y = 4.46x + 0.100  $\Delta$ CFSE of Co<sup>2+</sup> is  $0.27\Delta_0$ Therefore,  $D = \exp(4.46 \times 0.27 + 0.100) = 3.68 (= 3.7)$ 

Whether the graph is drawn does not affect grading. If the coordinates of  $Mn^{2+}$  and  $Cr^{2+}$  are correctly plotted and the *D* is estimated with guide of the graph, full mark is given.



**3 points** for the calculation of *D*.

Partial credit of 2 points if the  $\ln D$  is correctly estimated from the linear regression line or the graph. If the intercept of the linear regression line is assumed as zero (i.e.,  $Mn^{2+}$  is at the origin of the coordinate), full mark is given.

In order to avoid double punishment with A.1: If the answers of A.1 were wrong but the coordinates of  $Mn^{2+}$  and  $Cr^{2+}$  are correctly plotted in the graph (or simultaneous equations are given) according to the answers of A.1, and D of  $Co^{2+}$  is correctly estimated from lnD assuming a linear relationship, full mark is given.

Metal oxides MO (M: Ca, Ti, V, Mn, or Co) crystallize in a rock-salt structure wherein the  $M^{n+}$  adopts an  $O_h$  geometry with a high-spin electron configuration. The lattice enthalpy of these oxides is mainly governed by the Coulomb interactions based on the radius and charge of the ions and some contributions from the CFSE of  $M^{n+}$  in the  $O_h$  field.





	CaO	TIO	vo	MnO	CoO
(a)	3460	3878	3913	3810	3916
(b)	3460	3916	3878	3810	3913
(c)	3460	3913	3916	3810	3878
(d)	3810	3878	3913	3460	3916
(e)	3810	3916	3878	3460	3913
(f)	3810	3913	3916	3460	3878

The lattice enthalpy is determined by the Coulomb interactions, which are proportional to the product of the valences of the constituent ions and inversely proportional to the sum of the ionic radii. As the target compounds are oxides of divalent metal ions, we should consider the ionic radii of the metal ions. The radii of divalent metal ions within the same period decrease with increasing atomic number. Let us compare the lattice enthalpies of CaO and MnO with no contribution from the CFSE: The ionic radius of  $Mn^{2+}$  is smaller than that of  $Ca^{2+}$ , and therefore, the lattice enthalpy is higher for MnO. So, the participants should choose (a), (b), or (c). Then, let us compare the lattice enthalpies of TiO (d<sup>2</sup>) and VO (d<sup>3</sup>): The ionic radius of V<sup>2+</sup> is smaller than that of Ti<sup>2+</sup>, and the CFSE is higher for VO than for TiO. Accordingly, the lattice enthalpy is also higher for VO. Based on these observations, the answer should be (a) or (c). Finally, let us compare the lattice enthalpies of TiO (d<sup>2</sup>) and CoO (d<sup>7</sup>): The ionic radius of Co<sup>2+</sup> is smaller than that of Ti<sup>2+</sup>, while their CFSEs are equal. Thus, the lattice enthalpy is higher for CoO. Thus, the correct answer is (a). Partial credit is given for (b) and (c).

**3 points** for the correct answer (a). Partial credit of 2 points for (c) and 1 point for (b).

#### Part B

A mixed oxide **A**, which contains La<sup>3+</sup> and Cu<sup>2+</sup>, crystallizes in a tetragonal unit cell shown in Fig.1. In the  $[CuO_6]$  octahedron, the Cu–O length along the *z*-axis ( $l_z$ ) is longer than that of the *x*-axis ( $l_x$ ), and  $[CuO_6]$  is distorted from the regular  $O_h$  geometry. This distortion removes the degeneracy of the  $e_g$  orbitals  $(d_{x^2-y^2} \text{ and } d_{z^2})$ .







Fig. 1

**A** can be synthesized by thermal decomposition (pyrolysis) of complex **B**, which is formed by mixing metal chlorides in dilute aqueous ammonia solution containing squaric acid  $C_4H_2O_4$ , i.e., a diacid. The pyrolysis behavior of **B** in dry air shows a weight loss of 29.1% up to 200 °C due to the loss of crystallization water, followed by another weight loss up to 700 °C due to the release of  $CO_2$ . The total weight loss during the formation of **A** from **B** is 63.6%. It should be noted that only water and  $CO_2$  are released in the pyrolysis reaction.

The unit cell shown in Fig. 1 contains four La<sup>3+</sup>, two Cu<sup>2+</sup>, and eight O<sup>2-</sup> ions. Therefore, **A**: La<sub>2</sub>CuO<sub>4</sub>. As the formula weight of La<sub>2</sub>CuO<sub>4</sub> is 405.3, that of **B** should be 1113.5 considering the following equation: 405.3 ÷ (1 – 0.636). Given that the weight loss due to crystallization water is 29.1%, the number of molecules of crystallization water is 18.00 considering the following equation: (1113.5 × 0.291) ÷ 18 (18H<sub>2</sub>O; M = 324). Complex **B** is a trinuclear complex that consists of two La<sup>3+</sup> and one Cu<sup>2+</sup> ions. Considering that the synthetic solution is basic, the squaric acid is deprotonated and coordinates to the metal ion as C<sub>4</sub>O<sub>4</sub><sup>2-</sup>. The number of squaric acid molecules is 4.00 based on the following equation: (1113.5 – 138.9 × 2 – 63.5 – 324) ÷ 112 (C<sub>4</sub>O<sub>4</sub><sup>2-</sup>; M = 112). B: La<sub>2</sub>Cu(C<sub>4</sub>O<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>18</sub> (La<sub>2</sub>CuC<sub>16</sub>O<sub>34</sub>H<sub>36</sub>)

**6 points in total** (2 and 4 points for **A** and **B**, respectively). Partial credit of 2 points for the correct number of crystallization water  $(La_2Cu(H_2O)_{18})$  for **B**. (full marks are also given for **A**:  $La_4Cu_2O_8$  and **B**:  $La_4Cu_2(C_4O_4)_8(H_2O)_{36}$  ( $La_4Cu_2C_{32}O_{68}H_{72}$ ), which correspond to the numbers of elements in the unit cell)

B.2	<u>Calculate</u> $l_x$	and $l_z$	using	Fig.	1.
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 $l_x$ : 0.3833 ÷ 2 = 0.1917 (= 0.192 nm).  $l_z$ : (1.3313 – 0.2520 × 2) ÷ 4 = 0.2068 (= 0.207 nm)

**4 points in total** (2 points for each correct answer).

**B.3** For  $Cu^{2+}$  in the distorted  $[CuO_6]$  octahedron in **A** of Fig. 1, <u>write</u> the names of the 4pt split  $e_g$  orbitals  $(d_{x^2-y^2}$  and  $d_{z^2})$  in (i) and (ii), and <u>draw</u> the electron configuration in the dotted box in your answer sheet.

(i)  $\mathsf{d}_{x^2-y^2}$  , (ii)  $\mathsf{d}_{z^2}$ 



4 points in total: 2 points for the correct names of the orbitals in (i) and (ii), and 2 points for the correct electron configuration in the dotted box. Full mark is given even spin up and down directions of the electrons are not shown (the electrons can be shown in arrows, lines, circles etc.).

**A** is an insulator. When one La<sup>3+</sup> is substituted with one Sr<sup>2+</sup>, one hole is generated in the crystal lattice that can conduct electricity. As a result, the Sr<sup>2+</sup>-doped **A** shows superconductivity below 38 K. When a substitution reaction took place for **A**,  $2.05 \times 10^{27}$  holes m<sup>-3</sup> were generated.

**B.4** Calculate the percentage of  $Sr^{2+}$  substituted for  $La^{3+}$  based on the mole ratio 4pt in the substitution reaction. Note that the valences of the constituent ions and the crystal structure are not altered by the substitution reaction.

The corresponding reaction equation, where the amount of  $Sr^{2+}$  is x%, is:  $La_2CuO_4 + (2x/100)Sr^{2+} \rightarrow [La_{2(1-x/100)}Sr_{(2x/100)}CuO_4]^{(2x/100)-} + (2x/100)La^{3+}$ The charge of  $[La_{2(1-x/100)}Sr_{(2x/100)}CuO_4]$  is negative, and the amount of doped holes is  $(2x/100)h^+$ per mole. The volume of the unit cell is  $0.3833^2 \times 1.3313 = 0.1956$  nm<sup>3</sup>. The unit cell contains four  $La^{3+}$ , two  $Cu^{2+}$ , and eight  $O^{2-}$  ions, i.e., the unit contains two  $La_2CuO_4$ . Accordingly, the number of holes per unit cell is (4x/100). Since the concentration of holes is the number of holes divided by the unit cell volume, the following equation is satisfied:  $(4x/100)/(0.1956 \times 10^{-27}) = 2.05 \times 10^{-27}$ , x = 10%Alternative answer without giving the substitution reaction; density of  $La^{3+}$  in the unit cell  $4/(0.3833^2 \times 1.3313) = 20.45$  nm<sup>-3</sup> Density of holes in the unit cell is 2.05 nm<sup>-3</sup> Therefore, the percentage of substitution is  $2.05/20.45 \times 100 = 10\%$ 

partial credit of 1 point for 20% (forgetting that the unit cell contains two  $La_2CuO_4$ ).





#### Part C

 $Cu_2(CH_3CO_2)_4$  is composed of four  $CH_3CO_2^-$  coordinated to two  $Cu^{2+}$  (Fig. 2A).  $Cu_2(CH_3CO_2)_4$  exhibits high levels of structural symmetry, with two axes passing through the carbon atoms of the four  $CH_3CO_2^$ and an axis passing through the two  $Cu^{2+}$ , all of which are oriented orthogonal relative to each other. When a dicarboxylate ligand is used instead of  $CH_3CO_2^-$ , a "cage complex" is formed. The cage complex  $Cu_4(L1)_4$  is composed of planar dicarboxylate L1 (Fig. 2B) and  $Cu^{2+}$  (Fig. 2C). The angle  $\theta$  between the coordination directions of the two carboxylates, indicated by the arrows in Fig. 2B, determines the structure of the cage complex. The  $\theta$  is 0° for L1. Note that hydrogen atoms are not shown in Fig. 2.



**C.1** The  $\theta$  of the planar dicarboxylate **L2** below is fixed to 90°. If the composition 5pt of the cage complex formed from **L2** and Cu<sup>2+</sup> is Cu<sub>n</sub>(**L2**)<sub>m</sub>, **give** the smallest integer combination of *n* and *m*. Assume that only the CO<sub>2</sub><sup>-</sup> groups of **L2** form a coordination bond to Cu<sup>2+</sup> ions.









A zinc complex,  $Zn_4O(CH_3CO_2)_6$ , contains four tetrahedral  $Zn^{2+}$ , six  $CH_3CO_2^{-}$ , and one  $O^{2-}$  (Fig. 3A). In  $Zn_4O(CH_3CO_2)_6$ , the  $O^{2-}$  is located at the origin, and the three axes passing through the carbon atoms of  $CH_3CO_2^{-}$  are oriented orthogonal relative to each other. When *p*-benzenedicarboxylate (Fig. 3B, **L3**,  $\theta$  = 180°) is used instead of  $CH_3CO_2^{-}$ , the  $Zn^{2+}$  clusters are linked to each other to form a crystalline solid (**X**) that is called a "porous coordination polymer" (Fig. 3C). The composition of **X** is  $[Zn_4O(L3)_3]_n$ , and it has a cubic crystal structure with nano-sized pores. One pore is represented as a sphere in Fig. 3D, and each tetrahedral  $Zn^{2+}$  cluster is represented as a dark gray polyhedron in Fig. 3C and 3D. Note that hydrogen atoms are not shown in Fig. 3.



**C.2 X** has a cubic unit cell with a side length of *a* (Fig. 3C) and a density of 0.592 5pt  $g \text{ cm}^{-3}$ . **Calculate** *a* in [cm].

The molecular weight of Zn<sub>4</sub>O(**L3**)<sub>3</sub> is 770. According to Figure 3C, there are eight Zn<sub>4</sub>O(**L3**)<sub>3</sub> units in the unit cell. Therefore, the molecular weight per unit cell can be calculated as 770 × 8 = 6160. The weight of the unit cell is  $6160 \div N_{\rm A} = 1.02 \times 10^{-20}$  g Let the length of the side of the unit cell be *a* [cm], then,  $(1.02 \times 10^{-20})$  g /  $a^3$  [cm<sup>3</sup>] = 0.592 g cm<sup>-3</sup>.  $a = 2.6 \times 10^{-7}$  cm

#### 5 points in total.

Partial credit of 3 points for the correct formulation to derive the molecular weight of the unit cell; 2 points for the correct value of *a*.

**C.3** X contains a considerable number of pores, and 1 g of X can accommodate 5pt  $3.0 \times 10^2$  mL of CO<sub>2</sub> gas in the pores at 1 bar and 25 °C. <u>Calculate</u> the average number of CO<sub>2</sub> molecules per pore.





#### There is one pore per Zn<sub>4</sub>O(L3)<sub>3</sub> unit. Number of pores [mol] per 1 [g] of X: 1 [g] / 770 = 0.00130. Based on the ideal gas equation, $3.0 \times 10^2$ [mL] of adsorbed CO<sub>2</sub> corresponds to: $(1 \times 10^5$ [Pa] × $3.0 \times 10^{-4}$ [m<sup>3</sup>]) / (8.31 × 298 [K]) = 0.0121 [mol] of CO<sub>2</sub>. Therefore, 0.0121 ÷ 0.00130 = <u>9.3 molecules</u> of CO<sub>2</sub> per pore.

#### 5 points in total.

Partial credit of 3 points for the correct formulation to calculate the number of pores in 1 g; 2 points for the correct calculation of the number of molecules of  $CO_2$  per pore.





## **Playing with Non-benzenoid Aromaticity**

13 % of the total						
Question	A.1	A.2	A.3	B.1	Total	
Points	5	2	19	10	36	
Score						

Prof. Nozoe (1902–1996) opened the research field of non-benzenoid aromatic compounds, which are now ubiquitous in organic chemistry.



Photo courtesy: Tohoku Univ.

#### Part A

Lineariifolianone is a natural product with a unique structure, which was isolated from *Inula linariifolia*. From valencene (1), a one-step conversion yields **2**, before a three-step conversion via **3** yields ketone **4**. Eremophilene (**5**) is converted into **6** by performing the same four-step conversion.







Inula linariifolia



**A.1 Draw** the structures of **2** and **6** and clearly identify the stereochemistry where 5pt necessary.







Then, ketone **4** is converted into ester **15**. Compound **8** (molecular weight: 188) retains all the stereocenters in **7**. Compounds **9** and **10** have five stereocenters and no carbon-carbon double bonds. Assume that  $H_2^{18}O$  is used instead of  $H_2^{16}O$  for the synthesis of <sup>18</sup>O-labelled-lineariifolianones **13** and **14** from **11** and **12**, respectively. Compounds **13** and **14** are <sup>18</sup>O-labelled isotopomers. Ignoring isotopic labelling, both **13** and **14** provide the same product **15** with identical stereochemistry.













essary. Also, <u>indicate</u> the introduced <sup>18</sup>O atoms for **13** and **14** as shown in the example below.





Q7-6 English (Official)







#### 8 (3 pt in total):

-1 pt each for missing one double bond or drawing an allene instead of an alkyne,

0 pt for incorrect planar structure,

- -2 pt for an opposite stereochemistry next to the alkyne,
- -2 pt for other stereochemistry errors.

#### 9–12 (2 pt each, 8 pt in total):

-1 pt each for missing atoms (e.g., fluorine atom, oxygen of epoxide),
-1 pt for stereochemistry error,
Two sets of compounds 9, 11, 13 and 10, 12, 14 are interconvertible,

#### Structures of 13 and 14/<sup>18</sup>O labelling on hydroxy groups of 13 and 14 (3 pt each, 6 pt in total):

-1 pt each for incorrect or unclear <sup>18</sup>O labelling on the diol moiety,
-1 pt each for incomplete transformation (diol only, ketone only),
0 pt for incorrect planar structure other than the above,

-2 pt for stereochemistry error.

<sup>18</sup>O labelling on carbonyl group of 13 and 14 (1 pt each, 2 pt in total):

0 pt when <sup>18</sup>O is incorporated in the carbonyl group of neither **13** nor **14**.





#### Part B

Compound **19** is synthesized as shown below. In relation to non-benzenoid aromaticity, **19** can be used as an activator for alcohols, and **20** was converted to **22** via ion-pair intermediate **21**. Although the formation of **21** was observed by NMR, **21** gradually decomposes to give **18** and **22**.



**B.1 Draw** the structures of **17–19** and **21**. Identifying the stereochemistry is not 10pt necessary.



Q7-9 English (Official)



-1 pt when the alkoxide and chlorocyclopropenium are given.





## **Dynamic Organic Molecules and Their Chirality**

11 % of the total						
Question	A.1	A.2	A.3	B.1	B.2	Total
Points	9	3	7	3	4	26
Score						

#### Part A

Polycyclic aromatic hydrocarbons with successive ortho-connections are called [n]carbohelicenes (here, n represents the number of six-membered rings) (see below). [4]Carbohelicene ([4]C) is efficiently prepared by a route using a photoreaction as shown below, via an intermediate (Int.) that is readily oxidized by iodine.



The photoreaction proceeds in a manner similar to the following example.







## Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated $\pi$ systems.

	A (3 pt)	<b>B</b> (3 pt)	<b>C</b> (3 pt)			
<ul> <li>points each. When B and C are reversed, give 1 point each. When missing double bonds in B and , -1 point each.</li> <li>B is blank and C is the trans-isomer (i.e. B), give 2 points for C.</li> <li>I point for each "circled" answer (this is applied for all the following questions in Q8)</li> <li>A.2 Attempts to synthesize [5]carbohelicene from the same phosphonium salt and 3pt an appropriate starting compound resulted in the formation of only a trace</li> </ul>						











[5]- and larger [n]carbohelicenes have helical chirality and interconversion between enantiomers of these helicenes is significantly slow at room temperature. The chirality of [n]carbohelicenes is defined as (*M*) or (*P*) as shown below.



[n]Carbohelicenes with n larger than 4 can be enantiomerically separated by a chiral column chromatography, which was developed by Prof. Yoshio Okamoto.



Photo courtesy: The Japan Prize Foundation

Multiple helicenes are molecules that contain two or more helicene-like structures. If its helical chirality is considered, several stereoisomers exist in a multiple helicene. For example, compound **E** contains three [5]carbohelicene-like moieties in one molecule. One of the stereoisomers is described as (P, P, P) as shown below.









**A.3** The nickel-mediated trimerization of 1,2-dibromobenzene generates triphenylene. When the same reaction is applied to an enantiomer of **F**, (*P*)-**F**, multiple helicene **G** ( $C_{66}H_{36}$ ) is obtained. Given that interconversion between stereoisomers does not occur during the reaction, **identify all** the possible stereoisomers of **G** formed in this process, without duplication. As a reference, one isomer should be drawn completely with the chirality defined as in the example above, with numerical labels; the other stereoisomers should be listed with location numbers and *M* and *P* labels according to the same numbering. For instance, the other stereoisomers of **E** should be listed as (1, 2, 3) = (*P*, *M*, *P*), (*P*, *M*, *M*), (*P*, *P*, *M*), (*M*, *M*, *M*), (*M*, *P*, *P*), and (*M*, *P*, *M*).



(*P*)-F







0 points if no representative structure is drawn.





#### Part B

Sumanene is a bowl-shaped hydrocarbon that was first reported in Japan in 2003. The name "sumanene" derives from a Sanskrit-Hindi word "suman" that means sunflower. The synthesis of sumanene was achieved by a reaction sequence that consists of a ring-opening and a ring-closing metathesis.



Representative metathesis reactions catalyzed by a ruthenium catalyst (Ru\*) are shown below.



#### **B.1 Draw** the structure of intermediate **I** (its stereochemistry is not required).

3pt











**B.2** Starting from the optically active precursor **J**, the same reaction sequence gives 4pt the optically active sumanene derivative **K**. The stereocenters in **J** suffer no inversion during the metathesis reaction. **Draw** the structure of **K** with the appropriate stereochemistry.







## Likes and Dislikes of Capsule

10 % of the total						
Question	A.1	A.2	A.3	A.4	A.5	Total
Points	13	2	2	3	3	23
Score						

Good kids don't do this, but if you unseam a tennis ball, you can disassemble it into two U-shaped pieces.



Based on this idea, compounds **1** and **2** were synthesized as U-shaped molecules with different sizes. Compound **3** was prepared as a comparison of **1** and the encapsulation behavior of these compounds was investigated.







The synthetic route to **2** is shown below. The elemental composition of compound **9**: C; 40.49%, H; 1.70%, and O; 17.98% by mass.







# **A.1 Draw** the structures of **4–9**; the stereochemistry can be neglected. Use "PMB" 13pt as a substituent instead of drawing the whole structure of *p*-methoxybenzyl group shown in the scheme above.







In the mass spectrum of **1**, the ion peak corresponding to its dimer  $(\mathbf{1}_2)$  was clearly observed, whereas





an ion peak for  $\mathbf{3}_2$  was not observed in the spectrum of **3**. In the <sup>1</sup>H NMR spectra of a solution of  $\mathbf{1}_2$ , all the NH protons derived from **1** were observed to be chemically equivalent, and their chemical shift was significantly different from that of the NH protons of **3**. These data indicate that hydrogen bonds are formed between the NH moieties of **1** and atoms **X** of another molecule of **1** to form the dimeric capsule.



8 (because 8 NH protons were observed equally in the <sup>1</sup>H NMR spectrum of the dimer.) 2 points for the correct answer.

The dimeric capsule of **1** ( $\mathbf{1}_2$ ) has an internal space wherein an appropriate small molecule Z can be encapsulated. This phenomenon is expressed by the following equation:

$$\mathsf{Z} + \mathbf{1}_2 \to \mathsf{Z} @ \mathbf{1}_2 \tag{1}$$

The equilibrium constant of the encapsulation of Z into  $\mathbf{1}_2$  is given as below:

$$K_{\mathsf{a}} = \frac{[\mathsf{Z}@\mathbf{1}_2]}{[\mathsf{Z}][\mathbf{1}_2]} \tag{2}$$

Encapsulation of a molecule into a capsule could be monitored by NMR spectroscopy. For example,  $1_2$  in C<sub>6</sub>D<sub>6</sub> gave different signals in the <sup>1</sup>H NMR spectra before and after addition of CH<sub>4</sub>.

Compound **2** also forms a rigid and larger dimeric capsule ( $2_2$ ). The <sup>1</sup>H NMR spectrum of  $2_2$  was measured in C<sub>6</sub>D<sub>6</sub>, C<sub>6</sub>D<sub>5</sub>F, and a C<sub>6</sub>D<sub>6</sub>/C<sub>6</sub>D<sub>5</sub>F solvent mixture, with all other conditions being kept constant. The chemical shifts for the H<sup>a</sup> proton of **2** in the above solvents are summarized below, and no other signals from the H<sup>a</sup> in **2**, except for the listed, were observed. Assume that the interior of the capsule is always filled with the largest possible number of solvent molecules and that each signal corresponds to one species of the filled capsule.







solvent	$\delta$ (ppm) of H <sup>a</sup>
C <sub>6</sub> D <sub>6</sub>	4.60
C <sub>6</sub> D <sub>5</sub> F	4.71
C <sub>6</sub> D <sub>6</sub> / C <sub>6</sub> D <sub>5</sub> F	4.60, 4.71, 4.82

**A.4 Determine** the number of  $C_6D_6$  and  $C_6D_5F$  molecules encapsulated in  $2_2$  giving 3pt each H<sup>a</sup> signal.

1 point for the correct number of encapsulated  $C_6D_6$  and  $C_6D_5F$  molecules for each NMR signal.

$\delta$ (ppm) of H <sup>a</sup>	numbers of C <sub>6</sub> D <sub>6</sub>	numbers of C <sub>6</sub> D <sub>5</sub> F
4.60 ppm	2	0
4.71 ppm	0	2
4.82 ppm	1	1

The observation of the third signal in the mixed solvent indicates that two solvent molecules are initially encapsulated in the capsule. Thus, the signal at 4.82 ppm is ascribed to a capsule containing one molecule of  $C_6 D_6$  and one molecule of  $C_6 D_5 F$ .

<sup>1</sup>H NMR measurements in  $C_6D_6$  revealed that  $2_2$  can incorporate one molecule of 1-adamantanecarboxylic acid (AdA), and the association constants ( $K_a$ ) which are expressed below were determined for various temperatures. [solvent@ $2_2$ ] denotes a species containing one or more solvent molecules.

$$K_{\mathsf{a}} = \frac{[\mathsf{Z}@\mathbf{2}_2]}{[\mathsf{Z}][\mathsf{solvent}@\mathbf{2}_2]} \tag{3}$$

Similarly, the  $K_a$  values of CH<sub>4</sub> and  $1_2$  given as eq (2) at various temperatures in C<sub>6</sub>D<sub>6</sub> were also determined by <sup>1</sup>H NMR measurements. The plots of the two association constants (as ln  $K_a$  vs 1/*T*) are shown below.


No  $C_6D_6$  molecule is encapsulated in  $1_2$ . In line **II**, the entropy change ( $\Delta S$ ) is (1) and enthalpy change ( $\Delta H$ ) is (2), indicating that the driving force for the encapsulation in line **II** is (3). Therefore, line **I** corresponds to (4), and line **II** corresponds to (5).

A.5 <u>Choo</u> and	<b>ose</b> the correct B.	options in gaps (1)–(5) in	the following paragraph fro	om A 3pt	
		Α	В	]	
	(1)	positive	negative		
	(2)	positive	negative		
	(3)	$\Delta S$	$\Delta H$		
	(4)	$1_2$ and $CH_4$	$2_2$ and AdA		
	(5)	$1_2$ and $CH_4$	$2_2$ and AdA		
				-	
(1): A(2): A(3): A(4): A(5): B3 points in total2 points for correct answers for (1)-(3).1 point for correct answers for (4) and (5).No points when the former part ((1)-(3)) is incorrect even if the latter part ((4) and (5)) is correct.					
Transforming J $\ln K_a = -\frac{\Delta H}{RT}$ (If $\Delta H$ is negatThe relationshithe two compo0), indicating thplot with a posiTherefore, theThis is due to tcapsulation of o	$\Delta G = -RT \ln K$ $+ \frac{\Delta S}{R}$ ive, the slope is p between 1 <sub>2</sub> a nents become nat the enthalpy itive slope and plot with a neg- he release of the one molecule of	$T_a = \Delta H - T\Delta S$ gives s positive; if the y-intercept nd CH <sub>4</sub> is that the entropy one component. Neverthel y change is exothermic and a negative y-intercept for 1 gative slope ( $\Delta H > 0$ ) and p he two molecules of C <sub>6</sub> D <sub>6</sub> to f AdA.	is negative, $\Delta S$ is negative. change is unfavorable ( $\Delta S$ ess, the encapsulation of Cl favorable ( $\Delta H$ < 0). This re and CH <sub>4</sub> . positive y-intercept ( $\Delta S$ > 0 hat were initially encapsula	) I < 0) given that $H_4$ occurs ( $\Delta G <$ esult indicates a ) is $2_2$ and AdA. ted and the en-	

# Reference

## **Practical Tasks**

The 53rd International Chemistry Olympiad, IChO 2021 Japan, was held remotely, unfortunately we were not able to do the practical exams.

In order to reinforce the importance of laboratory work, the practical tasks prepared for the 53rd IChO 2021 Japan were made open, despite not being officially approved by the International Jury meeting for the 53rd IChO 2021 Japan.

We prepared videos in which all tasks were demonstrated with explanations and published the videos as one of the activities during the 53rd IChO 2021 Japan. We hope that many of you will take up the challenge of the practical tasks.

Practical Task 1. Partition coefficient of 2,5-furandicarboxylic acid in a 1octanol/water system

'Biomass chemistry' is attracting attention as a strategy to break away from the oildependence of human society. Furan derivatives are plant-derived chemicals that can be used as building blocks for new materials. They are made from furfural, which can be easily synthesized from agricultural waste containing sugars. One furan derivative, 2,5furandicarboxylic acid, has been extensively studied as a raw material for bioplastics. When using a new material, it is essential to elucidate the effects of the chemical on the human body, animals, and plants. It is known that the accumulation of a chemical in living organisms is related to its hydrophobicity. The 1-octanol/water partition coefficient is one

of the best indicators of hydrophobicity/hydrophilicity. The purpose of this experiment is to calculate the partition coefficient of 2,5-

furandicarboxylic acid in a 1-octanol/water system by examining the 2,5-furandicarboxylic acid concentrations in the 1-octanol phase and the aqueous phase and analyzing its aggregation state in 1-octanol.



Substance	Name	State	GHS Hazard Statement
C <sub>6</sub> H <sub>4</sub> O <sub>5</sub>	2,5-Furandi-	1-Octanol	H319
	carboxylic acid	Solution	
		(0.020	
		$mol L^{-1}$ )	
C <sub>8</sub> H <sub>17</sub> OH	1-Octanol	Liquid	H319, H412
NaCl	Sodium chloride	Aqueous	NA
		solution	
		(10%)	
NaOH	Sodium	Aqueous	H290, H314
	hydroxide	solution	
		(ca. 0.01	
		mol L <sup>-1</sup> ) *	
$C_{20}H_{14}O_{4}$	Phenolphthalein	Ethanol	H226, H320
		solution	

Chemicals

\*Exact concentration will be shown at the examination.

**Glassware and Equipment** 

- 2 Volumetric flasks, 100 mL
- 2 Pipettes
- 1 Silicone dropper
- 3 Erlenmeyer flasks with stopper, 100 mL
- 4 Volumetric pipettes, 20 mL
- 3 Volumetric pipettes, 10 mL
- 1 Pipettor
- 1 Laboratory stand with burette clamp
- 1 Burette, 25 mL
- 1 Funnel
- 3 Conical beakers, 50 mL
- 1 Magnetic stirrer
- 1 Stirrer bar

For the procedure "Taking an Aliquot of Aqueous Phase B"

- 3 Pipettes
- 3 Beakers, 50 mL

## Procedure

- Transfer two 20 mL portions of 0.020 mol L<sup>-1</sup> 2,5-furandicarboxylic acid solution (Solution A) to a 100 mL volumetric flask (total volume: 40 mL). Fill the flask with 1-octanol using a pipette. Homogenize the solution, which is henceforth called Solution B.
- Transfer 20 mL of Solution A to another 100 mL volumetric flask (total volume: 20 mL). Fill the flask and homogenize the solution as above. This solution is called Solution C.
- 3. **Transfer** two 20 mL portions of **Solutions A**, **B**, and **C** to 100 mL Erlenmeyer flasks with stoppers (total volume: 40 mL each).
- 4. Add two 20 mL portions of 10% aqueous NaCl solution to each Erlenmeyer flask (total volume of the aqueous solution: 40 mL). Seal the Erlenmeyer flasks.
- 5. Hold each Erlenmeyer flask firmly so that the stopper does not come off, shake it vertically 30 times, and let it stand for 5 minutes. Shake the flask and let it stand 5 times in total. (In general, the partition coefficient depends on the temperature. However, the partition coefficient does not change in the range of 20-30°C in this system. Therefore, this experiment can be conducted at room temperature without temperature control.)

6. Transfer 10 mL of the aqueous phase of Solution C to a conical beaker with a 10 mL volumetric pipette (\*Refer to "*Taking an Aliquot of Aqueous Phase A or B*"). Add a stirrer bar and 1 drop of phenolphthalein solution. Titrate using 0.01 mol L<sup>-1</sup> aqueous sodium hydroxide solution with stirring. Repeat the titration as needed (the titration can be done up to 3 times). Similarly, titrate Solution B and A in that order.

## \* "Taking an Aliquot of Aqueous Phase A"

- a. **Insert** a volumetric pipette into the solution so that the tip is near the center of the aqueous phase.
- b. Blow out a small amount of air using a pipettor and push out the solution at the tip.
- c. **Pull up** the aqueous phase so that the none of the oil phase remaining on the bottom and sides of the Erlenmeyer flask is drawn in.
- d. **Pull** the volumetric pipette out of the solution and **wipe off** the solution on the outside of the pipette.
- e. Align the meniscus of the solution and the line marked on the pipette.
- f. **Transfer** the aqueous phase to a conical beaker.

## \* "Taking an Aliquot of Aqueous Phase B"

- a. **Insert** a pipette into the solution so that the tip is near the center of the aqueous phase.
- b. **Blow out** a small amount of air using a silicone dropper and **push out** the solution at the tip.
- c. **Pull up** the aqueous phase (more than 10 mL) so that none of the oil phase remaining on the bottom and sides of the Erlenmeyer flask is drawn in.
- d. **Pull** the pipette out of the solution and **wipe off** the solution on the outside of the pipette.
- e. **Transfer** the aqueous phase to a beaker.
- f. **Transfer** the aqueous phase from the beaker to a conical beaker using a volumetric pipette.

## <u>Results</u> **Record** the titration volume.

Ne	Volume for	Volume for	Volume for
INO.	Solution A [mL]	Solution B [mL]	Solution C [mL]
1			
2			
3			
Volume determined [mL]			

\*It is not necessary to fill in all rows.

## Questions

1. **Calculate** the concentration of 2,5-furandicarboxylic acid in the aqueous phase,  $C_w$ , and  $\log C_w$  from the determined titration volume.

	Solution A	Solution B	Solution C
Cw [mol L <sup>-1</sup> ]			
log <i>C</i> w			

2. **Calculate** the concentration of 2,5-furandicarboxylic acid in 1-octanol,  $C_o$ , and  $\log C_o$  using the total amount of 2,5-furandicarboxylic acid.

	Solution A	Solution B	Solution C
Co [mol L <sup>-1</sup> ]			
log <i>C</i> o			

3. If 2,5-furandicarboxylic acid is present in water at a concentration of  $C_w$  as a single molecule and in 1-octanol at a concentration of  $C_o$  as an n-molecule aggregate, the partition coefficient *K* is calculated using the following equation.

$$\frac{C_o}{C_w{}^n} = K$$

Taking the logarithm of both sides, the equation can be transformed as follows:  $logC_o = nlogC_w + logK$  Taking points A, B, and C as  $(\log C_w(A), \log C_o(A))$ ,  $(\log C_w(B), \log C_o(B))$ , and  $(\log C_w(C), \log C_o(C))$ , respectively, **calculate** *n* and *K* from the equations of the straight lines AB, BC, and AC, and **average** them. If necessary, **use** the graph paper on the next page.

	n	K
AB		
BC		
AC		
Average		

4. **Draw** the structure of the aggregated 2,5-furandicarboxylic acid that is expected to be present in 1-octanol from the calculated value of *n*.





## Practical Task 2. Separation and determination of metal ions using anionexchange resins

## Introduction

The separation and quantitative analysis of metal ions is of pivotal importance in the compositional analysis of a variety of materials, such as alloys and metal complexes. In aqueous solution, most metal ions exist as cations (aqua complexes). In hydrochloric acid, on the other hand, some metal ions are in equilibrium with chloride complexes and can be present as anions. The ratio of the cationic and anionic forms in solution depends largely on the chloride concentration, and this mechanism can be used to separate metal ions. In this task, you will separate Co(II) ion impurities from a sample solution containing Fe(III) ions (Sample X) using an anion-exchange resin column and determine the Fe(III) content in Sample X by chelate titration.

## Background

The ion-exchange resin is a synthetic polymer with a three-dimensional network structure; the functional substituents responsible for the ion-exchange reaction are introduced on its surface. Resins that perform a cation-exchange reaction, i.e., the adsorption of cations and release of the initially adsorbed cations, typically protons, are called cation-exchange resins, while those that exchange anions are referred to as anion-exchange resins. Various types of ion-exchange resins with different characteristics are commercially available, and an example of the structure of an ion-exchange resin obtained from the copolymerization of divinylbenzene and a styrene derivative that bears a quaternary ammonium group is shown below.



This resin can exchange the anions contained in a solution for the chloride ions associated with the ammonium groups. The adsorption and dissociation of the anions are reversible reactions because they are based on the electrostatic interaction between the ammonium group and the anion. Therefore, specific anions can be retained or eluted by appropriately adjusting the concentration of chloride ions.

In this task, we will use a strongly basic anion-exchange resin manufactured by Dow Chemical Co., Ltd. (DOWEX<sup>TM</sup>  $1 \times 8 100-200$  Mesh Cl<sup>-</sup> Anion Exchange Resin), which can replace the anions in solution with chloride ions. In our experiment, we use a chromatographic column packed with the resin, and the analyte is passed through the column using hydrochloric acid as the eluent. Assuming that the generation of chloride complexes and their reaction with the resin are in equilibrium, it is possible to elute the desired anions from the column by appropriately adjusting the concentration of the hydrochloric acid.

The partition ratio, D, is defined as the ratio of the total concentration of the substance in the solid phase (mol g<sup>-1</sup>) to the total concentration of the substance in the liquid phase (mol cm<sup>-3</sup>).

 $D = \frac{\text{total concentration of the substance in the solid phase (mol g^{-1})}{\text{total concentration of the substance in the liquid phase (mol cm^{-3})}$ 

The relationship between D and the concentration of hydrochloric acid, [HCl], for Fe(III) and Co(II) ions is given below. The figure shows that Fe(III) has a large D and is more easily adsorbed on the resin at all [HCl] values. For example, when 4 M HCl is used as the eluent, Fe(III) is about 1000 times more likely to be adsorbed on the resin than Co(II). Therefore, under this condition, Co(II) ions will elute from the column first. By lowering [HCl] after removing the Co(II) ions, the adsorbed Fe(III) can be eluted.



## Chemicals

Substance	Name	State	GHS Hazard Statement
HCl	Hydrochloric acid	Aqueous solution	H290, H301, H314,
(6, 4, 0.5 M)			H318, H332, H334,
			H370, H372, H400
NH <sub>3</sub> (1 M)	Ammonia	Aqueous solution	H290, H302, H314,
			H318, H370, H401
VBB indicator	Variamine Blue B	Diluted with KCl	NA
EDTA	Disodium dihydrogen	Aqueous solution	NA
(0.01 M)	ethylenediaminetetraacetate		
Sample X		Acidic solution	NA

## Glassware and equipment

1 Column packed with DOWEX<sup>™</sup> 1×8 100-200 Mesh Cl<sup>-</sup> Anion Exchange Resin (i.d. = 10 mm)

- 1 Burette, 25 mL
- 1 Laboratory stand with burette clamp
- 7 Conical beakers, 100 mL
- 1 One-mark pipette, 2 mL
- 1 One-mark pipette, 20 mL
- 1 Volumetric flask, 100 mL
- **3** Pipettes
- 2 Pasteur pipettes
- **1** Pipetting bulb
- **1** Glass vial
- **1** Glass rod
- 1 Alcohol thermometer
- 1 Spatula (spoon)
- $1 \ {\rm Hot} \ {\rm plate}$
- Congo Red Paper

## Procedure

## A. Separation of the Co(II) and Fe(III) ions contained in Sample X

- The column is packed with anion-exchange resin and pre-conditioned with 6 M HCl. Lower the liquid level to the cotton on the top of the column, being careful not to let air bubbles enter.
- 2. **Transfer** 2 mL of Sample X into a sample bottle and then gently **load** the entire volume on the top of the column using a Pasteur pipette so that the sample is charged evenly.
- 3. Lower the liquid level to the cotton. **Rinse** the sample bottle and inner wall of the column with a small amount of 6 M HCl and **load** the washings onto the column in a similar manner. **Repeat** this operation several times to adsorb all the metal ions on the anion-exchange resin.
- 4. **Elute** the column with 4 M HCl and **collect** the first fraction in a 100 mL conical beaker. You can easily recognize the fraction by color.
- 5. **Elute** the column with 0.5 M HCl once you observe that all the first fraction has been collected. **Collect** the second fraction in another 100 mL conical beaker until all the second fraction has eluted.
- 6. **Elute** the column with  $H_2O$  to collect the remaining residue adsorbed on the resin.

## Note

To repeat the experiment, wash the column with 20 mL of water followed by 10 mL of 6 M HCl before repeating the procedure.

## B. Determination of Fe(III) ions

In this experiment, the concentration of Fe(III) ions contained in Sample X is determined using the fraction containing Fe(III) ions obtained in Experiment A.

- 1. **Dilute** the fraction containing Fe(III) ions separated in Experiment A to 100 mL.
- 2. Transfer 20 mL of the diluted solution to a 100 mL conical beaker.
- 3. Adjust the pH to 2-3 using 1 M aqueous ammonia. In this pH range, the Congo Red test paper turns purple. If a precipitate appears, add a small amount of HCl to redissolve all the precipitate.

- 4. **Warm** the solution to approximately 50 °C using a hot plate.
- Add VBB indicator to the solution until the solution turns dark purple. You do not have to weigh the VBB, but judge the appropriate amount by the color of the solution. Approximately 50 mg is required.
- 6. **Titrate** the sample solution with 0.01 M EDTA quickly so that the solution does not cool.
- 7. **Determine** and **record** the amount of EDTA added to reach the equivalence point where the sample solution changes from the initial purple color to a pale yellow, and the color does not change further even if additional EDTA solution is added.
- 8. **Repeat** the titration using the remaining diluted sample solution. Although titration can be performed up to 4 times, it is sufficient to perform it only as many times as you need.

## Questions

I. **Draw** the chemical structure of the chemical species that the Fe(III) ion is expected to form in 6 M HCl.



II. **Report** the amount of 0.01 M EDTA solution needed to reach the equivalence point. You only need to report the number of times you titrated.

#	1	2	3	4
Amount of 0.01 M EDTA solution / mL				

III. **Report** the number of Sample X analyzed and **calculate** the molar concentration of Fe(III) ions contained in Sample X.

# of Sample X



Molar concentration of Fe(III) ions in Sample X

mol  $dm^{-3}$ 

## Discussion

What causes the color change of the first fraction before and after elution from the column?

## Instructions for mentors

## Preparation of Sample X

Dissolve NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub> · 12H<sub>2</sub>O (M= 482.25) and CoCl<sub>2</sub> · 6H<sub>2</sub>O (M= 237.93) in 6 M HCl. Concentrations of Fe(III) ions between 0.1–0.2 M are appropriate, while that of Co(II) should be less than 0.1 M.

## Note

 $FeCl_3 \cdot 6H_2O$  can also be used as the source of Fe(III) ions. However, it may be difficult to know the prepared concentration accurately due to the hygroscopic nature of the salt.

## Preparation of VBB indicator diluted with KCl

Mix 1 part VBB with 200 parts KCl in a mortar. Store the mixture in a brown bottle.

## Preparation of the anion-exchange resin column

## Note

The following procedure can be included in the task if the students have time to spare.

Wash the anion-exchange resin (about 5 g per person) with deionized water (hereafter referred to as water) and let the resin swell in water overnight. Loosely pack absorbent cotton at the bottom of the chromatography column and add water to remove air bubbles. Using a funnel, pour the swollen resin into the column (10 cm in length) and open the cock to drain the excess water. Note that no air bubbles should enter the top of the resin. Place a small amount of absorbent cotton on top of the resin so that its surface is not disturbed and add a small amount of water to remove air bubbles. Check that there is no resin outflow from the column and that the flow rate is around 15 drops/min (typically 10–20 drops/min). If the column is not to be used immediately, add an appropriate amount of water so that the upper part of the column does not dry out. Prior to the experiment, lower the liquid level to the cotton and gently add 10 mL of 6 M HCl to flow through for conditioning.

## Practical Task 3. Brevity is the soul of wit in organic synthesis

#### Introduction

In organic synthesis, C–C-bond-forming reactions to build molecular frameworks are some of the most basic yet also most important reactions. Many C–C-bond-forming reactions require large amounts of organic solvents and complicated procedures for separation and purification of the target compounds and are thus associated with a relatively high environmental load. In this task, a C–C-bond-forming reaction is carried out between triphenylmethanol (1) and malonic acid (2) to synthesize 3,3,3-triphenylpropionic acid (3) as shown in equation (1). This is a well-designed synthetic method in which the reaction proceeds via the simple heating of two solid raw materials, and the target product 3 can be obtained in high purity using only recrystallization without performing complicated separation procedures. The purpose of this task is to consider the reaction mechanism based on the experimental results and understand the well-designed reaction system.



Chemicals

Substance	Name	State	GHS Codes
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> C–OH	Triphenylmethanol	Solid	H302
CH <sub>2</sub> (CO <sub>2</sub> H) <sub>2</sub>	Malonic acid	Solid	NA
C <sub>2</sub> H <sub>5</sub> OH	Ethanol	Liquid	H225- H320

Glassware and equipment

- 1 Erlenmeyer flask (30 mL)
- 1 Hot plate with digital temperature display (or a thermometer for the surface temperature)
- 1 Pipette (5 mL)
- 1 Spatula
- 1 Screw-top bottle (20 mL)
- 1 Apparatus for filtration
- 1 Paper for wrapping powdered medicine
- 1 Pair of work gloves

## Experimental procedure

## Caution

In this task, gases with low toxicity but a strong smell are generated. Perform in an environment where a fume hood or other air exhauster can be used appropriately. During heating, the hot plate reaches high temperatures. Be careful to avoid burns.

- 1. Set the surface temperature of the hot plate to 170 °C. Control of the surface temperature is essential. If the hot plate does not have a digital temperature display, its surface temperature should be measured using a thermometer (such as a radiation thermometer).
- Add triphenylmethanol (Ph<sub>3</sub>C–OH, 1.041 g) and malonic acid (2.082 g) to an Erlenmeyer flask (30 mL) and mix the reactants by gently swirling the flask by hand.
- 3. **Place** the Erlenmeyer flask on the hot plate at 170 °C.
- 4. **Heat** the Erlenmeyer flask for 30 min while observing the reaction.
- 5. Wearing the work gloves, **remove** the Erlenmeyer flask from the hot plate and **place** it on a stack of Kimwipes on the workbench.
- 6. **Set** the surface temperature of the hot plate to 120 °C.
- 7. Allow the flask to cool for 1 min.
- 8. Add a solution of EtOH:H<sub>2</sub>O (5/1, v/v, 1 mL) to the reaction mixture and stir the solution to initiate crystallization.
- 9. If no crystals form, **rub** the wall with a spatula to induce crystallization.
- 10. Add additional EtOH:H<sub>2</sub>O (5/1, v/v, 5 mL).
- 11. Place the Erlenmeyer flask on the hot plate at 120 °C.
- 12. After complete dissolution, move the Erlenmeyer flask onto the Kimwipes on the workbench.
- 13. Allow to cool for ca. 2 h. Caution: even after cooling to room temperature, the crystals continue to grow slowly.
- 14. Break the crystals gently with a spatula.
- 15. **Collect** the crystals by filtration under reduced pressure.
- 16. Place the crystals into a screw-top bottle (20 mL) and submit the sample.

## For the evaluation of the purity

1. Melting point

Pure 3,3,3-triphenylpropionic acid has a melting point of 182 °C.

2. <sup>1</sup>H NMR spectroscopy

The methylene protons and the aromatic protons of pure 3,3,3-triphenylpropionic acid show an

integration ratio of 2:15. Use a deuterated solvent other than CDCl<sub>3</sub>, C<sub>6</sub>D<sub>6</sub>, or methanol- $d_4$ , because the residual protons in CDCl<sub>3</sub> and C<sub>6</sub>D<sub>6</sub> overlap with the aromatic protons, while methanol- $d_4$  causes deuterium exchange of the methylene protons in 3,3,3-triphenylpropionic acid.

## 3. HPLC

The main contaminant would be triphenylmethanol, which can be quantified by high-performance liquid chromatography using a reversed-phase column such as an octadecylsilicate column.

### Questions

- 1. **Calculate** the theoretical yield, showing the details of the calculation method. It should be noted that the crystal water and solvent are not included.
- 2. Write the chemical formulae of the products X and Y that are generated by the reaction of triphenylmethanol (1) and malonic acid (2) in equation (1).
- Draw the chemical structure of the ionic intermediate A that is generated from triphenylmethanol (1).
- 4. **Describe** the most important experimental evidence suggesting the formation of the ionic intermediate **A**.
- 5. In this task, malonic acid plays multiple roles. **Write** the role of malonic acid other than as a stoichiometric reagent and a solvent.
- 6. This task requires an appropriate air exhauster (such as a fume hood) for removing compound **B** generated during the reaction. **Write** the formula of compound B.
- 7. The procedure in this task is well designed. If the reaction conditions are changed as described below, **what** will occur?
  - (i) using a 1:1 mole ratio of triphenylmethanol and malonic acid to avoid using a large amount of malonic acid.
  - (ii) using a solvent for the enhancement of the reaction selectivity.
  - (iii) using a Liebig condenser, the generated compound **B** is refluxed to prevent it from leaving the system.
  - (iv) the reaction is carried out at 150 °C to implement milder conditions, or at 200 °C to enhance the reaction rate.
    - To further enhance the efficiency of the reaction (e.g., yield, purity, reduced raw material

consumption, reduced energy consumption, reduced waste, simpler procedure), what kind of method might you propose? **Discuss** this with your mentor.

" The best is not, so long as we can say, 'This is the best." - modified from King Lear.



## **Catalyzer 0**



## Welcome Message

The 53rd International Chemistry Olympiad IChO2021 will be held in Osaka, Japan, from Saturday, July 24 to Monday, August 2, 2021. On behalf of the Organizing Committee, I look forward to welcoming many talented high school students who love chemistry to Japan.

Chemistry is all around us as the central science. Chemistry has a mission to create new materials. Chemistry is the only scientific discipline that can understand and transform the structures and function of materials at the atomic and molecular levels. Chemistry thus must play a key role in finding solutions for many global issues, including energy, environmental, and resource related issues, that humanity is now facing. I hope that IChO2021 Japan contributes to foster many young talents who will be involved in the states of art of such aspects of chemistry.

Osaka, the venue for IChO2021 is surrounded by two old capitals, Nara and Kyoto, as the birthplace of Japan's politics and culture. Osaka is not just a lively, modern commercial city, but also is the birthplace of chemical research in Japan. I really hope that IChO2021 Osaka, Japan serves as a catalyzer for all participants to make many friends through personal communications and cultural exchanges.

However, the situation surrounding us has changed significantly last year, 2020. We have been experiencing a difficult situation due to the COVID-19 global pandemic. The IChO2020 Turkey was forced to be held online. I would like to express my heartfelt appreciation and congratulations to all members of the IChO2020 Turkey Organizing Committee and the Steering Committee for their great efforts to make the IChO2020 so successful with the Online Theory Exam on July 25 and the Online Closing Ceremony on July 30. I am convinced that the great success of Online IChO2020, as the first attempt in IChO history, should be worthy of note in the following three points: (1) It provided precious opportunity to many talented high school students around the world to enjoy chemistry in their own countries. (2) They were given hope and courage to overcome unprecedented difficulties. (3) International friendships and trust have been strengthened among over 60 participating countries. We have learned a lot from the Online IChO2020.

At the end of the Closing Ceremony, I was invited to hand over the IChO flag through the computer from Professor Hasan Mandal, Chairman of the Organizing Committee for IChO2020 Turkey.

It is finally our turn, but the situation is still uncertain. We have started preparations assuming an Online IChO2021, as well as a real event in Osaka, Japan. In any case, we, organizing committee all together, will concentrate our efforts to lead a successful IChO2021 Japan.

Our final decision will be announced in due course. We ask for the understanding and cooperation of all those involved.



Chairman, Organizing Committee for the 53rd ICh02021 Osaka, Japan

# Japan

Area: 377,975 km² (61st in the world) Population: 126.86 million (11th in the world in 2019) Currency: JPY (103 JPY = 1 USD, 05/01/2021) Language: Japanese (with many dialects)



he 53rd International Chemistry Olympiad (ICh053) 2021 will be held in Osaka, Japan. This is the second time for Japan to host it; the first time (IChO42) was in 2010 in Tokyo. Japan has approximately 6,800 islands, including the four major islands of Hokkaido, Honshu, Shikoku, and Kyushu, and is situated on the Eastern edge of the Eurasia continent. There are mega cities such as Tokyo and Osaka. However as soon as one steps out of such ultra-urban areas, one is greeted by beautiful mountains and streams. Japan is a country whose land stretches from north to south with various climates ranging from subarctic to subtropical, four seasons, and distinctive local regions rich in nature. As the Japanese archipelago is part of circum-Pacific volcanic zone, Japan has several active volcanoes and a countless number of hot springs all around the country. These springs result from volcanic activities and provide a rich resource for bathing. Additionally, Japan has a total of 300,000 kilometers of coastline, and consists of many islands where people can enjoy swimming, fishing, boating, and other marine leisure activities. Japan's islands are mostly mountainous, and offer many spots suitable for trekking, skiing, and other activities.

A long the Pacific coast, major industrial zones were constructed from which various chemical, mechanical, electronic, and automotive products are exported globally. Osaka prefecture, where the 53rd International Chemistry Olympiad (IChO53) will be held, belongs to the Kansai region and is located about 400 kilometers from Tokyo, Japan's capital. It can be reached in only two and a half hours by the Shinkansen bullet train.

J apan's traditional culture has become increasingly popular among international travelers to Japan. This includes not only traditional crafts, *kimono*, and architecture, as seen in its historical shrines and temples. Japanese cuisine and its unique gastronomic culture are also attracting much interest, particularly among those who are health conscious. Japanese animation has become a focus of popular culture and is enjoyed by wide range of generations globally.

The Kansai region

Olsaka OTokyo



SPring-8, photo provided by RIKEN

# Science & Technology



# **Osaka** and the Kansai region

The Kansai region refers to the area in the midwestern part of the island of Honshu, which is the largest of the four main Japanese islands. This region consists of six prefectures, namely, Osaka, Kyoto, Hyogo, Shiga, Nara, and Wakayama. It is one of the largest economic zones in Japan, second only to the Tokyo area, and has three large cities, Osaka, Kyoto, and Kobe, whose populations exceed one million. Kindai University, the venue of IChO53, is located in Osaka Prefecture, which is a metropolis with a population of 8,800,000.

H istorically, this area was once the political, economic, and cultural center of the nation. In the 7th century Japan's first capital and imperial castle were situated in present-day Nara (Asuka Itabukinomiya). The capital was transferred to Osaka (Naniwanomiya) followed by Nara (Heijokyo). It was then relocated to Kyoto (Heiankyo) where it remained for approximately 1,200 years before finally being officially moved to Tokyo in 1868. Given the long history of this area, there are many historical buildings that have been designated as UNESCO World Heritage Sites. Kyoto and Nara are especially well known as Japan's ancient capitals, making them highly popular destinations for domestic and international travelers.



## Food

J apanese cuisine is well known worldwide. Among the most popular dishes are sushi, ramen, tempura, and curry and rice. In the Kansai region, Kyoto, which is surrounded by mountains, did not have good access to fresh seafood. Nonetheless, Kyoto is renowned for its cuisine made with unique local vegetables known as *Kyoyasai* and dried foods. Osaka, which is a center for fresh foods, has a rich and varied gastronomic culture that has flourished for centuries. Today it is known for *konamon*, a general term used for savory foods made from flour as well as fresh ingredients. Dishes such as *takoyaki* and *okonomiyaki* have become very popular, even among international visitors, as casual and inexpensive dishes with a savory taste.

T he climate of this area may be divided into the Sea of Japan climate zone, the Pacific climate zone, and the Setouchi climate zone, which is sandwiched between the two. Given these different climate zones, the area is blessed with exquisite natural scenery. The Kii Mountain area that straddles the three prefectures of Wakayama, Nara, and Mie, is famous for its beautiful nature. The sacred sites and pilgrimage routes of the Kii Mountains are registered as World Heritage Sites.



## Language

**S** tandard Japanese language is used nationwide, but there are also various dialects particular to each region. It is often possible to tell which region a person is from by his or her intonation. Some dialects are distinctive which can make it difficult for someone who is not from that area to understand. The Tokyo dialect is now considered standard Japanese. However, in the Kansai region, there are many distinctive dialects spoken in different areas within the region, forming a group of Kansai dialects or *Kansai-ben*. There are slight differences among the dialects in the region making it possible to distinguish the part of the region from which the speaker comes. Further details regarding the Kansai dialect will be mentioned in Catalyzer No. 1.

# The Venue Kindai University Ata Glance

3-4-1 Kowakae, Higashiosaka City, Osaka 577-8502, Japan https://www.kindai.ac.jp/english/

https://www.kinddi.dc.jp/english/

K indai University was founded in 1925. Now one of Japan's largest universities, it has six campuses in western Japan and boasts research facilities across the nation - from Hokkaido in the north to Kagoshima in the south. Currently, Kindai University comprises 14 faculties with 48 departments, 11 graduate schools, a law school, 18 research facilities, two junior colleges, 18 associated primary and secondary schools, and two teaching hospitals. The university has over 30,000 students and more than 500,000 alumni and has about 500 international students enrolled from all over the world. Kindai University has 250 partner universities in 50 countries and regions, and continues to interact with universities around the world. Kindai University conducts research in a wide range of fields and is making a name for itself as a leader in aquaculture, most notably for

its work with bluefin tuna. Dedicated to meeting the needs of today's rapidly changing society, Kindai University will continue expanding its educational programs and facilities.



## **Useful Japanese Phrases**

## English

Good morning Good afternoon Good evening Good night Good-bye Excuse me I am sorry I don't understand Thank you Yes No Please Ohayou gozaimas Kon' nichiwa Kon' banwa Oyasumi nasai Sayounara Sumimasen Gomen nasai Wakarimasen Arigatou Hai lie Onegai shimasu

## Japanese



These five elements spell "OMoTeNaSi", the Japanese word for hospitality. It means to wholeheartedly take care of guests without expecting anything in return. Attention is paid to even the smallest details in order to bring guests the best experience possible. As you make your way across Japan, you will find *omotenasi* everywhere.

# Chemistry/ It's Cool/



Catalyzer No Official Website https://www.icho2021.org/



Weather information (Average in late July) **Osaka** 

### **Contact Information**

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## Catalyzer 0.5



Dear Students, Mentors, Guests, Distinguished Scholars, Observers, SC Members and Colleagues:

W elcome to the IChO2021 Japan 53rd International Chemistry Olympiad. I am delighted to serve as the Chair of the Executive Committee of IChO2021, a very important scientific event especially for students at secondary school level.

This past January, we carefully discussed whether we could hold a real or remote Olympiad in 2021. We eventually decided to hold a remote Olympiad this summer, owing to the ongoing global COVID-19 pandemic. The most important priority was to be able to organize IChO2021 safely and smoothly. Our remote IChO2021 will be held from 25 July to 2 August, 2021. The three key concerns of the Chemistry Olympiad are as follows: (1) The safety of all participants, including secondary school students; (2) Equal opportunity for every student; and (3) International experiences via competition and cooperation, despite the Olympiad being held remotely.

I hope you have already visited our website, https://www.icho2021. org. There you can find our motto for IChO2021, "Chemistry! It's Cool!", as well as our first Catalyzer newsletter. We are sure that you can still enjoy chemistry and experience O-Mo-Te-Na-Si during this remote Olympiad.

The opening ceremony will be held online on our website on 25 July, 2021, and the examination will be conducted in each country on 28 July. Students will be able to take the examination in their home countries. The duration of the examination is five hours. The examination may start at any time between 4:00 pm and 9:00 pm JST, and each country can decide the starting time that suits them.

After grading is complete, an online closing and award ceremony will take place on 2 August. Students may attend the ceremony with their avatars. Medals and the certificates will be sent to participants via surface mail together with commemorative gifts.

Between the opening and closing ceremonies, Olympiad participants can enjoy a series of remote events. These include virtual visits to tourist spots such as Himeji Castle and other famous world-heritage temples and shrines in the Kansai region (Kyoto, Nara, Osaka, and Kobe). Interesting cultural events are also planned, including a visit to a special site at which repair work to an ancient Buddha statue is being carried out. Students can take part in a scientific virtual visit to SPring-8, the world's largest synchrotron radiation facility. Communications among participating students are also important. Virtual reality avatars will be available for all students to enhance their remote communication experiences. We also plan to make the practical examination available to the general public so they can try their own experiments.



# Remote Examination FAQ

Due to the COVID-19 pandemic, ICh02021 Japan will be held remotely. The safety of every participant is our first priority. Even though we might be far apart, we still aim to provide special experiences to the participants in July.

Several changes to regulations for the examination are listed below. For more details, please see website.

#### Q What are the time zones for the remote IChO?

All dates and times on this document are based on Japan Standard Time (JST), which is Coordinated Universal Time (UTC) +9 hours. Japan does not use daylight saving time during the summer.

Q When is the date for the examination?

A The theoretical examination will take place on 28 July, 2021.

#### Q How long is the examination?

A The duration of the examination is 5 hours. The details of the examination must be reported by invigilators. A report form to be completed by invigilators will be provided with the student examination papers.

#### Q What is the start time of the examination?

A The examination may start at any time between 16:00 and 21:00 JST, and each country can decide its own starting time. However, all competitors in each country must have the same examination timetable to avoid ill-intentioned communication among competitors. Countries with multiple time zones must set their timetable on the basis of one specific time zone and conduct the examination accordingly.

## Q How will be the examination conducted remotely?

A The preparation of the examination (discussions, voting, translation, printing) will be done using Oly-Exam software. Mentors will read, comment and vote on, and translate the examination text using the Oly-Exam software.

## Q Where should the examination be located?

A The examination location must be a calm and quiet room with electricity, and equipped with a computer or smartphone, web camera, microphone, high quality printer, scanner with PDF-conversion software, and stable internet connection. Each location will be checked via Zoom before the examination.

A single location for the full number of 4 students is highly preferred. If legal travel restrictions in the country forbid a single location, multiple locations for one country are acceptable.

Q What help/tools are allowed for the examination?

J:JST CET E:EST

52

e

197 .

A Only a non-programmable calculator, good writing pen and a ruler can be used during the examination. Students should write their answers only using a pen with dark ink.

#### Q What are the important dates for the IChO2021?

A See the following Table.

0

95 95

## Schedule of Remote IChO2021 (Tentative)

Date	Student	Mentor		
Jul 23, Fri		Training of Oly-Exam	02:00 0 14:00 <u>0</u> 8:00	
	Opening Ceremon	<b>Y</b> (Start time to be determined)		
Jul 25, Sull		Receive the problem	00:80 <b>0</b> (4:00 <b>0</b> :8:00	
Jul 26 Mon		Deadline of feedback	00:05 <b>0</b> 00:500 00:900	
Jul 20, Wolf	Activity (To be announced)	Jury meeting	00:80 <b>0</b> 14:00 📴 8:00	
Jul 27. Tue	Activity (To be appounced)	Receive the authorized problem	0:0:00 0:0:00 0:0:00	
		I ranslation/submission		
	Start remote examination at 1500 0300 1300	Deadline of translation	00:05 00:2:00 00:2:00	
Jul 28, Wed		[Invigilator] Receive and print out the problem	J 14:00 C07:00 E0 1:00	
		[Invigilator] Submit the solutions (Within one hour after the end of the examination)		
lul 20 Thu		Receive the solution and the grading schen	ne 🕽 19:00 C 12:00 E 20:00	
	Activity (To be announ	ced)		
		Receive grading	0:0:00 0:2:00 0:0:00	
Jul 30, Fri	ACTIVITY (To be announced)	(from Organizer, Request arbitration)		
		Deadline of request, Jury meeting	<b>1</b> 5 :00 <b>0</b> 14:00 <b>6</b> 18:00	
Jul 31, Sat		Arbitration	0:9:00 0:2:00 02:00	
		Receive final results	<b>No:00 No:00 B2000</b>	
Aug 1, Sun				
			<b>N</b> 2 100 <b>N</b> 1400 <b>N</b> 800	
Aug 2, Mon	Closing Ceremony			



## Seimi-kyoku 會密局 the Origins of Modern Chemistry in Japan

D uring the Edo period (1603 to 1868), when the Tokugawa shoguns ruled the country, Japan adopted a policy of seclusion and closed its borders to the outside world for more than 250 years; international trade was allowed only with China (mainly under the Qing dynasty) and the Netherlands. Any information on the natural sciences that emerged in Europe in the early 18th century came only from the Netherlands through *Dejima*, a small artificial island in the bay of Nagasaki on the west end of Japan.

The first systematic chemistry lectures in Japan were given by Johannes Lijdius Catharinus Pompe van Meerdervoort, a physician who came to Japan in 1857. Pompe began teaching Western medicine in Nagasaki, and after he found that the students lacked fundamental knowledge in science, he also started teaching a course in basic science. After Pompe left Japan, Dr Anthonius Franciscus Bauduin was invited to succeed him, and taught chemistry as well as medicine. Following Bauduin, the Dutch chemist Koenraad Wolter Gratama was invited to teach in Japan as a specialist in science and chemistry teaching.

In 1867, Gratama was set to be transferred to the *Kaiseijo*, the shogunate's Western education and research center located in Edo (present-day Tokyo), but this plan was thwarted when the shogunate collapsed during the Meiji Restoration in 1868. The new Meiji government, however, established a college called the *Seimikyoku* in Osaka to replace the *Kaiseijo*, and welcomed Gratama as head lecturer there. The word *seimi* was a transliteration of the Dutch word *chemie*, though it is no longer used today. One reason behind the new government's move to establish the *Seimi-kyoku* in Osaka is said to have been their initial intention to move the capital from Kyoto to Osaka, rather than to Tokyo. Ultimately, however, the Emperor moved to Edo Castle where the Tokugawa shogunate was based, after the castle was surrendered bloodlessly to the new government. Eventually, Edo was renamed Tokyo and became the new capital city of Japan.

In 1868, the new *Seimi-kyoku* (also known as the *Osaka Seimi-kyoku*) was completed, and Gratama started teaching physics and chemistry there. Gratama not only taught students, but also initiated training programs for physics and chemistry teachers. The



Koenraad Wolter Gratama (1831-1888)

following year, a medical school and hospital were established nearby, where Bauduin also taught. Many students from the medical school also came to attend the lectures at the *Seimi-kyoku*, among them Jokichi Takamine, who later became well-known for his research on adrenaline (Catalyzer, No. 2). Kikunae Ikeda, who discovered the "umami"



ingredient *Ajinomoto* (Catalyzer, No. 6), studied chemistry under the tutelage of Jiro Murahashi, Gratama's assistant at the *Seimikyoku*. Hiroakira Akashi, who worked at the medical school hospital, deepened his knowledge by listening to Gratama's lectures, and eventually established the *Kyoto Seimi-kyoku* in his home town Kyoto, with the support of the Kyoto prefectural government. Genzo Shimazu, a blacksmith who had been a contractor at the *Kyoto Seimikyoku*, was taught by the German teacher there, and later established Shimadzu Corporation, the chemical equipment manufacturer (Catalyzer, No. 5). These are just a few examples of the many students and teachers who received direct or indirect instruction from foreign teachers and who later drove the development of medicine, chemistry, and pharmacy in Japan.

In 1870, Gratama completed his term of office and returned to the Netherlands the following year. The German chemist Georg Hermann Ritter was invited to replace him. In 1872 however, all the personnel and assets of the *Seimi-kyoku* were transferred to the *Tokyo Kaisei Gakko* school, which later became the University of Tokyo. The *Seimi-kyoku* underwent several organizational and name changes, finally becoming the Third Higher School in 1889, which would later be merged into Kyoto University. At the site of the former *Osaka Seimi-kyoku* near Osaka Castle, there is a large camphor tree in a corner surrounded by a stone wall that appears to block the walkway, and at the base of the tree stands a stone pillar and monument that reads "Site of the Former *Seimi-kyoku*." On the reverse side of the monument is a majestic bust of Gratama. Although the *Seimi-kyoku* disappeared in the turbulent times for Japanese society in the early Meiji era, its legacy lives on as the foundation



## Element #1 Japanese mineral resources AU, Ag, and CU

**T** oday, Japan depends mostly on imports of the mineral resources it needs, but in the past it used to produce large amounts of gold, silver, and copper. Marco Polo, the 13th-century merchant and explorer who travelled throughout Asia, introduced Japan to Europe as "Japan, Land of Gold" in his travelogue *The Travels of Marco Polo*, which later became the driving force for adventurous explorers during the Age of Discovery.

Long ago, gold mines such as those on the island of Sado (part of Niigata prefecture today) and in Koshu (Yamanashi prefecture) produced significant amounts of gold. In the Edo era, from the 16th to the 19th centuries, the Tokugawa bakufu (shogunate) established an official gold guild known as the Kin-za, and gold coins called Keicho Koban and Oban were issued.

I n terms of silver production, one of the major operations was the *Iwami Ginzan* silver mine, where production of silver continued for approximately 400 years from the 16th century. The *Iwami Ginzan* silver mine was located in what is the city of Oda in Shimane Prefecture today, and production reached its peak during the Edo period, when the mine was directly managed by the *bakufu*. Production then gradually decreased until the mine was closed in 1923. The *Iwami Ginzan* silver mine site was registered as a UNESCO World Heritage (Cultural) Site in 2007, listed as the Iwami Ginzan Silver Mine and its Cultural Landscape, with special mention made of its environmentally friendly operation.





The Besshi copper mine located in what is the city of Niihama in Ehime Prefecture, discovered in 1690, produced a total of 700,000 tonnes of copper in 283 years until it was closed in 1973. The former mine site is now the location of Minetopia Besshi, a historical theme park where people can learn how the mine operated in the olden days.

These five elements spell "OMoTeNaSi", the Japanese word for hospitality. It means to wholeheartedly take care of guests without expecting anything in return. Attention is paid to even the smallest details in order to bring guests the best experience possible. As you make your way across Japan, you will find *omotenasi* everywhere.

# Chemistry! It's Cool!



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## **Catalyzer 1**



# Message

I tis our great pleasure to host the 53rd International Chemistry Olympiad (IChO2021), a competition so rich in history since the first one in 1968, and to welcome very talented young students from 79 countries and regions around the world.

As important as it is as an academic subject, chemistry is also the basis for creating materials and substances with a vast range of functions that constantly supports our daily lives.

The COVID-19 pandemic is still plaguing the world. Chemistry is playing a vital role in the fight against COVID-19 by being applied for PCR and antigen testing to detect infection and its history and for the manufacture of COVID-19 treatment drugs.

Moreover, we expect chemistry to greatly contribute to achieving the Sustainable Development Goals, including the stable supply of food, the recycling of waste, and so on.

All the students participating in IChO2021 have the potential to address these various shared problems of the world and to open up a new path for humankind. It is a crucial issue for governments around the world to discover their talents and create an environment to develop fully these capabilities.

The International Science Olympiads, including IChO, have provided various opportunities for talented students to challenge, and contributed to discovering such students and fostering their capabilities. As the host country, Japan will make its utmost efforts to support this mission.

Because of COVID-19, like the previous Olympiad, IChO2021 will be held online. The organizers are planning to make full use of VR technology and avatar technology to provide remote tours to both state-of-the-art and traditional science and technology facilities, which large groups of people cannot usually visit. Unfortunately you will not be able to have direct interaction, however, with the creative use of these technologies, you will be able to overcome the barriers of distance and space to connect with your peers.

We hope that all of you representing your countries at this Olympiad will fully demonstrate your real abilities and the results of your efforts, improve yourselves through competitions, and make lasting friendships with peers.

It is our sincere wish that you all continue your self-improvement and make the most of your experiences to play active roles in leading your countries and the world.

HAGIUDA Koichi the Minister of Education, Culture, Sports, Science and Technology



# ICh02021 Japan Welcome Address at the Opening Ceremony on July 25

am Kohei Tamao. Thank you for your kind introduction. It is a great pleasure and honor for me to say a few words at the opening ceremony of the 53rd International Chemistry Olympiad, IChO2021 Japan.

Dear talented high school students, mentors, scientific observers, guests, distinguished scholars, invigilators, Steering Committee members, and colleagues from all over the world, welcome to the Opening Ceremony of ICh02021 Japan.

Originally, we had been preparing to hold IChO2021 Japan at Kindai University, one of the biggest private universities in Japan, located in the lively and modern commercial city of Osaka in midwest Japan, also known as the birthplace of chemical research in this country.

However, in light of the ongoing COVID-19 pandemic, we had no choice but to hold IChO2021 remotely, following the lead of IChO2020 Turkey last year.

This is the result of giving top priority to the safety of our young talented students and all participants, even at the expense of practical examinations and opportunities for in-person international exchange. I would like to thank all the International Steering Committee members led by Dr. Gábor Magyarfalvi for their enthusiastic discussion and acceptance of our decision.

Even under the difficult conditions presented by the COVID-19 pandemic, the good news is that we have accepted registrations from 85 countries and regions of the 89 to which we sent invitations. More than 320 students have been registered. I would like to express my sincere gratitude and respect for the wonderful efforts of mentors, teachers, and all concerned in each country to select talented students and set up the examination sites.

The theoretical examinations will be held on July 28th in each country, and the examination results, including gold, silver and bronze medalists, will be announced in the closing ceremony on August 2nd.

I am confident that the remote examinations on July 28th will be carried out in an atmosphere of justice, fairness, and trust, maintaining the spirit of IChO across space and time. It is my sincere hope that all the participating students will do their very best, showcasing the talents and skills they demonstrate every day.

As we are unable to hold the practical examinations, we have prepared a demonstration video of the practical tasks.

To compensate for the fact that the participants cannot meet in person, we will offer various initiatives for students to create international friendships and become familiar with Japanese culture and the state of art, science, and technology in this country.

For that purpose, VR avatars for all students have been prepared to facilitate remote networking and to give greater realism to virtual visits to sensitive areas such as the restoration site of an ancient Buddha statue and the world's largest synchrotron radiation facility, SPring-8, to which access is normally prohibited. Dear students, now I would like to ask you to keep the following three things in mind, as you are about to enjoy a once-in-a-lifetime valuable experience.

First, you have been given hope and courage to overcome difficulties through your participation in this remote ICh02021 Japan.

Second, the unprecedented difficulties we have been facing can only be overcome by international friendships and trust. Thus, you should show gratitude and respect to your mentors, teachers, invigilators, and all others who have contributed to make this major international event a reality, despite the obstacles faced.

Third, I want you to remember that chemistry, the central science, is all around us. Chemistry must therefore play a key role in finding solutions for many global challenges, including energy, environmental, and resource-related issues that humanity is now facing.

I hope that IChO2021 Japan helps to foster many talented young people who will go on to play roles as future world leaders. While you do not have the opportunity to meet each other in person this time, I am convinced that one day you may meet each other somewhere in the world when you go to university or graduate school. I sincerely hope that you take the opportunities given to you as participants in this remote IChO2021 to create strong networks of international friendship, with the slogan "Chemistry! It's Cool!" as your watchword.

Finally, I would like to thank the Ministry of Education, Sports, Science and Technology (MEXT Japan) and the Japan Science and Technology Agency (JST) for their meaningful support, and the more than 180 chemical companies and trading companies in Japan as our sponsors for their substantial financial assistance, as well as numerous personal donations.

My special thanks are also due to all the members of the Japan Committee and Organizing Committee for IChO2021 Japan, as well as our secretariat and KNT Corporate Business Company, Ltd., as represented by the Vice President of the Japan Committee and Chair of the Fundraising Committee Dr. Kyohei Takahashi, Chairs of the Finance Committee the late Dr. Tadao Kondo and Dr. Teiji Koge, Chair of the Executive Committee Professor Yoshiki Chujo, Chair of the Scientific Committee Professor Hiroshi Nishihara, and member of the International Steering Committee Professor Nobuhiro Kihara. Without their remarkable support and endeavors, this remote

IChO2021 Japan would not be possible.

Now, it is my great pleasure to officially declare remote IChO2021 Japan open. Thank you very much for your kind attention.



President, ICh02021 Japan Committee Chairman, Organizing Committee for the 53rd ICh02021, Japan



## Schedule of Remote ICh02021

Date	Student		Mentor		
Jul 25 Sup	Opening Ceremony (Virtual Reality Venue)		J 15:00 C08:00 E02:00		
Jui 25, Sun	VR Closed		Receive the problem	02 1:00 C 14:00 E08:00	
Jul 26 Mon	VP Closed		Deadline of feedback	00:00 00:00 00:00	
JUI 20, IVIUII	VRCIOSEU		Jury meeting	U2 ::00 C 14:00 C08:00	
Jul 27, Tue	VR Closed		Receive the authorized problem Translation	009:00 002:00 02:00	
	Start between Examination (5 hours)	Start between	Deadline of translation	00:00 00:00 <b>0</b> 20:00	
Jul 28, Wed		[Invigilator] Receive and print out the problem	0:55 <b>0</b> 00+00 00:1 0		
		(Jul 29)	[Invigilator] Submit the solutions (Within 2 hours after the e	nd of the examination)	
lul 20 Thu			Receive the solution and the grading scheme	00:00 00:00 00:00	
Jui 29, mu	Activity (SPring-8 Virtual tour)				
Jul 30, Fri	Video: Practical Examination ex	rolanation	<b>Receive grading</b> (from Organizer, Request arbitration)	00:00 00:00 00:00	
			Deadline of request, Jury meeting	02:00 0 14:00 00:00	
Jul 31, Sat	Activity Video:History and Culture of Nara		Arbitration America (west) >>> Asia >>> Europe >>> America (east)	009:00 002:00 02:00	
	Activity		Receive final results	00:00 C02:00 C20:00	
Aug 1, Sull	Video:Himeji Castle, Osaka, and Kyoto		Activity Video:Himeji Castle, Osaka, and Kyoto		
Aug 2, Mon	Closing Ceremo		) <b>Y</b> (Virtual Reality Venue)	J2 1:00 C 14:00 E08:00	

[]: JST = UTC + 9 []: CET = UTC + 2 (summer time) []: EST = UTC - 4 (summer time) []: CET = UTC + 2 (summer time) []: CET = UTC + 2

## Nobel Prize Research from Japan (1) (2) (3)

# Frontier Orbital Theory Kenichi Fukui

H ow do chemical reactions occur? For chemistry students, the frontier orbitals called HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) are extremely important. This concept of frontier orbitals was conceived by Kenichi Fukui, who in 1952 proposed that electrophilic substitution reactions in aromatic hydrocarbons occur at the position with the highest coefficient of HOMO, while nucleophilic reactions are determined by the coefficient



Frontier orbitals of naphthalene. a) HOMO. b) LUMO. The arrows show locations where reactivity is higher.

of LUMO. This was an epoch-making concept, completely different from the conventional theory of organic electronics, which was based mainly on electron density.



Dr. Kenichi Fukui (1918–1998)

In 1964, he further developed this theory by pointing out that the symmetry and phases of the HOMO and LUMO of the reacting molecule play important roles in cycloaddition reactions such as the Diels–Alder reaction. In 1981, he was awarded the Nobel Prize in Chemistry for "the theories concerning the course of chemical reactions," together with Roald Hoffmann, who separately published the Woodward–Hoffmann rules in 1965. Fukui was the first Japanese chemist and Asian person to be awarded the prize, which had until then been won by researchers from Europe and the United States. Today, the concept of HOMO–LUMO is widely used not only in chemical reactions and physical properties of molecules themselves, but also in molecular electronics, organic electroluminescence, enzymatic reactions, and electron transfer in interactions in biomolecules such as proteins.

# COVID-19 and mRNA Vaccines

or certain infectious diseases, it is empirically known that once a person is infected they will not contract the disease again. This is due to the function of the immune system, which remembers the disease they have been infected with and can quickly eliminate the pathogen on the second infection. Vaccines make use of this biological function. Less virulent viruses or bacteria, as well as a portion of the pathogen (protein or polysaccharide), can be administered as a vaccine. This allows the immune system to remember the pathogen and prevent infection. Vaccines against COVID-19, a new type of coronavirus, which has had a major impact on our lives since 2020, are being vigorously developed around the world, resulting in the development of mRNA vaccines. Unlike conventional vaccines, mRNA vaccines deliver mRNA, the gene for the pathogen protein, into the human body. Although mRNA vaccines have been studied since the 1990s, they have not been put to practical use due to a number of drawbacks, including the following: 1) mRNA is not stable in vivo, 2) mRNA is not very efficient in the production of proteins, and 3) it is not easy to deliver mRNA into cells. Development of effective mRNA vaccines proceeded by solving these issues one by one. This was done through introducing artificial structures into the mRNA to prevent degradation by metabolism, and optimizing the RNA sequence to increase the efficiency of conversion into protein. Furthermore, by encapsulating the mRNA in lipid nanoparticles, researchers succeeded in efficiently delivering it into the cell. As a result, an extremely effective vaccine against coronaviruses has been developed.

#### How vaccines work

Conv

mRN

entional vaccine	
Culture Inactivation (Loss of infectivity)	njection Synthesized coronavirus surface protein
A Vaccines	
Lipid coating to promote delivery to the target cells 19 A Comparison of the virus surface is analyzed and stable and efficient mBNA is surface; with the virus surface is analyzed	Captured and memorized by immune cells The next time the real virus invades the body, it is rapidly eliminated





n the era of Toyotomi Hideyoshi (1537 to 1598), drug wholesalers were concentrated in the Doshomachi area of Osaka in accordance with the government's commercial policy. During the isolationist period of the Tokugawa shogunate (1603 to 1867), exchange with foreign nations was restricted to China and Holland. Drug wholesalers who imported drugs from those two countries established their businesses in Doshomachi, forming an officially approved guild, or Kabunakama, called the Yakushunakagainakama. In 1721, the Tokugawa government established an agency in Doshomachi for checking the quality of medicinal products made in Japan (Wayakushu aratame kaisho). Hence, all medicines commercially traded throughout Japan passed through Doshomachi first. All these historical connections led to Doshomachi being home to many pharmaceutical companies, making it Japan's first "medicine town," followed later by Nihonbashi Honcho in Tokyo.



he Doshomachi Pharmaceutical and Historical Museum (Kusurinomachi Doshomachi Shiryokan) is a great place to see exhibits of prescription medicines, instruments, equipments, and other related items used by medical wholesalers. The Sukunahikona Shrine, a Shinto shrine that is dedicated to medical deities, can also be found in Doshomachi.



# Participating Teams

Armenia	📧 Costa Rica	25 Hungary	Iithuania	🜆 Oman	Slovenia	Inited Arab Emirates	
Australia	💶 Croatia	26 Iceland	38 Luxembourg	50 Pakistan	🔯 South Africa	Inited Kingdom	
3 Austria	Cyprus	27 India	💷 Malaysia	Philippines	🔤 Sri Lanka	75 United State	s of America
Azerbaijan	16 Czech Republic	Indonesia	40 Mexico	52 Poland	🛯 Sweden	76 Uruguay	
Bangladesh	🔟 Denmark	29 Iran	41 Moldova	53 Portugal	Switzerland	7 Uzbekistan	
6 Belarus	El Salvador	Ireland	🛯 Mongolia	54 Qatar	66 Syria	78 Venezuela	
Belgium	19 Estonia	Israel	43 Montenegro	55 Romania	🔯 Tajikistan	79 Vietnam	
Brazil	20 Finland	📴 Japan	4 Netherlands	56 Russian Federation	n 🔤 Thailand		
Bulgaria	21 France	33 Kazakhstan	45 New Zealand	5 Saudi Arabia	📴 Trinidad and Tobago	Observer	r Teams
🔟 Canada	📨 Georgia	Korea	46 Nigeria	58 Serbia	🔟 Turkey	<ul> <li>Afghanistan</li> </ul>	<ul> <li>Kuwait</li> </ul>
🔟 China	📧 Germany	55 Kyrgyzstan	47 North Macedonia	Singapore	📶 Turkmenistan	<ul> <li>Ecuador</li> </ul>	<ul> <li>Nepal</li> </ul>
Chinese Taipei	24 Greece	36 Latvia	🚳 Norway	💷 Slovakia	🔁 Ukraine	<ul> <li>Egypt</li> </ul>	<ul> <li>Paraguay</li> </ul>




## Short short | A Papier-mâché Tiger

In ancient Asia, tigers were considered to be messengers from the Gods, and their bones were used as a medicine and in lucky charms. In 1822, when Osaka was hit by the cholera epidemic that was sweeping the world at the time, an apothecary in Doshomachi, Osaka, created a Japanese herbal medicine containing tiger skulls and distributed it with a tiger-shaped charm made of paper called

1 (Nd, Pb, B)

3 (Nd, Fe, Co)

Hariko-no-tora, meaning a papier-mâché tiger. Although the medicine itself became obsolete, Hariko-no-tora are still handmade as traditional crafts. They are popular in the Kansai region as lucky charms that protect people from disease and express the wish for healthy growth of children.



## Useful Japanese Phrases +a the Kansai dialect

**F** ollowing on from the useful Japanese phrases introduced in Catalyzer No. 0, this edition features *Kansai-ben*, a dialect spoken in the Kansai region, where we had originally planned to hold the in-person ICh02021. Let's all try speaking *Kansai-ben*!

English	Standard Japanese	Kan Dial	sai ect	
Good bye	Sayounara	Sainara	さいなら	
l'm sorry.	Gomennasai	Sunmahen	すんまへん	
My bad.	Gomen	Suman	すまん	
Thank you!	Arigatou	Ohkini	おおきに	
Yes	Hai	Soya	そや	
No	lie	Chau	ちゃう	
foolish	bakamitai	ahokusa	あほくさ	
nonsense	kudaranai	shoumona	しょうもな	
strange	okashina	kettaina	けったいな	
because	$\sim$ nanode	$\sim$ yasakai	~やさかい	
tired	tsukareru	shindoi	しんどい	
How about?	Dou?	Donai?	どない?	
McDonald's	Mac	Makudo	まくど	
Father	Tousan	Oton	おとん	
Mother	Kasan	Okan	おかん	

\* These words are just some examples.



A neodymium magnet, known as the world's strongest permanent magnet, is made of three elements. Which of the following is the correct combination?

2 (Nd, Pd, Fe) 4 (Nd, Fe, B)



## Chemistry/ It's Cool/





Jul. 25 1908 Patented! Production method of Umami flavor (AJINOMOTO)

#### **Contact Information**

## **Catalyzer 2**



symmetric Reactions

**Cover illustration : Jury Meeting** 

## Nobel Prize Research from Japan (2)

 $S \ \ \, \text{ome organic compounds exist as two stereoisomers that} \\ are mirror images of each other (chiral molecules); the relationship resembles that of a person's right hand and left hand. Many chiral molecules are found in nature, typical examples of which are the amino acids that make up proteins in living$ 



organisms. Interestingly, proteins in living organisms are composed of only one of the mirror-image isomers (L-type amino acids). Since living organisms

· Ryoji Noyori



Dr. Ryoji Noyori (1938–)

distinguish chiral molecules, asymmetric synthesis is extremely important in the development of pharmaceuticals, flavors, and food additives. Ryoji Noyori developed unique chiral phosphorus ligand BINAP as a source of chirality essential for the synthesis of chiral compounds. BINAP has a beautiful structure with  $C_2$ symmetry, and its metal complexes enable various catalytic asymmetric reactions. One of the best known applications of BINAP is the Rh-BINAP-catalyzed asymmetric hydrogen transfer reaction, a key step in the synthesis of (–)-menthol used in flavors and pharmaceuticals. This technology has been commercialized by Takasago International Corporation (Japan), a world leader in the fragrance and flavor industry. For developing such a truly practical method for catalytic asymmetric synthesis, Ryoji Noyori was awarded the Nobel Prize in Chemistry in 2001, together with William S. Knowles and Karl Barry Sharpless.



## <u>Chemistry//It</u>sJapan// The Discovery of Umami Component ••• Kikunae Ikeda

ur sense of taste includes sweetness, sourness, saltiness, and bitterness as well as umami. The umami component was discovered by Kikunae Ikeda. Back then, the taste was thought to consist of a combination of four tastes: sweet, sour, salty, and bitter. Ikeda believed that dashi or broth made of dried bonito flakes and kelp,



contained ingredients that made people feel that a food was delicious. Motivated by this somewhat unique Japanese sensibility, he

Dr. Kikunae Ikeda (1864-1936)

attempted to identify the source of umami from kelp, and in 1908, determined that monosodium glutamate was indeed the umami component. Although glutamate itself had already been described as a chemical compound, Ikeda was the first to formulate the concept of glutamate as a component of umami. Based on this discovery, the company Ajinomoto was established, which has grown to become one of Japan's leading food companies. Ikeda also discovered the umami component of bonito, and together with his student Shintaro Kodama, discovered inosinic acid as the second umami component. Whether umami is a taste or not has been debated for a long time, but the discovery that the taste buds on the tongue contain sensors (glutamate receptors) that sense umami as well as the other four tastes has scientifically proven that humans can actually



Structure of monosodium glutamate

sense umami as a taste. The Japanese word umami has now gained currency in English and has become internationally recognized.





reld throughout the country, many of Japan's festivals are religious events. The Tenjin Festival in Osaka, the Gion Festival in Kyoto, and the Kanda Festival in Tokyo are known as Japan's three top festivals; two of them in the Kansai region of western Japan. The Tenjin Festival is held at the Osaka Tenmangu Shrine, which enshrines Sugawara no Michizane, a 9th century scholar and politician. On the night of July 25, the anniversary of Michizane's death, a boat procession is held on the Okawa River, accompanied by a fireworks display. It is known as the festival of fire and water because of the splendid sight of bonfires, lanterns, and fireworks reflected on the Okawa River. Aside from the festival, the Osaka Tenmangu Shrine also attracts students who come to pray for success in their entrance exams, as Michizane is worshipped as the god of learning. The Gion Festival has been

held at Yasaka Shrine since the 9th century. Thirty-two large floats called Yamahoko are paraded through the center of Kyoto on July 17 each year.



Teniin Festiva





## **Hinokitin :** Let a Deep-red Natural Pigment Inspire Your Curiosity

Practical Task 4 of the preparatory problems deals with nonbenzenoid aromatic compounds, a collection of which is designated in Japan as Certified Chemical Heritage No. 036. Reading the related literature, we found an article containing a comment by Tetsuo Nozoe\*, looking back on his research into a seven-membered ring compound named hinokitiol, which reads: "I was attracted by the red pigment hinokitin in the wood of the Formosan Hinoki Cypress tree (Chamaecyparis obtuse var. formosana) derived by Nenokichi Hirao". Hirao had published a paper on hinokitin in 1926 (Nihon Kagakukaishi, vol. 47, pp. 666-671). Nozoe unexpectedly discovered that hinokitin contained iron, and obtained hinokitiol by removing the iron content, leading to the discovery of a new family of chemical compounds, the nonbenzenoid aromatic compounds. Hinokitin is an iron trivalent complex with hinokitiol as a ligand. In Practical Task 4, you are to synthesize hinokitin from hinokitiol and iron (III) nitrate nonahydrate. Watch in awe as the reaction produces a compound with an impressively deep-red color (see photo). I hope that the red color of hinokitin will catalyze the curiosity and passionate spirit of inquiry of young people who will create the future of chemistry.

\*Tetsuo Nozoe (1902–1996) : Japanese Chemist, Professor of National Taiwan University (1936–1948) and Tohoku University (1948–1966)



## ╞ CHEER UP? Participants? 🗧

Welcome to IChO! I hope you are enjoying your virtual stay in Japan and getting ready for the exam. More than anything, however, enjoy your time with participants from other countries. I made many lasting friendships in IChO and I am sure you will too! When you hesitate to talk with someone because they speak a different language or come from a different culture, remember your passion

for chemistry will be the bond that connects you together. Have fun!



Tomohiro Soejima (Japan) University of California, Berkeley Department of Physics

PhD student



IChO 43rd in Ankara, Turkey Gold medal IChO 44th in Washington D.C., USA Gold medal



Stainless steel is an alloy made by adding two metals to iron. Which of the following is the correct combination of the two non-iron metal elements?

 1 (Co, Mn)
 2 (Zn, Ni)

 3 (Ca, Mn)
 4 (Cr, Ni)

## 

A s the COVID-19 pandemic continues to rage around the world, Japan too is battling waves of cases and new variants, and has started vaccinating its population in stages. Tsutenkaku Tower, the symbolic tower of Osaka, lights up in different colors to call on the local citizens to help prevent the spread of the disease. In accordance with the model adopted by the Osaka prefectural government in its countermeasures against COVID-19, the color

is red during a state of emergency, yellow when an alert is issued, and green when the alert is lifted. The tower has also been illuminated with blue lights to express gratitude to the medical personnel who are struggling on the front lines.





## Answer for Q1

## 4 (Nd, Fe, B)

A neodymium magnet contains iron and boron in addition to neodymium, as shown by the chemical formula  $Nd_2Fe_{14}B$ .

The iron generates magnetization and the neodymium directs the magnetization in one direction.

The boron keeps the distance between the iron and the neodymium atoms at an optimum level.







Chemistry/ It's Cool/

## **Contact Information**

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Catalyzer 3
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# Nobel Prize<br/>Research from<br/>Japan (3)Natural Product Chemistry that<br/>Leads to MedicinesLeads to MedicinesSatoshi Ōmura

N ature is host to countless compounds that can be used as medicines and yet remain undiscovered by humans. Satoshi Ōmura has isolated and determined the structures of many useful natural organic compounds produced by microorganisms in soil, many of which have been put to practical use. One such compound is avermectin, a substance produced by the bacterium Actinomycetes that was isolated from the soil of a golf course in Shizuoka Prefecture. Ōmura's research in collaboration with William C. Campbell showed it has strong activity as an anthelmintic, a treatment for parasitic diseases. Subsequently, a structurally modified version of this compound, ivermectin, was developed as an anthelmintic for livestock.



Dr. Satoshi Ōmura (1935-)

Furthermore, ivermectin has been shown to be effective against onchocerciasis, a disease which may lead to loss of sight, caused by filarial nematodes transmitted by mosquitoes in Africa and other tropical regions, and is now widely used as an anthelmintic. The 2015 Nobel Prize in Physiology or Medicine was awarded to Satoshi Ōmura, William C. Campbell, and Youyou Tu for "their discoveries concerning a novel therapy against infections caused by roundworm parasites." Youyou Tu also discovered artemisinin, which is the basis of a group of drugs used to treat malaria.



## Chemistry Lites Japans Studies on Urushiol ••• Rikō Majima

U rushi lacquerware is one of Japan's well-known traditional crafts. Urushi, which has a beautiful black luster, is a natural resin obtained from the sap of the lacquer tree and consists mainly of a catechol derivative called urushiol. The structure of urushiol was determined by Rikō Majima, and the research process became the starting point for the development of organic chemistry in Japan. When Majima started his research around 1900, chemistry in Japan was still in its infancy, and there was a serious shortage of skilled chemists to guide experimental research. Majima studied organic chemistry almost entirely on his own and became acutely aware



of the gap in ability between Japan and the Western countries; at the same time he came to the conclusion that if he could conduct research on lacquer, which is native to the Orient, he would be able to develop his own original research without being outdone by researchers from other countries.

Urushiol: originally a light-yellow resin, it turned blackish after 100 years

A fter studying in Germany, Majima began to determine the structure of urushiol in earnest at Tohoku Imperial University. With the latest European methods such as advanced vacuum distillation, ozonolysis, and catalytic reduction, he tried to determine the structure of urushiol. After several steps, he finally determined that urushiol exists as a mixture of the compounds shown in



**Dr. Rikō Majima** (1874–1962)

the figure. Majima began to determine the structures of many other natural products found only in the Orient such as indole and aconite alkaloids, in addition to urushiol, and trained many of his students as organic chemists. His students eventually established organic chemistry laboratories at universities around the country and laid the foundation for modern organic chemistry in Japan.

Figure: Structure of Urushiol



#### Tale related to Preparatory Problem



## Green tea, a part of Japanese culture

What would you drink when you are thirsty? Water, juice, soda, or tea? Tea, particularly green tea, is very popular in Japan among other countries. Tea is classified into three major types: green tea (unfermented), black tea (fermented), and the rest such as oolong tea (semi-fermented). As introduced in preparatory problem 23, green-tea culture in Japan started in the early 1200s. The most famous form is the traditional 'tea ceremony', during which *matcha* is prepared and drunk. In addition, green tea is largely consumed as a regular beverage on a daily basis and has been associated with a variety of health benefits. Tea leaves contain several catechins such as epicatechin, epigallocatechin, epicatechin gallate, and epigallocatechin gallate, which are responsible for the characteristic taste (*shibumi*) of green tea. Japan also made significant contributions to green-tea chemistry. For instance, Michiyo Tsujimura, the first Japanese female doctor of agriculture, isolated catechin from green tea for the first time in 1929. Green tea also contains caffeine, which has a bitter taste (nigami), and theanine, which adds a savory (*umami*) flavor. While green tea is produced by suppressing the oxidation of tea leaves, black tea is produced by fermentation of the tea leaves, promoting oxidative dimerization of catechins to give theaflavins, which have a benzotropolone core structure and are characteristic pigments of black tea.

## Himeji Castle Kansai Scenes

Himeji Castle (or *Himeji-jo* in Japanese) is an excellent surviving example of a modern Japanese castle. Described as a *Hirayama Jo* in Japanese, meaning a hilltop castle, it is located in the north of present-day Himeji. It is one of the original 12 castle towers (tenshu) which were built in the Edo period (1603 to 1868), and is designated as one of the 100 Great Castles in Japan. Himeji Castle was designated as a National Treasure in 1951, and a UNESCO World Heritage Site (Cultural) in 1993; so becoming Japan's first cultural World Heritage Site. The present castle tower was built in 1609 by Ikeda Terumasa, a warlord who married Tokuhime, the second daughter of Tokugawa Ieyasu, the founder of the Edo bakufu (shogunate). The castle is also known fondly as Shirasagi-jo (White Egret Castle), as its elegant figure resembles an egret with its wings outstretched. The castle is characterized by brilliant white stucco exterior walls and features a huge *tenshu* (main tower) with five layered roofs and seven stories (one underground and six above ground), which is interconnected with smaller towers (the East, the West, and the Northwest) by watari-yagura roofed passages. The tenshu was restored to its current beautiful condition after five-and-a-half years of restoration work that stretched from 2009 to 2015.







## ╞ CHEER UP? Participants? 🗧

Not just IChO, but even the months leading up to it, are like a dream come true. Not only are you stimulated intellectually but you get to meet remarkable people at truly amazing places in the world. The knowledge, the drive, and encouragement you take away are unparalleled and stay with you for life.



from Maaha Ayub (Pakistan)

IChO 49th in Nakhon Pathom, Thailand Bronze Medal

## Answer for Q2

## 4 (Cr, Ni)

Stainless steel was developed to strengthen iron's rust resistance, and a number of researchers contributed to its improvement during the 19th and 20th centuries. The metals added to iron are typically chromium and nickel, which form a passive layer on the surface, preventing rust caused by air or water. Today, stainless steel is widely used, for example, in cooking utensils, vehicles, and machine parts.

## Element # 2



dine, with atomic number 53 and an atomic weight of 126.9, is represented by

the symbol I. It belongs to Group 17, the halogen group, together with elements such as bromine, chlorine, and fluorine. Although Japan is usually characterized as a country poor in natural resources, it is placed second in the world after Chile in the production of iodine. Eighty percent of iodine is produced from sodium iodide dissolved in ancient seawater in natural gas wells in Chiba Prefecture. Japan even exports iodine to other countries around the world.

I odine is a dark purple solid at room temperature and <sup>127</sup>I is its only stable isotope, with a natural abundance of almost 100%. The isotope <sup>131</sup>I is a fission product of uranium and other radioactive elements, and it has a half-life of around 8 days transforming <sup>131</sup>Xe with beta and gamma emissions. Therefore, stable <sup>127</sup>I can be used to protect people from health hazards caused by a nuclear accident. Iodine as an element has a variety of uses in our lives such as X-ray contrast agents, bactericidal disinfectants, and polarizers used in screens of LCD TVs, PCs, and smartphones.

→ ince iodine is a component of thyroid hormones, a shortage of iodine

S ince iodine is a component of thyroid hormon in the body may lead to the condition known as hypothyroidism. However, such shortages are rare in Japanese because the country is surrounded by sea and sufficient iodine can be obtained from a diet rich in seaweed and a variety of seafoods. By contrast, many people living in other parts of the world are exposed to the risk of iodine deficiency. Thus, potassium iodide or potassium iodate is added to the table salt to prevent it.









Chemistry! It's Cool!

Insulin extraction

#### **Contact Information**

**Catalyzer 4** 



## Message from Dr. Akira Yoshino

H ello, everyone. This is Akira Yoshino. Congratulations to all the representatives from all over the world who participated in the 2021 International Chemistry Olympiad in Japan. I congratulate you on your daily interest in chemistry and the fruits of your enthusiastic learning. We would also like to extend our congratulations and respect to the mentors from each country who have nurtured such wonderful athletes.

The International Chemistry Olympiad is an international event in which high school students from all over the world compete for their chemistry skills. Not only that, but it also builds a human resources network for young people through international exchange and deepens their understanding of Japanese culture. It will be of great significance to develop human resources who will be in a leadership position in the future.

Unfortunately, due to the influence of the new coronavirus pandemic, it has become a remote competition, but even in such a difficult situation, it is the relationship of international trust that has been built up so far. I would like to once again recognize with you that it is supported by the depth of friendship, and I would like to express my sincere gratitude to all the people concerned and the executive committees of each country for their efforts.

Chemistry is central science. It plays an important role in creating new substances by making full use of the properties of elements. I received the Nobel Prize in Chemistry in 2019 for developing a lithium-ion secondary battery and leading it to practical use. In this development, after a long basic research based on the properties of lithium, cobalt, carbon, etc., it was put into practical use. In this way, the results of basic research in chemistry have the power to change the social system. Chemistry must play a leading role in solving various problems such as environment, resources, energy, and health that are currently facing on a global scale. And they are entrusted to a younger generation like you.

You are the leaders of each country and the world in the future. Please take pride in participating in the International Chemistry Olympiad, and remind yourself of the importance of these roles in chemistry for further development.

Please do your best in the written test and enjoy the VR videos of various research facilities and cultural activities that are prepared to deepen your exchange. This is my greeting.

Dr. Akira Yoshino Honorary Fellow, Asahi Kasei Corp. 2019 Nobel Laureate in Chemistry



Catalyzer 221

## Nobel Prize Research from Japan **Development of Lithium-ion** Secondary Batteries ----- Akira Yoshino

How to make rainbow indica

ithium-ion batteries (Li-ion batteries) are used in all aspects ▲ of modern life, from small smartphones and notebook computers to electric vehicles, due to their features such as light weight, rechargeability, and high capacity. It would not be an exaggeration to say that Li-ion batteries enable us to freely carry electricity around. It all started in 1976 when Stanley Whittingham developed a revolutionary rechargeable battery using metallic lithium for the anode and titanium disulfide for the cathode, which intercalates lithium ions. Later, John B. Goodenough developed a battery using lithium-cobalt oxide (LiCoO<sub>2</sub>) as the cathode, but the practicality of this battery was challenged by the fact that it used metallic lithium as the anode, which posed the risk of explosion and ignition. Akira Yoshino(photo: previous page) overcame these safety and stability issues by using carbon materials for the anode, and laid the foundation for practical Li-ion batteries. For these achievements, Akira Yoshino, John Goodenough, and Stanley Whittingham were awarded the Nobel Prize in Chemistry in 2019. Akira Yoshino was born and raised in Osaka, where IChO2021 was to be held. He says he was inspired

to pursue chemistry by the book "THE CHEMICAL HISTORY OF A CANDLE", written by Michael Faraday, which his homeroom teacher in elementary school recommended he read.



## Tale related to Preparatory Problem ••• Theoretical Task 10

Universal indicators are widely used to check the pH values of aqueous solutions. Nowadays, the most popular universal indicator shows red in acidic conditions and blue in basic conditions, the same color variation as that of the rainbow and therefore easy to remember. Is there a suitable molecule that will show such a drastic color change alone? The answer is no: universal indicator is a mixture of several indicators. The original recipe was proposed by a Japanese researcher, Shinobu Yamada, in 1933. Let's see how he cleverly mixed the individual indicators to achieve a rainbow of colors. Thymol blue (TB) changes from red to blue via yellow. To generate the color orange, methyl red (MR) is added. Because of the pKa gap between TB and MR, we can generate an orange color, which is the mixture of red (MR) and yellow (TB), around a pH of 3 to 4. Bromothymol blue (BTB) is used to generate a green color. Using the pKa gap between TB and BTB, we can generate green, which is a mixture of yellow (BTB) and blue (TB), around a pH of 7 to 8. Note that MR in basic conditions and BTB in acidic conditions are yellow. Therefore, too much MR makes the solution green in basic conditions, and too much BTB makes the solution orange in acidic conditions. Fortunately, phenolphthalein (PP) is colorless

in acidic and neutral conditions, and therefore the purple color in basic conditions can be adjusted relatively easily. The appropriate constituent ratio is determined by human eyes with a trial-and-error process. We are thankful for Yamada's keen eyes that gave us this universal indicator today.



Color chart of indicators used for Yamada universal indicator (note that the colors and their variations are qualitative).

## Chemistry#It<sup>1</sup>s-Japan#

## Spectrochemical Series ... Ryutaro Tsuchida

G ems and pigments have attracted human beings with their beautiful colors since ancient times. Such colors are mainly caused by transition metal ions: the colors depend on not only types of metal, but also the ligands attached to the metal, and the coordination structures. However, the colors we see are mere sensory expression, which differs from individual to individual. Thus, quantifying the colors derived from inorganic compounds as energy and understanding the causes of these colors has been a major challenge for complex chemistry.

C omplex chemistry was first brought to Japan by Yuji Shibata (1882-1980), who learned from Alfred Werner, the founding father of modern complex chemistry, and later taught at Tokyo Imperial University and Nagoya Imperial University as a Professor. His student Ryutaro Tsuchida, who later taught as professor at Osaka Imperial University, became interested in the relationship between color and ligands in metal complexes. After conducting measurement of the electronic absorption spectra of a numerous kind of metal complexes, he discovered a quantitative relationship between the wavelength of the absorption band and the ligand. Based on this





Company logo of

Kagaku-Dojin

Complexes synthesized and organized by Tsuchida in the order of the spectrochemical series. Source: *Kinzoku Sakutaino Iro To Kozo (The color and structure* of metal complexes). 1944. Zoshinsha.

finding, he proposed the spectrochemical series (1938), in which ligands and metal ions are arranged in the order of the energy difference of the d-d transition of octahedral metal complexes. Later, it was theoretically supported by ligand field theory, which considers the covalent nature of the metal-ligand bond, and it became clear that the spectrochemical series is an



Dr. Ryutaro Tsuchida (1903–1962)

order of ligand field splitting energies. In addition to colors, Tsuchida was also strongly interested in the steric structure. He assumed the coordination bonds in complexes to be in the same bonding state as the covalent bonds in organic compounds, and the most stable molecular structure is the one that minimizes the repulsion between all electron pairs. This model that Tsuchida conceived was actually almost the same as the model known as the VSEPR rule today; however, this would not be known globally, since Japan was at midst of war. This achievement is very typical of Tsuchida, we may say, who was always conscious of correlations between "structure and properties" of complexes.

In addition to his chemical research, Tsuchida also devoted himself to the expansion of chemical education as well as his own research. He was involved in producing teaching guidelines for high school chemistry and handbooks to chemical experiments, and he was also involved in launching and publishing chemical magazines for general public. In particular, he was a long-time member of the editorial board of the monthly magazine *"Kagaku* (Chemistry)" (first published in 1951) : this periodical is still published today, and the logo he designed for the magazine is still used as company logo of Kagaku-Dojin.



## Fushîmî Inarî Taîsha Shrîne

F ushimi Inari Taisha, also known as Oinari-san, is the most important of the Inari shrines that are dotted throughout Japan, and is located in Fushimi-ku, Kyoto. Since the shrine was established in 711, it has been worshipped as a god of good harvest, prosperous business, safety in the home, and fulfillment of wishes. The foxes that serve as messengers of the shrine are also cherished by the people. From the first *torii* gate on the main approach to the shrine, the outer hall of worship (maiden), inner hall of worship, and main hall of worship are arranged in a straight line. It is said that there are about 10,000 *torii* contributed





by followers, including the beautiful vermilion *senbon torii* (one thousand gates) that line the mountain. *Fushimi Inari Taisha* is one of the most popular tourist spots among people visiting Japan.





## ╞ CHEER UP! Participants! 🗧

Hello, dear Olympians! My name is Edith Leal and I represented the mexican delegation in the 45th and 46th IChO and now I'm studying my PhD in Chemistry. Looking back from the future, the best advice I can give to you is to give your personal best. Meeting so many young people, who are very intelligent and who seem better prepared for the tasks than you can be very overwhelming, however, remember that just by being here, you have already won a lot of knowledge, from the fundamentals of Chemistry, beyond your usual high school program, to the very specialized Preparatory Problems, which some of them are so specialized, they can be difficult to encounter, even as an undergraduate Chemist. So, stop worrying about anything else and focus into putting everything you know on the questions in the exam, so that when you finish, you feel satisfied and happy with yourself.

Greetings and my very best wishes!



IChO 45th In Moscow, Russian Pederaton Participant IChO 46th in Hanoi, Vietnam Bronze medal





## Japanese mineral resources

-	- Basic Information				
	Origin of the name: Greek word <i>lithos</i> (stone)				
	Discovered by: J. A. Arfvedson (Sweden) [1817].				
	Global reserves: 21 million tons				
	Maior reserve countries: Chile. Australia. Argentina				
	Global production: 82.000 tons				
	Maior producers: Australia, Chile, China				
	·····, -····				

L ithium-ion batteries are widely used in smartphones and notebook computers today. The applications of these lightweight and high-performance secondary batteries in electric vehicles have grown, in part due to a shift towards a decarbonized society. Akira

Yoshino, a Nobel laureate in chemistry in 2019, developed a new battery using a lithium oxide compound as the cathode and a carbon material as the anode (See page 2 of this issue).



© The Courtyard of our Mineral

#### Answer for Q3

#### 1 Ba

In 1938, German Chemists Otto Hahn and Fritz Strassmann discovered that when uranium-235 is bombarded with neutrons, radioactive barium, krypton, neutrons, and an enormous amount of energy are released. This discovery led to the development of nuclear energy.



Assume you have the same volume of gold, silver, copper, and mercury, and they are all at the same temperature. Which of these metals is the heaviest among them?

Gold 2 Silver 3 Copper 4 Mercury

## Chemistry/ It's Cool/





#### **Contact Information**

## **Catalyzer 5**



# Nobel Prize Soft Laser Desorption for Mass Research from Spectrometry Japan (3) Spectrometry

R ecent years have seen a growing need for methods to determine the structure of biomolecules such as proteins, carbohydrates, and lipids. Koichi Tanaka, an engineer at Shimadzu Corporation, has developed an innovative method to enable mass spectrometry of such large biomolecules. Mass spectrometry (MS) is an analytical method for measuring the mass of a material in its ionic state, based on its mass-to-charge ratio, and to do this, the sample (analyte) must first be ionized. Previously, electron ionization (EI), in which the sample is irradiated with thermal electrons, was mainly used for this process, but this did not provide useful information on the mass of biological macromolecules with high molecular weights such as proteins, because they are hard to volatilize and are easily



decomposed by heat. On the other hand, in the soft laser ionization method such as the matrix-assisted laser desorption/ionization (MALDI) method, the analyte is mixed with a viscous liquid known as a matrix and irradiated with an ultraviolet laser beam, which causes rapid heating and ablation of the matrix as well as vaporization and ionization of the sample, enabling a soft ionization of the



Dr. Koichi Tanaka ( 1959– )

analyte. It is said that this method was conceived when a sample was mistakenly prepared using glycerin instead of acetone, and the sample was analyzed so as not to waste it. This method becomes a particularly powerful tool when analyzing compounds with large molecular weights, making it possible to measure compounds with molecular weights of 100,000 or more. MALDI, and another method known as electrospray ionization (ESI), developed by John B. Fenn, are currently the main methods used for ionizing organic compounds for mass spectrometry. The 2002 Nobel Prize in Chemistry was awarded "for the development of methods for identification and structure analyses of biological macromolecules" to Koichi Tanaka, John B. Fenn, and Kurt Wüthrich for their achievements in protein structure analysis. This particular year's Nobel Prize in Chemistry was unique in that it was awarded for the development of fundamental technologies that support advanced research.

# <image>

## Chemistry//It<sup>1</sup>s-Japan//

New Nomination

**Periodic Table** 



N ihonium is the 113th element (symbol: Nh) of the periodic table. This element was first discovered in July 2004 by Kosuke Morita and his group at RIKEN, Japan's largest multidisciplinary research institution. After two successful follow-up tests and certification of the element's discovery at the end of December 2015, the name nihonium and the symbol Nh were officially ratified in November 2016. This became the first element to be named in the Asian region, as all the elements identified until then had been found in Western countries. Nihonium (278Nh), was artificially synthesized by fusing two types of nuclei: a thin film of bismuth (209Bi) with atomic number 83 and mass number 209 was irradiated with a beam of zinc (70Zn) with atomic number 30 and mass number 70 that had been accelerated to about 10% of the speed of light. In this experiment, a large linear accelerator (RILAC) with the world's highest beam intensity and a gas-filled recoil separator (GARIS), which extracts only the 113th element from the countless particles produced by irradiation, played a major role. The probability of nuclei fusing is extremely small, and only three atoms of nihonium were obtained after 400 trillion collisions. It was also revealed that the lifetime of nihonium is only 344 microseconds.

E lements up to the 118th, oganesson (Og), have now been reported, completing the 7th period of the periodic table.



## Akashi Kaikyo Bridge Kansai Scenes 5 the longest suspension bridge in the world

The Akashi Kaikyo Bridge is one of the world's longest bridges. It crosses the Akashi Strait (or Akashi Kaikyo in Japanese),



linking Kobe on the mainland of Honshu with Iwaya on Awaji Island, and has a total length of 3,911 meters and central span of 1,991 meters. Awaji is then linked with the island of Shikoku by another suspension bridge called the Onaruto Bridge that crosses the Naruto Strait, well-known for the massive Naruto Whirlpools. Together, these two great bridges provide a seamless route for people travelling between the islands of Honshu and Shikoku.

The suspension cables of the Akashi Kaikyo Bridge are supported by two main towers, which rise 288.3 meters above the sea. The main cables of the supporting towers consist of 290 strands (wire bundles with regular hexagonal cross sections), each of which is made of 127 high-tensile galvanized steel wires. Each cable has a diameter of 112.2 centimeters and can support a load of up to 60,000 tonnes. To protect the wires from wind and rain and to prevent corrosion, their surfaces are coated with rubber, and the cable interiors are protected with desalted and dehumidified air, maintaining the strength and durability of this marvelous suspension bridge.











## **Japanese mineral resources**

Basic Information Origin of the name: the Latin name of the River Rhine. Rhenus Discovered by: W. Nodak, I. Tacke, and O. Berke (Germany) [1925] Global reserves: 2,400 tons Major reserve countries: Chile, the USA, Russia Global production: 53 tons Major producers: Chile, Poland, the USA

n 1908, Masataka Ogawa, who was studying at the University of London at the time, reported his discovery of element 43, which he named nipponium (Np), in the mineral trianite produced in Sri Lanka (then Ceylon). Unfortunately, his analysis was later

found to be inaccurate, and the element Ogawa had discovered was actually element 75, rhenium, which is one row down on the periodic table. If his analysis had been accurate, there might have been an element named after Japan more than 100 years before nihonium (Nh).



## **Answer for Q4**

#### 1 Gold

Density (weight per cubic centimeter =  $g/cm^3$ ) is used to compare the weights of substances. The density of water is defined as 1.0 g/cm<sup>3</sup>. The densities of the four metals are 19.3, 10.5, 8.96, and 13.6 g/cm<sup>3</sup> for gold, silver, copper, and mercury, respectively; thus, gold is the heaviest of the four. The heaviest of all known metals is osmium, with a density of 22.6 g/cm<sup>3</sup>.

**Jul. 29** 1836 Completed! Triumphal arch in Paris

#### **Contact Information**

## **Catalyzer 6**



# Nobel Prize<br/>Research from<br/>Japan (1) (2) (2)Development of Palladium-Catalyzed<br/>Cross Coupling ..... Akira Suzuki / Ei-ichi Negishi

M any of the functional materials and pharmaceuticals that are indispensable to modern life are created by organic synthetic reactions. In order to synthesize such useful materials, carbon-carbon bond formation reactions are indispensable to link the carbon atoms of organic molecules. A typical example of such a cross-coupling reaction is the chemical transformation of benzene rings. This reaction is difficult to achieve by traditional methods using carbocations and carbanions, but was found to be more easily accomplished by using transition-metal catalysts. It is no exaggeration to say that the field



of cross-coupling reactions has been led by Japanese researchers, and in particular, the palladiumcatalyzed cross-coupling reactions of aryl halides with arylmetal (boron or zinc) reagents developed by Akira Suzuki and Ei-



Dr. Akira Suzuki Dr. Ei-ichi Negishi (1930–) (1935–2021)

ichi Negishi in the 1970s are extremely versatile. They have a wide range of applications, and are currently being used in the synthesis of numerous pharmaceuticals and organic electroluminescent materials. In 2010, Akira Suzuki and Ei-ichi Negishi were awarded the Nobel Prize in Chemistry, together with Richard F. Heck, for the development of such a truly practical synthetic reaction.

## Unsaturated bonds between heavier main-group elements

In the late 1800s, the periodicity of the properties of elements was discovered; this concept suggests that elements that exhibit similar properties appear in a periodic order when arranged according to their atomic numbers. Ultimately, the stringent application of this principle resulted in the creation of the periodic table of elements by Mendeleev in 1869. In general, elements in the same group, *i.e.*, those located in the same column in the periodic table, are thus expected to exhibit similar properties. *What do you think about this statement? Is this true for all the elements in the same group?* 

Silicon is the heavier homologue closest to carbon in the periodic table, and the analogies between carbon and silicon have been discussed controversially for a long time. For example, while the chemistry of unsaturated compounds of the main-

group elements of the second row such as olefins  $(R_2C=CR_2)$ is plentiful, that of the heavier-element homologues of these



multiple-bond compounds has remained underdeveloped in comparison, which is predominantly due to their extremely high reactivity and inherent instability under ambient conditions. Prior to the 1970s, all attempts to synthesize compounds with multiple bonds between heavier main-group elements were unsuccessful, and only cyclic oligomers or polymers with single covalent bonds between the main-group elements were obtained. Accordingly, the scientific consensus at the time was that such heavier main-group elements are probably not able to form  $\pi$ -bonds ('double-bond rule'). However, ambitious chemists were ultimately able to isolate and characterize several kinds of such compounds with unsaturated bonds between heavier main-group elements using bulky substituents for steric protection ('kinetic stabilization'). For example, the first distannene (R<sub>2</sub>Sn=SnR<sub>2</sub>, Lappert 1973), diphosphene (RP=PR, Yoshifuji 1981), disilene (R₂Si=SiR₂, West 1981), and disilynes (RSi≡SiR, Wiberg and Sekiguchi 2004) have been synthesized as stable compounds by using sterically demanding substituents, which disproved the double-bond rule. Since then, the unique features of unsaturated compounds of heavier main-group elements have been investigated in detail, attracting much attention to the area of main-groupelement chemistry. For example, it has been reported that disilenes (R<sub>2</sub>Si=SiR<sub>2</sub>) and disilynes (RSi=SiR) exhibit pyramidalized and bent geometries, respectively, which stands in sharp contrast to the planar geometry of ethylene and the linear structure of acetylene. These different structural features should in turn cause different reactivity and properties, and thus, the chemistry of unsaturated silicon compounds can be expected to be characterized by unprecedented functions and chemistry that is different from that of carbon. Thus, it should be noted here that the structure and chemistry of the second-row elements is considerably different in from those of the heavier main-group elements, as exemplified by the case of H<sub>2</sub>O (bp: 100 °C;  $\checkmark$  HOH  $\approx$  104.5°) vs. H<sub>2</sub>S (bp: -60 °C;  $\checkmark$  HSH  $\approx$  92°)



Chemistry//It<sup>2</sup>s-Japan//

## **Discovery of Adrenaline**

## ••• Jokichi Takamine / Keizo Uenaka

When one feels anxious, excited, or nervous, such as during important exams, public presentations, cheering on sports teams, muscle training, or when in love, our blood pressure rises and our heart rate increases. A hormone called adrenaline is secreted by the adrenal medulla when the sympathetic nervous system becomes dominant. Adrenaline was the first hormone to be isolated by scientists, in the year 1900. Jokichi Takamine and Keizo Uenaka (1876–1960) played key roles in this discovery. They succeeded in obtaining 7 grams of adrenaline crystals from 9 kilograms of bovine and sheep adrenal tissue by



Dr. Jokichi Takamine ( 1854–1922 )

ansai

repeated acid and base extraction. Only after the first successful isolation did the hormone become commercialized as adrenaline preparation. Since then, it has become an indispensable agent for raising blood pressure in surgery, ophthalmology, and internal medicine. The number of lives adrenaline has saved to date is testament to the importance of this achievement for humanity. In vivo, adrenaline is biosynthesized via L-tyrosine, L-dopa, dopamine, and noradrenaline.



Adrenaline

## **Daibutsuden**The world's largest wooden structure

onstruction of the Great Buddha of Nara started in the year 📕 745, after Emperor Shomu decided to build a huge statue of Buddha to placate social disturbances in the wake of multiple coups and rebellions. The Buddha statue was completed in 752. The current Buddha is approximately 14.7 meters tall, and the circumferences of the platform, the head, and the palm are 70 meters, 2.6 meters, and 2.6 meters respectively. The head was restored in the Edo (Tokugawa) period (1603 to 1868), and most of the body was restored during the Kamakura period (1185 to 1333), but parts of the original statue still remain. The amount of copper used for building the Buddha varies slightly, depending on the historical record, but it is estimated to be 500 tons. Mercury used as a solvent in the plating process and arsenic contained in copper are said to have caused poisoning of nearby residents, and a medical center was established to treat these patients. The Hall where the Great Buddha



(*Daibutsuden*) is enshrined today is 57.5 meters wide in the east-west direction, 50.5 meters deep, and 49.1 meters high to the ridge of the roof. It is the largest wooden frame building in the world, and was designated by the Japanese government as a National Treasure in 1952.



## Early Bird Communication





## Answer for Q5

## 2 Davy

Humphrey Davy discovered as many as six elements from nature in his lifetime by electrolyzing a huge number of substances using Volta batteries.



Basic Information

## Japanese mineral resources Palladium

Origin of the name: Named after the asteroid Pallas Discovered by: W. H. Wollaston (the UK) [1803] Global production: 210 tons

Major producers: Russia, South Africa, Canada

P alladium catalysts are vital to the efficient formation of carboncarbon bonds. The compounds produced by cross-coupling reactions with these catalysts are indispensable to industry, from pharmaceuticals and agricultural chemicals to liquid crystals and organic light-emitting diodes. About 60% of palladium production is used in catalysts (three-way catalysts) for the removal of incomplete combustion products and unburned gasoline in automobile exhaust.



© Crystal Museun



## Chemistry! It's Cool!





## **Contact Information**

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Catalyzer 7
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#### **Green Fluorescent Protein** Research from ······· Osamu Shimom Japan 🛛 🍘 🛞

samu Shimomura became interested in how the bioluminescent jellyfish Aequorea victoria glows in the dark, and went to Friday Harbor in the U.S. state of Washington with his family every summer to solve the mystery. They collected as many as 850,000 jellyfish and investigated the nature of the substance that made them glow. He isolated the substance in question, a kind of protein called green fluorescent protein (GFP). This protein undergoes a structural transformation to become a chromophore



and emits fluorescence; specifically, via cyclization and oxidation of three amino acid residues, Ser65-Tyr66-Gly67. In the jellyfish body, the calcium-responsive protein aequorin absorbs light, and then emits blue fluorescence; in turn, GFP absorbs this blue light and glows green. However, GFP can also glow on its own, so Martin Chalfie and Roger Y.



Dr. Osamu Shimomura (1928-2018)

Tsien used genetic engineering to develop a method of attaching GFP to other proteins and making them glow. This tool enabled the analysis of various biological phenomena in cells to reveal the subcellular localization of proteins (GFP tags), and advanced research in a wide range of fields including cell and molecular biology, developmental biology, and medicine. The 2008 Nobel Prize in Chemistry was awarded to Osamu Shimomura, Martin Chalfie, and Roger Y. Tsien for "the discovery and development of the green fluorescent protein, GFP." Today, artificial fluorescent proteins that glow in a variety of colors are being produced.



**Nobel Prize** 

## ••• IChO2021 Problem Q6 ••• **Coordination polymers: found in minerals - promising** rage materials for small molecules

An enormous variety of minerals exist in nature. Most of these are inorganic compounds, while some are known as organic minerals. For example, there are currently 23 known organic minerals that contain carboxylic acids such as formic acid, oxalic acid, or acetic acid. In oxalate minerals, the two carboxylate groups (-COO<sup>-</sup>) of oxalic acid are linked to various metal ions by coordination bonds to form network crystal structures (Fig. 1). Although not an organic mineral, Prussian blue, which was accidentally discovered in Germany in the early 17th century and has ever since been valued as a blue dye, adopts a crystal structure in which iron cations and cyanide anions (CN<sup>-</sup>) are linked by coordination bonds (Fig. 2). Prussian blue was also used in Katsushika Hokusai's famous woodblock print "Under the Wave off Kanagawa" (ca. 1831; Fig. 2). Such crystalline network structures, which arise from coordination bonds between metal ions and bridging ligands, are called 'coordination polymers'.

In the middle of the 19th century, in parallel to the development of X-ray crystallography, chemists began to synthesize new

(left) Photo of a macroscopic crystal of calc te and (right) its microscopic crystal struc mined by single-crystal X-ray diffraction analysis

ussian blue the Mave

coordination polymers using organic ligands that do not necessarily exist in nature. The crystal structure of an organic ligand-bridged coordination polymer that consists of adiponitrile and copper ions was firstly reported by Yoshihiko Saito et al. in 1959 (Fig. 3; left). We can only wonder how amazed these scientists must have been at the time by the complexity of the "reticular" networks of these crystal structures. After that, various other crystal structures were reported and chemists started to think about useful applications for these characteristic crystal structures.

In 1997, Susumu Kitagawa of Kyoto University discovered that the nanometer-sized small pores formed inside coordination polymers that consist of cobalt ions and bipyridine could be used as a gas-storage material (Fig. 3; right). Such "porous coordination polymers" can store large amounts of gas inside the crystals and are now being put to practical use. The applications of these materials can be expected to continue to expand in the future and probable applications include storing  $H_2$  to power fuel cells, capturing  $CO_2$ to ameliorate global warming, and storing H<sub>2</sub>O to water the desert.





## Kumano Kodo Scenes 7

▼umano Kodo (literally means the old ways of Kumano) is a K general term for the network of pilgrimage routes that lead to the three main Kumano Shrines: Kumano Hayatama Taisha, Kumano Hongu Taisha, and Kumano Nachi Taisha. Located in the southwestern part of the Kii Peninsula and starting eastwards from the city of Tanabe, the network spans Mie, Nara, Wakayama, and Osaka Prefectures. It was registered as a UNESCO World Cultural Heritage Site in 2004. Kumano is regarded by the Japanese people as a sacred place for mountain worship, a practice that originates from the worship of nature in which the gods dwell in rivers, waterfalls, and huge rocks. The Kumano Kodo is also mentioned in the ancient history book Nihon Shoki, written during the Nara period (710 to 794). People walking the routes today can see the same scenery as the pilgrims who visited Kumano to gain enlightenment in the old days, including such joys of nature as the large cypress trees that are more than 800 years old, and the smooth cobblestones on the paths.



## Other Local Dialects in the Kansai Region

In Catalyzer No. 0, we presented a list of useful Japanese phrases, and in Catalyzer No. 1, a comparison of everyday phrases in Standard Japanese and *Kansai-ben*, a dialect spoken in the Kansai region. There are several subregional dialects too, each with distinctive expressions, spoken in various parts of Kansai. When a Kansai person speaks, we can often tell which part in the region they come from. The English phrase "Very Good!", for example, is Totemo line! in standard Japanese, *Meccha Eeyan*! in Osaka; *Erai Yoroshiyan*! in Kyoto; *Erai Eegai*! in Hyogo; *Erai Eenaa*! in Shiga; *Gottsu Eena*! in Nara; and *Yanikoo Eewaisho*! in Wakayama. Look at some of the other differences in the table below.



English	Standard Japanese	Osaka	Hyogo	Kyoto	Shiga	Nara	Wakayama
l agree.	Sou-dane.	Seya-na.	Seya-na.	Soya-na.	Hoya-na.	Seya-na.	Soya-ne.
No, you can't!	Dame-dayo!	Akan-de!	Akkai-ya!	Akan-shi!	Akasen!	Akan-de!	Akanaa!
Lots	Takusan	Gyousan	Jousan	Tanto	Yokke	Youke	Yousan
No problem.	Kamaimasen.	Kamahen.	Becchonai.	Dannai.	Dannai.	Kamahin.	Kitsukainai.
l can't.	Dekinai.	Dekehen.	Dekihin.	Yousimahen.	Dekihin.	Dekiyan.	Yousen.
Bottom	Saikai	Dobe	Getta	Bebetako	Gebeccha	Bebeta	Betta
Do not come	Konai	Kēhen	Kōhen	Kīhin	Kiyahen	Kyahen	Kēhen

\* These words are just some examples.



#### A message from the student narrators of the practical examination video

We are fortunate to be given this opportunity to help the International Chemistry Olympics in this way. We are students who like both English and chemistry. We believed challenging ourselves to try new things would give us new perspectives, and we thought taking this opportunity would give us new discoveries and experiences. Being able to participate in this event with friends was another incentive as well.

Although it wasn't an easy task to pronounce the long names of chemical substances or highly technical chemistry terms properly, we enjoyed dealing with it.

Most of us hope to work in a science field such as medicine. biology, or space aeronautics. Some of us would like to deal with environmental problems in the future as well. We are sure we need to use English to work in this field with the global scene. We will make good use of this experience that has given

us a chance to get to know what practical English is like. Thank you.













## **Short short from Editors**

# The book to take you to the world of Chemistry

Do you remember what made you fell in love with Chemistry? In Japan, there are illustrated books that introduce chemistry to children and fascinates chemists at the same time. Kako is also a scientist himself and has written many Chemistry stories for children. One of

them is "Nakayoshi Ijiwaru Genso no Gakkou." It means "School of ELEMENTS with good friends and mean friends." This book introduces the process of creating the periodic table by comparing the properties of elements to the personalities of human classmates.



Little Daruma series





Origin of the name: Latin word *indicum* (indigo) Discovered by: H. T. Richter and F. Reich (Germany) [1863] Global production: 900 tons Major producers: China, South Korea, Japan

Indium is an essential material for liquid crystal displays (LCDs), which are widely used for flat-screen TVs and notebook computers. Indium tin oxide (ITO) is used for electrodes in LCD panels because it is both transparent and conductive. Most of the

world's indium is now produced in China, but in the past, the Toyoha Mine in Sapporo on the Japanese island of Hokkaido was the world's largest producing mine of indium. However, the mine was closed in 2006 because of its low profitability and the depletion of the resource.



© Crystal Museu



A shape memory alloys is made by mixing two metals in a 1:1 ratio. Which of the following is the correct combination of two metals? **1** (Zn, Cu) **2** (Al, Cu)

4 (Ni, Fe)

3 (Ni, Ti)

## Answer for Q6

## 1 2 Palladium

Osmium was used in the oxidation by Dr. Sharpless, and ruthenium and rhodium were used in the hydrogenation by Dr. Noyori and Dr. Knowles. Palladium was not used in either of these reactions.

## 2 Chlorine

Vancomycin is an antibiotic that belongs to the family of glycopeptides, which contain chlorine.

## Chemistry/ It's Cool/





## **Contact Information**

## **Catalyzer 8**



## Medal Design Concept: "The Chemical Vortex Leading to the Future" Designer: Sakiko Matsumoto

**F** rom the center to the edge, the entire medal forms the shape of a vortex, giving the impression of a whirling motion. This movement represents the global impact and upcoming success of young students, originating at IChO2021 Japan. Through the designs found on both sides of the medal, IChO2021 supports the bright future of the contestants.

The obverse side features three kinds of popular auspicious patterns to express aspects of Japanese culture.

The reverse side contains the logo, which is represented in a simple and emphatic way through an image that spreads across the world.



Seigaiha (青海波) translates to blue ocean waves. The endlessly calm waves are a prayer for long-lasting happiness and a peaceful life.

Shippō Tsunagi (ビボウなぎ) is a pattern of connecting circles, expressing a wish for happiness, harmony, and connection. This connection is as valuable as the Seven Treasures of Buddhism: gold, silver, lapis lazuli, agate, seashell, amber, and coral.

Asanoha (條の策) is a pattern representing hemp leaves. Because hemp is resilient, grows vigorously, and requires little care, it is often used as a pattern in the *kimono* of young children in the hope that they grow up big and strong. It is also meant to ward off evil.

The ribbon represents the image of a whirlpool flowing from the medal in indigo, black, and vermillion, which is the color of Japan. The design also expresses the impact that the students will have in the world.

# Nobel Prize<br/>Research from<br/>Japan (3)Discovery and Development of<br/>Conductive Polymers ---- Hideki Shirakawa

**P** lastics (polymers) are used in all aspects of our daily living and enrich our lives with their low cost, light weight, and flexible formability. Initially, plastics were thought not to conduct electricity and were used as insulators. However, various conductive polymers have now been developed and boast a wide range of applications, including touch panels for smartphones and electrodes for lithium-ion batteries. The development of conductive polymers that led to innovation in the world of plastics



was triggered by a s e r e n d i p i t o u s (unexpected) discovery by Hideki Shirakawa. When a student in his laboratory accidentally used one thousand times the required amount of catalyst to synthesize polyacetylene, he obtained a shiny, filmlike material that was completely different from the conventional black powdery polyacetylene. Although polyacetylene has many  $\pi$ -electrons, they cannot move freely, and the film-like polyacetylene did not show sufficient conductivity in its original state. However, through trial and error, they came up with a method to dope



Dr. Hideki Shirakawa ( 1936- )

carriers that act as electron acceptors, and when they added a small amount of bromine or iodine, the conductivity surged 10 million times. This discovery led to a dramatic development in research on conductive polymers. For this series of achievements in laying the foundation for the development of conductive polymers, which became indispensable to modern society, Hideki Shirakawa was awarded the Nobel Prize in Chemistry in 2000, together with Alan Jay Heeger and Alan Graham MacDiarmid.

## Japan is a "fermentation powerhouse"

J apan, with its warm and moist climate, is a "fermentation powerhouse" where microorganisms are very efficacious. Fermented foods such as soy sauce, *natto* (fermented soybeans), and *katsuobushi* (dried bonito flakes), which are made by growing mold on fish to remove moisture, are world-famous.



K ansai is also home to many fermented foods rooted in the local climate. In Wakayama, facing the Pacific Ocean, "Narezushi", salted fish wrapped in plant leaves

with rice and then lacto-fermented, is served on celebratory occasions. *"Funa-zushi"*, a kind of *Nare-zushi*, is made along the shoreline of Lake Biwa. *Funa-zushi* is made by marinating spawning crucian carp in salt and fermenting it with rice for one to three years. The



lactic fermentation gives it a novel cheese-like flavor and sourness, and the acidity increases its shelf life. There are two types of pickles in Japan: those made of lactofermented vegetables, and those made by soaking veges in *koji* (rice malt) or sake lees to add to their flavors. For example, *"Suguki-zuke"* is a lacto-fermented turnip and *"Nara-zuke"* is a type of cucumber





Nara-zuke

or squash pickle that has been pickled in sake lees for years.

*Koji* and yeast are crucial for making sake and basic seasonings such as soy sauce, miso, mirin, and vinegar. Jokichi Takamine who succeeded in crystallizing adrenaline (Catalyzer No. 6), devised a method to extract a type of diastase (digestive agent), named Takadiastase later, during the process of growing *koji*. *Koji* is deeply connected to the history of biochemical research in Japan. Against this background, *Aspergillus oryzae*, the main body of *koji* that supports Japanese food culture, was designated as Japan's national fungus in 2006 by the Brewing Society of Japan.

# **IChO2021 Participating Teams**













## main

Avanhaf



Ganada





Brach\_Rand







**El Salvador** 





Belanus





Chinese-Taipei













## Kazakhstar



Korea



France

÷

Germany

Greece

Hungar







Ireland



lsæd





# Kyrzyzsten



**հերբայ**ե

## Luxembourg





## Mexico



## Moldova

Allocatory





## Norway

Pakistan

Poland

119







## Romania



## **Russian Federation**



## Saudi Arabia





## Natharlands



New-Zealand









## Singapore



## Slovalda



## Slovenia-



## South-Africa



## Stilanka





Thailand











## **Uphaktatan**

Venezuela







# Turkmenistan

## Ukraine



















# Looking Back Remote ICh02021



## Nobuhiro Kihara

Vice-chair of Executive Committee, Vice-chair of Science Committee for the 53rd ICh02021, Japan

The 53rd International Chemistry Olympiad (IChO) 2021 Japan was originally planned to follow the 2020 Olympic and Paralympic Games in Tokyo, Japan. The interest to chemistry from the people was expected to be enhanced when a scientific Olympiad would be held after the excitement of a sporting Olympiad.

W hen we heard the first reports of COVID-19 early in 2020, it appeared to be a minor concern. Despite the virus being thought of as causing a new kind of cold, we knew that the common cold is inactive in summer, when the IChO was to be held. However, shortly after the pandemic spread across the globe, it became evident that COVID-19 was active in summer, too. The 2020 Olympics and Paralympics were postponed, and the 52nd IChO2020 in Turkey was held remotely, because the University venue could not be used for an in-person event in the period of IChO.

#### The IChO is composed of three key elements:

#### (1) Examination

Chemistry is an experiment-based science, with every theory coming out of the laboratory. Therefore, both theoretical and practical examinations play important roles in the IChO.

#### (2) Communication

Talented students from all over the world come together to take part in the IChO. Conversation, cooperation, and communication with each other provide a great opportunity for promising youngsters to enjoy international experiences and to make friends with other participants via their common interest, chemistry.

#### (3) Culture

The venue chosen for IChO2021 Japan was the ancient capital of Japan, where the first government of Japan was established 2681 years ago (according to Japanese legend). Several places were to be visited, including not only very old temples but also state-of-theart scientific institutes. In the middle of January 2021, the Organizing Committee of IChO2021 Japan met with the Steering Committee (SC) of the IChO. We discussed two proposals; for an in-person IChO and a remote IChO. Unfortunately, it was already clear that all the elements of the IChO described above could not be included in an in-person IChO during the COVID-19 pandemic, due to difficulties in immigration control and of the need for social distancing.

The first priority of IChO is, of course, the safety of all participants. After our meeting with the SC, we finally decided to hold IChO2021 Japan as a remote event. At the end of February, when we had a second meeting with SC, the holding of a remote IChO was approved.

## Even in a remote format, all elements essential to the IChO had to be maintained as much as possible:

#### (1) Examination

The competition involves theoretical problems, and was strictly monitored to avoid cheating. However, in order to reinforce the importance of laboratory work, an activity was developed in which the practical tasks prepared for IChO2021 Japan were demonstrated. We are delighted if those who are inspired by the demonstration can prepare and submit original videos in which they attempt the practical tasks and discussions. Reports on the tasks will also be highly welcome.

#### (2) Communication

We prepared avatars for all participants. Everyone participated in events and activities via their avatars. We also prepared virtual venues in which avatars can enjoy close conversation, cooperation, and communication with others. Some events also took place in such virtual venues.

#### (3) Culture

IChO participants were offered the opportunity for virtual visits to several locations. As well as those locations that had been planned for the in-person IChO, we have added several that are very interesting to experience but not suitable for in-person visits due to hazards, sensitivity, space limitations, or language difficulties. However, the participants' avatars can readily visit such restricted locations. The menu of cultural tours for our remote IChO holds more interest than would otherwise be possible.

This remote IChO has given us the chance to make the latest technology to provide great opportunities and special experiences to all participants.





Which country is the largest producer of selenium in the world?

1 USA 2 Japan 3 Mexico 4 China

## Answer for Q7

## 3 (Ni, Ti)

Zinc-copper alloy is brass, aluminum-copper alloy is duralumin, and nickel-iron alloy is called permalloy. A nickel-titanium alloy that consists of same ratio of the two metals is called a shape-memory alloy because it has the property of returning to its original shape when heated above a certain temperature, even after deformation.

## Element # 7

## Japanese mineral resources Silicon

- Basic Information Origin of the name: Latin word *silex* (hard stone, flint) Discovered by: J. J. Berzelius (Sweden) [1823] Global production: 8 million tons Major producers: China, Russia, Brazil

**S** ilicon does not exist in its pure metal form in nature; however, massive amounts of silicon can be found in soil, stones, and minerals in oxide forms, typically SiO<sub>2</sub>, a major constituent of sand. Yamanashi Prefecture in Japan is famous for its natural quartz crystal. Silicon metal is a very important material for industry today, used widely in semiconductors, microchips, and photovoltaic panels.





Daisenryo Kofun Kansai 8

The Daisenryo Kofun, located in the city of Sakai in Osaka Prefecture, was built in the early to mid-5th century and is considered to be Japan's largest *kofun* (Emperor's tomb). It is one of the more than 200 burial mounds that make up the Mozu Tumulus Group, which were built between the late 4th and early 6th centuries. The three-tiered, keyhole-shaped tomb is 486 meters in length and 654 meters at its widest, and is surrounded by a threetiered moat. Although the actual identity of the Emperor buried there is unknown, the Daisenryo Kofun was recorded as the tomb of Emperor Nintoku in a collection of laws compiled by the Imperial Household Agency in the early 10th century. The Daisenryo Kofun is one of the three largest tombs in the world, together with the

pyramid of King Khufu in Egypt and the tomb of Qin Shi Huang in China. It was designated as a UNESCO World Heritage Site in 2019.



## Chemistry/ It's Cool/





#### **Contact Information**
**Catalyzer 9** 



## Welcome Message from China ··· IChO2022

e are looking forward to welcoming you from all over the world to participate in the 54th Chemistry Olympiad in 2022, at Nankai University, in Tianjin city. Tianjin, a meaning of the 'emperor's docks,' resides in Northern China, the key junction of transportation and communication for China and its connection with the world.

As the Vice-Chancellor of Nankai University, it is my greatest pleasure to introduce Nankai University as the 54th IChO host. Founded in 1919, Nankai University has played a vital role in Chinese education over the last 100 years. Today, Nankai has grown to three modern university campuses, plus a full range of educational institutions. Nankai University is a leading multidisciplinary and research-oriented state university, consisting of 26 colleges, covering areas from natural science to humanities, at all levels. As a member of the Global University Leaders Forum, Nankai University strives continuously to deepen its internationalization and globalization process, both in education and research. Not only does Nankai offer opportunities for students to study abroad, but it also provides a growing number of well-supported international studentships and scholar bursary programs each year. These broaden our academic horizons and contribute to building a worldwide academic community and a shared future for humankind.

As a chemist, I have found that Chemistry can start from simple concepts and extend to understand the complexities of the world. Here at Nankai, one is always encouraged to develop social responsibility, practical capabilities, and a creative spirit. This spirit is coincidently shared with the IChO, so we are genuinely looking forward to welcoming the young Olympians to Nankai University, bringing sparks of inspiration and ideas, scientific talent, and starting friendships. Right now, we are working as hard as possible to ensure you will have a safe, and a special IChO in China. We sincerely hope that the pandemic will be over and the world will go back to normal quickly.

Finally, we are looking forward to welcoming you to Tianjin, in 2022!



The Chair of the Organizing Committee of ICh02022 The Vice-Chancellor of Nakai University



# ICh02021 Japan Closing Remarks by Vice President of ICh02021

T hank you for kind introduction. My name is Kyohei Takahashi, and I'm originally from a Japanese chemical company, and also ex-Chairman of Japan Chemical Industry Association, an association of all Japanese chemical companies. In Japan, academic society and industry association jointly continue to contribute to overall chemical society, and it is my honor to work as a representative from the chemical industry in this International Chemistry Olympiad Japan Committee.

The 53rd International Chemistry Olympiad in Japan, or IChO2021 Japan, will be closed today after the fruitful session of 9 days. Although due to the ongoing COVID-19 pandemic, we had to have the meetings by WEB system, we had participants from 85 countries and regions. This is the largest number IChO has ever had.

This was made possible by the devoted efforts of the Steering Committee and Chairman Dr. Gábor Magyarfalvi, all national contacts of each country and region, and those who conducted selection of student representatives. I would like to express our sincere thanks to all of you. In addition, thanks to the grate efforts of all mentors, science observers, and invigilators, examinations in all countries and regions were fairly conducted. I really appreciate your efforts and cooperation.

In the host country Japan, sponsorship was provided for us by many governmental agencies including Ministry of Education, Culture, Sports, Science and Technology, Ministry of Economy, Trade and Industry, Japan Science and Technology Agency, and more than 180 chemical companies and associated companies. Here I would like to report that this IChO has been operated under the partnership of All-Japan. Let me express my heartfelt thanks to all organizations and persons who supported us.

Now all of more than 300 students from all over the world taking part in IChO2021 Japan, thank you for your on-line participation despite this difficult situation! Did you demonstrate your ability and results of your daily efforts to the full? I believe all of you did! Properly speaking, you should come to Japan, become good friends with other students, and directly feel Japanese science, technology, society, and culture. However, we could not invite you to Japan due to the pandemic. Nevertheless, we provided you with many extraordinary programs and events only an on-line would be capable of. We provided you with virtual-tour of SPring-8, which is the world's largest radiation facility, and on-line visit to Buddhist temples, Himeji Castle, Kyoto, and Osaka. I am sure you enjoyed these virtual tours! We also hope you enjoyed communication with many new friends from all over the world in the virtual space.

For all of you who gloried as gold, silver, and bronze medal winners, congratulations! Your past effort comes into full bloom now! Also, let me congratulate all other students participated, because taking part in the IChO as representatives from your country or region is an honor you should be proud of. Your experience of this time will let you gain great self-confidence and support in your future.

Chemistry has infinite potential. The chemical industry is the only industry which has a name of science in its name, while other industries, such as the automobile industry and the steel industry, are called with names of products. This is because the chemical industry is based on chemical technology. Our industry manufactures various products, and chemistry is utilized in every possible scene of our life. Therefore, we can say that the chemical industry is the blood for all other industries.

Today we are facing global-scale problems such as global environmental issues, natural resource problems, and energy problems. These problems may jolt the future of human beings. As you know, the UN Sustainable Development Summit held in September 2015 adopted a set of international development goals called "Sustainable Development Goals" known as SDGs and most of such 17 goals requires innovations by chemistry. We believe and hope young people like you, who have rich knowledge and capability about chemistry, will lead the achievement of such goals. My dear students, this time you represented your home countries. But in the future, you must lead chemistry in the world, you must work together with other participants in this IChO, and you must make great contribution to the solution of difficult global problems. My young friends, please have high aims, and attempt new challenges!

At the end of my closing address, I wish you great success in your bright future. Thank you very much and good luck!



Vice President, ICh02021 Japan Committee Vice Chair, Organizing Committee for the 53rd ICh02021, Japan



# **Awards and Closing Ceremony**

#### Program

- Opening Movie
- Introduction of Sponsors
- Explanation of Examination by Prof. Hiroshi Nishihara Chair of the Science Committee
- Awards Ceremony
- Message from Prof. Gábor Magyarfalvi Chair of the Steering Committee
- Closing Remarks by Kyohei Takahashi Vice President of ICh02021 Japan Committee Vice Chair of ICh02021 Organizing Committee
- Introduction of Organizing Committee Members
- IChO Flag Handover Ceremony
- Welcome Message from Prof. Jun Chen Chair of the Organizing Committee of IChO2022 Vice-Chancellor of Nankai University
- Closing Movie





Honorable Mention





alists #1st, Shu Y #3 avatars with





Chair of the Steering Committee







Prof. Hiroshi Nishihara Chair of the Science Committee



Chair of Organizing the Committee of ICh02022 Vice-Chancellor of Nankai University



# Congratulations!!



#### IChO2021 Japan

Jul. 25 (Sun.) - Aug. 2 (Mon.) 2021

China

#### **Remote Examination**

Jul. 28 (Wed.)

Participants (85 Teams) 521 Total Participants **312 Students** 157 Mentors 52 Observers and Guests **183 Invigilators** 

#### Awards

Gold Medal: 33 Silver Medal: 67 Bronze Medal: 94 Honorable Mention: 24







# Gold

#### Shu Yang China Zhangyi Huang China Xinyu Cai China China Bangsen Zhao Sobirjon Amanov Uzbekistan Mircea Raul Bodrogean Romania Aleksandr E. Trofimov **Russian Federation** Vietnam Anh Duy Nguyen Bo-An Chen Chinese Taipei Georgii M. Zhomin Russian Federation **Chun-Cheng Ting** Chinese Taipei Phuong Duc Nam Pham Vietnam United States of America **Qiyang Zhou** Berkan Tarak Turkey Chen Yizhou Singapore Alexander Ramsay Thow United Kingdom Rui-Xi Wang Chinese Taipei

Cheng Jun Nicholas Goh Singapore Nir Cohen Israel Timofey A. Charkin **Tudor Lile** India Adarsh Reddy Madur Mahbod Alian Fini Iran Deniz Guner Turkey Andrei S. Tyrin Dhananjay Raman India Yitian Zhu Filip Hůlek Harry John List Anh Le Thao Nguyen Mahyar Afshinmehr Iran Myeongjin Shin Korea Alexandru Catalin Dianu Romania

**Russian Federation** Romania **Russian Federation** United States of America Czech Republic United Kingdom Vietnam



**Duong Hoang Nguyen** Vietnam Stefan Dimitriu Romania Sebnem Gul Turkey Uladzislau Hlatankou Belarus Alphonsus Yu Xiang Neo Singapore **Michal Piotr Lipiec** Poland Oscar Dong Australia Korea Seung Jae Kang Nikhil Seshadri United States of America Faatih Regind Qashash Roman Indonesia Bernard Tze Wei Kwee Singapore Hsuan-Ting Lin Chinese Taipei Mahit Rajesh Gadhiwala India Seved Mohammad Hossein Barakati Iran Oisín Colm Ó Feinneadha Ireland **Oleksandr Zaporozhets** Ukraine **Goktug Gulsoy** Turkey Shahzod Nazirov Tajikistan Hee Seong Yoon Korea Jirapat Rujirayuk Thailand Jovan Marković Serbia Linus Albert Schwarz Germany Muhammad Barotov Tajikistan Vinicius da Silveira Lanza Avelar Brazil Lucio Saracco Hungary Ioannis Karageorgiou Greece Nichawadee Kanjanakosit Thailand Turkmenistan Davut Muhammetgulyyev Takahiro Takemoto Japan Kohei Nishiura Japan Bruno Andrzej Skoczen Poland Khaidar Kairbek Kazakhstan Mohammad Solaiman AlHadlag Saudi Arabia Marek Pavlica Czech Republic

Ehsan Naderi Donig Iran Patrik Žnidaršič Slovenia Seoyeon Kim Korea Gerel Bayarmagnai Mongolia Temujin Orkhon Mongolia **Kien Phuong** United States of America Tong Wu Ireland United Kingdom Zachary John McGuire India **Rishit Singla** Andy Cai Canada Lita Tantipraphat Thailand Džonatans Miks Melgalvis Latvia Yuya Koike Japan Mohammad Rashed AlHudaithi Saudi Arabia Abdulaziz Abdulrahman AlJuaid Saudi Arabia Matúš Tomčo Slovakia Itamar Steinitz Israel Gozel Dovranova Turkmenistan Ron Angelo A. Gelacio Philippines Simon Bukovšek Slovenia Michael Schembera Austria Sanzhar Bissenali Kazakhstan **Tim Bastian Enders** Germany Pavel Atanasov Nikolov Bulgaria Berdigylych Rejepbayev Turkmenistan Dávid Benkő Hungary Yusup Dovletmyradov Turkmenistan Kazakhstan Madiyar Kassymaly **Povilas Dapsys** Lithuania Nathan Wayne F. Ariston Philippines Daniils Kargins Latvia Jakub Krzysztof Kwiatkowski Poland Ihor Kholomieiev Ukraine



## Bronze

Kevin Lius Bong **Tadas Danilevicius** Khanim Yagublu Sathira Jantarakulchai Irmuun Altankhuyag Kamil Mambetov Neta Eiger István Babcsányi Samuil Vladimirov Petkov Durdona Muxtarxujayeva Lazar Savić Hanif Muhammad Zhafran Darko Stojchev Vladislavs Tiščenko Maciej Swiatek Keith Wong Johann Sora Blakytny Andrei Banica Firdavs Sobirov Ketevan Peranidze Abdur-Raheem Idowu Ruben Tapia Austin Lin Patrik Fábrik Aigerim Turuspekova Nathanael Reza Putra Widjaja Indonesia Edvards Jānis Treijs Georgi Neliyanov Nedyalkov Bulgaria Salman Huseynov Cassia Caroline Aguiar da Ponte Brazil Angelina Rogatch Benedek Sajósi Alina Tumashyk Nariman Shirinli

Indonesia Lithuania Azerbaijan Thailand Mongolia Kyrgyzstan Israel Hungary Bulgaria Uzbekistan Serbia Indonesia North Macedonia Latvia Austria Australia Germany Canada Uzbekistan Georgia Norway France Australia Slovakia Kazakhstan Latvia Azerbaijan Belarus Hungary Belarus Azerbaijan

Saeed Sultan Baghdadi	Saudi Arabia	
Ahmad Thaer Ater	Syria	
laha Ali Syria		
Jorge García-Ponce	Mexico	
Michael Li	Canada	
Lukas Rost	Austria	
Teodor Svilenov Maslyankov	Bulgaria	
Nadun Naveendra Rajapaksha	Sri Lanka	
Yurii Okis	Ukraine	
Dimitrije Gligorovski Serbia		
Achira Hansindu Kelambi Arachchige Sri Lanka		
Marina Malta Nogueira Brazil		
Fran Miletic Croatia		
Haruhi Isse Japan		
Jernej Birk Slovenia		
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Vid Kavčič	Slovenia	Mahin Kamal Sawdager	Bangladesh
Jessica Rebekka Kurmann	Switzerland	Khalid Hasan Tuhin	Bangladesh

out of 309 students

### Element # 8 Japanese mineral resources

Basic Information Origin of the name: Greek word *anti-monos* (not alone) Discovered by: known since early history Global reserves: 1.9 million tons Major reserve countries: China, Russia, Bolivia Global production: 153,000 tons Major producers: China, Russia, Tajikistan

Antimony is still used as an electrode material and as a wear-resistant material for secondary batteries, as well as for flame retardants, type metals, and semiconductors.



© The Courtyard of our Minerals

We deeply regret that editing of Catalyzer has mostly been done by remote. We have had little chance to meet and discuss face-to-face upon editing. The photo below is the immersive view in the Zoom meeting of the Team Catalyzer. We hope that human overcomes COVID-19 pandemic soon and the next Chemistry Olympiad the 54th IChO2022 will be held as the really REAL mode. The Team Catalyzer IChO2021



#### Answer for Q8

#### 1 amber

When J. J. Thomson (1856–1940) discovered that cathode ray was actually a stream of particles, G. J. Stoney (1826–1911) named it "electron" after the Greek word *aelectron*, which means amber. It was given the name because the particles were produced by rubbing an amber rod.

#### 2 2 Japan

Japan produces 28% of the world's selenium (770 tons; 2019 data). Selenium has a range of industrial uses; it is found in applications from electronic devices to pigments, beauty products, and other daily items.



This popular word has the meaning of "thank you". Many people in the Kansai area say "Ohkini" at the end of conversation to smooth relations with the person. Ohkini was originally an adverb that indicated large quantities. Therefore, "Ohkini Arigato" is the equivalent of "Thank you very much." Over the years, this was abbreviated to just "Ohkini."

## Chemistry/ It's Cool/





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#### Chemistry! It's cool!

The 53rd IChO 2021 Japan Public Relations Subcommittee organised three pre-events to inform junior high and high school students about the IChO and to show them the fun of chemistry.

The first event was held at Kyoto University during Chemistry Week in October 2019, with lectures and hands-on experiments. A large number of junior and senior high school students attended the event, where they heard about the latest research results and the experiences of the former head of IChO 2021 Japan, and also had the opportunity to try out the precision analysis equipment.

In 2021, due to the pandemic of COVID-19, the events were held online twice, with more than 300 junior high school students, high school students and members of the general public, including those from overseas.

These students must have thought that "chemistry is cool", "chemistry is fun" and "I will challenge the International Chemistry Olympiad".



#### IChO 2021 Japan Pre-event

#### **Pre-event Lectures**

Event planner	and	Facilitator
Akihito Konishi		Osaka Univ.

#### 10/19/2019

Atsushi WakamiyaKyoto Univ.Hayate SaitoKyoto Univ.Takuya YamakadoKyoto Univ.Kohei TamaoIChO 2021 Japan CommitteeSHIMADZU CORPORATIONJEOL Ltd.JEOL Ltd.KOMYO RIKAGAKU KOGYO K.K.Toyota Physical and Chemical Research Institute

#### 3/13/2021

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Aiko Fukazawa	Kyoto Univ.
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Yoshiki Chujo	IChO 2021 Japan Committee
Yoshito Tobe	IChO 2021 Japan Committee

#### 7/10/2021

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Aya Eizawa	Air Liquide Laboratories	
Kenichi Endo	Kyoto Univ.	
Shinsuke Sando	UTokyo	
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# See you also in the future host countries

## 2023 Zurich, Switzerland July 16~25 2024 Riyadh, Saudi Arabia 2025 Dubai, United Arab Emirates







