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Study of Clathrate Hydrates

from Keio's Faculty of Science and Technology

Crystal engineering for energy and environmental technologies.

Ryo Ohmura
Associate Professor
Department of
Mechanical Engineering

Introducing

Researchers

Featured in this issue is Associate Professor Ryo Ohmura,
who tackles new technological development in the energy field by utilizing clathrate hydrates.

Clathrate hydrates useful for natural gas storage and CO_2 extraction

Effective utilization of materials that are similar to but are not ice

Clathrate hydrates have a cage-like structure made of water molecules in which a substance other than water has been sealed and crystallized. Substances that can be sealed in the cage structure include hydrophobic gases such as methane, nitrogen, and carbon dioxide (CO_2). While clathrate hydration is a focus of attention as an effective gas solidification technology, many mysteries still remain as to its principles and mechanism. Keio University's Faculty of Science and Technology boasts one of the world-leading achievements in the study of clathrate hydrate application technology. Associate Professor Ryo Ohmura, the person who spearheads this research activity, explained what clathrate hydrates are like.

Water molecules form a cage in which a guest substance stays.

Dr. Ohmura explains the characteristics of its structure: "Clathrate hydrate is a crystal of orderly arranged water molecules. Though it resembles ice in appearance, it differs from ice in the way water molecules are arranged. Unlike ice, in which water molecules are closely arranged leaving no space between them, clathrate hydrate features a polyhedron cage structure made of water molecules. The cage structure takes in a non-water guest substance and is then crystallized."

Imagine the traditional "Kagome-kagome" game of Japanese children and it will easily explain the clathrate hydrate structure. In the center of a circle is a tagger bending his or her body with eyes closed. The surrounding children, tanking each other's hands, are compared to water molecules. The tagger is not left out of the game but is surrounded at a distance from the others. The tagger can neither get hand-in-hand with the others nor is allowed to get out of the circle. The guest substance in clathrate hydrate is something like the tagger in the "Kagome-kagome" game.

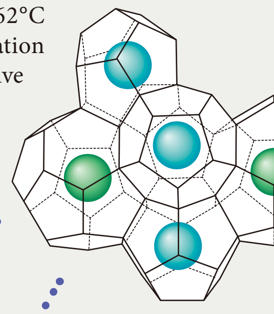
It solidifies a hydrophobic gas and enables its efficient storage and transport

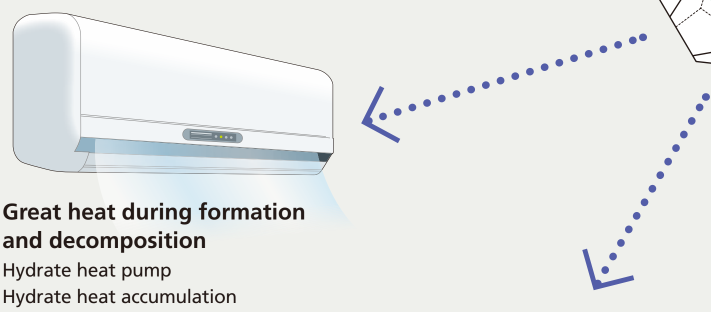
Clathrate hydrates with such characteristics also exist in the natural world. Methane hydrate, recently in focus of attention as a promising natural resource, is a kind of clathrate hydrate with its guest substance being methane molecules.

Similar to ice, methane hydrate is attracting attention as a medium capable of storing methane gas at a high density. Mr. Ohmura addresses the research project of taking advantage of such excellent storage capacity of clathrate hydrates for energy utilization of natural gas.

"Methane hydrate is a crystal containing water and methane molecules at a ratio of 46 to 8. Methane hydrate's storage capacity is 170 times greater in volume than that of methane gas. I came up with the idea of sealing natural gas as a guest substance. This marked the beginning of my study of natural gas hydrates. This research endeavor has come to the stage just before commercialization or engineering practice. The foremost merit of natural gas hydration is its ease of temperature management. Normally, natural gas is stored and transported as liquefied natural gas (LNG) after being cooled down to −162°C or less. By making it into the hydrate form, natural gas can be compressed to 1/170 in volume at a temperature of only −20°C. Though the volume of natural gas hydrate increases 3.5 times greater than that of LNG, it eliminates extra maintenance and management costs associated with cooling it to the cryogenic temperature of −162°C or less, making methane hydration highly promising as an alternative technology."

Since hydration enables





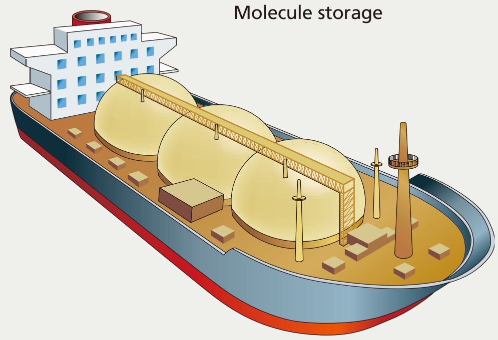


Fig.1 Application technologies that make the most of clathrate hydrate's physical characteristics
Highly efficient use and handling of clathrate hydrates becomes possible by incorporating their superb physical characteristics (greater gas storage capacity and greater decomposition heat) peculiar to clathrate hydrates into existing technologies and systems. Examples of application include natural gas storage and transport technology, carbon dioxide separation and extraction technology, and application to high-efficiency heat pumps. As future possibilities, innovative technologies, such as a hydrate engine, are also being conceived.

a guest substance to be stored at the molecular level, its application for the storage of hard-to-store or dangerous substances is being examined positively.

"Ozone (O_3) that exhibits superb bactericidal actions is a very unstable substance. In principle, ozone cannot be stored as is since its molecules react to each other and turn into more stable oxygen ($2O_3 \rightarrow 3O_2$). Once hydrated, however, it can be separated and preserved in the molecular form, thus enabling storage over a period of long time," he remarks.

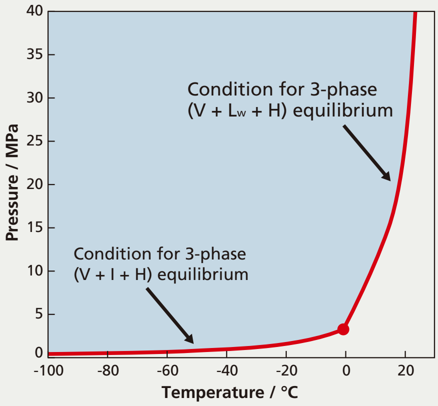
Can extract a specified substance and is promising as a CO_2 removal technology.

Clathrate hydrate cannot be formed by simply mixing water and a guest substance together. The formation of clathrate hydrate requires conditions of low temperature and high pressure. However, such conditions vary according to the guest substance in question. For example, at the temperature of 0°C, methane can be hydrated under 26 atmospheres (approx. 2.6 MPa), while carbon dioxide (CO_2) and nitrogen require 12 atmospheres and over 150 atmospheres, respectively.

"By taking advantage of such differences in hydrate-forming conditions, it is possible to hydrate particular guest substances selectively. Attracting attention as an application of this is the technology for CO_2 separation and removal from exhaust gas emitted by thermal power plants. It is an attempt to selectively solidify CO_2 only. In this process, exhaust gas, which consists of carbon dioxide and nitrogen, is given an optimum condition for hydration by having it react with water. Currently, the amine process* is used commonly as a CO_2 removal technology, but it involves the necessity to handle amine, a dangerous substance. Contrary to the amine process, the removal process, based on hydration of CO_2, uses water only, making it a highly promising process as an alternative to the amine process."

Fig.2 Conditions required for methane hydrate formation

Methane hydrate can be formed only when methane, water molecules, and temperature and pressure conditions become complete. The graph on the right shows the relationship between temperatures and pressures. When the temperature is low, the required pressure is low accordingly. But a higher pressure is required as the temperature rises. However, the low temperature and pressure required for control remain within a controllable range. Thus, ease of handling is another characteristic of methane hydrate. These physical characteristics can be seen commonly among all clathrate hydrates.



Also expected as a highly efficient thermal storage medium substituting for ice thermal storage

As clathrate hydrate is formed, its water molecules turn into a solid ice-like state, which can be controlled at a temperature range of between 5°C and 15°C. The creation of an efficient thermal energy storage medium for cooling can be expected as an application of this physical characteristic.

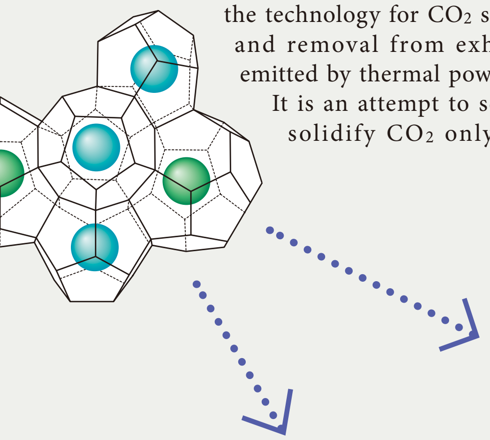
"Currently, most large buildings employ an ice thermal-energy storage system for their air-conditioning, which uses nighttime power to make ice and uses its cold air as the air-conditioning thermal source. From an efficiency viewpoint, however, it is pointed out that the thermal source of 0°C is too low since a thermal source temperature of approximately 10°C is optimum for producing cool air of 15°C needed to maintain the room temperature of 28°C. In fact, as much as 40% power conservation can be expected if the thermal source temperature is raised to 10°C. With hydrate thermal storage, it is possible to create a thermal source of approximately 10°C by controlling the guest substance and pressure – a thermal storage system far surpassing the efficiency of conventional ice thermal storage systems."

As Dr. Ohmura puts it, however, hydrate thermal-energy storage is not without problems. To realize practical application of clathrate hydrates, not only must the safety of guest substances be verified beforehand, but also the technology's principles and mechanism must be brought to light, the knowledge of which should be shared by many researchers and opinion leaders.

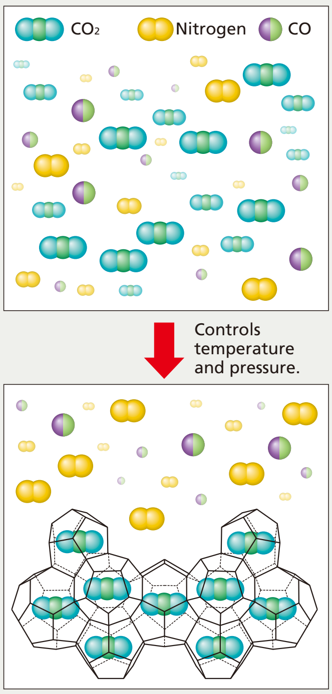
"As the stage of practical application of this technology approaches, now is the time for us to devote ourselves to basic studies. As a person in the academic world and as a leading researcher in this field, I think we now have to approach the clathrate hydrate phenomenon from a broader perspective, not biased for a particular engineering field," he concluded.

Studies of clathrate hydrates are steadily in progress.

(Reporter & text writer: Kaoru Watanabe)

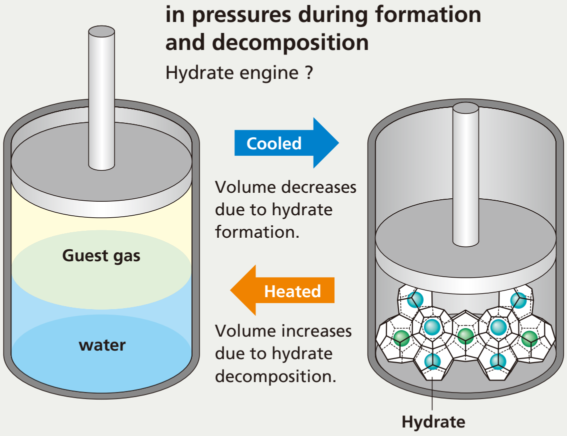


Guest substance selectivity
Separation/extraction technology



Hydrates CO_2 only.

Significant changes in pressures during formation and decomposition
Hydrate engine ?



* One of the CO_2 separation/removal methods. As an absorbent liquid, it uses an alkanolamine solution, the molecular structure of which incorporates an amino group that causes a combination reaction with carbon dioxide. The problem of cost reductions for absorbent liquid renewal still remains unsolved. Amine shows strong alkalescence, which requires utmost care for handling.

Logical thinking is essential for persuasive research

I'd like to address vis-à-vis what I feel is interesting

Dr. Ohmura has been tackling research on clathrate hydrates ever since he was an undergraduate. While he continues to pursue his career as a researcher, he also devotes his energies to fostering the next generation. When it comes to thermodynamics, his specialty, he smiles and jokingly says, "For students, this must be one of the toughest and 'worst' subjects to deal with." Contrary to his self criticism, his students favorably comment on Dr. Ohmura's lectures as being easy to understand. Some say that the study of physics has become interesting thanks to Dr. Ohmura.

What was the impetus for you to choose the science and technology course at a university?

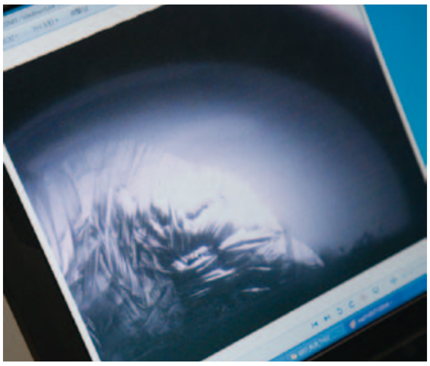
I'm now a teacher of mechanical engineering at Keio's Faculty of Science and Technology. It may surprise you to say that mathematics and physics were my weakest points as a high school student. My favorites were social-study subjects, such as politics, economics, ethics, and history.

Why did a liberal arts-oriented boy like me choose to study science and technology at a university? It was because of my father's advice. When I was pondering which subjects to choose at university, my father said, "A university can offer great opportunities because you can meet good teachers who are specialists in their respective science and technology fields. Why don't you learn your weak subjects from them?" Fortunately, my scores in entrance exam mathematics and physics tests were passable, so I decided to choose the science and technology course and went on to the Department of Mechanical Engineering of Keio University's Faculty of Science and Technology.

How did you manage your weak points – scientific subjects?

Although my perception of mathematics as being my weak point remained unchanged, my impression of physics totally changed immediately after admission to Keio. My teachers in charge of lectures on mechanics and thermodynamics were so professional that I was truly impressed by the fact that those teachers with thorough knowledge could make lectures so exciting.

At the university, I could learn everything about physical phenomena and machine functions through lectures and experiments – why is it so and why does it move like that? – from their principles through to mechanisms. These lectures were totally different from my high school physic class where I studied while asking myself "What on earth would this study be useful for?"



Using this equipment which looks like a cylinder placed in a horizontal position, we can observe the crystal growth process of clathrate hydrates under high pressures and low temperatures. The image above shows a hydrate crystal that is growing through a reaction between methane + CO_2 mixture gas with water.

What was the impetus for you to begin studying clathrate hydrates?

It was when I joined Prof. Yasuhiko Mori's laboratory as a senior. In those days, Dr. Mori focused on research into heat transfer, one of its themes being clathrate hydrates. Although I found clathrate hydrate phenomena intriguing back in those days, I didn't give it much further thought. But my perception of clathrate hydrates changed dramatically when I had an opportunity to meet Prof. E. D. Sloan Jr. of the Colorado School of Mines.

Prof. Sloan is the leading figure in the field of clathrate hydrate study with outstanding achievements in engineering. When I was studying in the master's program, a special course was held in our School of Science and Technology inviting Prof. Sloan. Though the special course lasted only for two months, it was a truly inspiring experience for me as it allowed me to acquire systematic knowledge from Prof. Sloan, whose research activity had focused on clathrate hydrates for years.

When I was thinking of continuing my clathrate hydrate research pursuit after acquisition of a doctor's degree, I happened to know that the National Institute of Advanced Industrial Science and Technology (AIST) was looking for young researchers in the field of hydrates. I was quick to apply for a position there. I belonged to the AIST for four years, during which period I experienced practical aspects of engineering science – the field where I could engage in fundamentals of applied physics while simultaneously observing research targets from the engineering perspective. It was a truly valuable experience as it concerns my current research activity.

Aside from jogging, my regular physical exercises are football and bench press. Currently, the maximum mass I can lift is 95kg. I'm continuing twice-a-week training together with my teacher, Prof. Mori, aiming at 100kg.

After leaving AIST, you returned to Keio. Was there any special reason for doing so?

Since my student days, I had thought I'm of the type who encourage others and draw out their potential abilities, which I became strongly aware of during my service with the AIST.

While AIST researchers sometimes work with their subordinates and part-timers, most of them normally devote themselves to their own research tasks. But I came to feel more motivation in thinking and working with students and fostering students who are willing to contribute to society and universities, and to shoulder the future for all. So I chose a career as university teacher, seizing an opportunity of an offer for a post of assistant professor. In my view, I'm a type of teacher who develops students' potentials by encouraging them while maintaining sternness. I know I'm viewed as a stern teacher among students, but think it's okay to some extent.

Aside from your research work, what are you interested in, or what are your pursuits?

I like to move my body. Jogging is a longtime pursuit. These days, I make it a rule to run a distance of about 16 kilometers daily, or one hour and 40 minutes. Since my home is in the Tsunashima area, my regular route is heading toward Shin-Yokohama along the Tsurumi River to the Nissan Stadium and back. It's almost a habit rather than a hobby. While running, I can put my thinking in order, whereas being able to refresh myself when I have a problem and waver in my judgment.

Please tell us what you are doing consciously as a teacher to draw out and develop students' potentials.

"Always be logical," I would say. I'm convinced that the ability to think logically is essential to make the best use of oneself in a given organization or society. Another point: Make it a rule to think about things by putting yourself in the shoes of others. One tends to be self-assertive when one has a strong message to deliver to others. But it's wise to restrain yourself. I'm trying to experience and prepare such environments through research activities and academic presentations.

From a mechanical engineering point of view, I'd like my students to acquire the practical application ability based on the laws of physics, with which they can judge things correctly. I know that mechanics and thermodynamics are extremely hard to understand, but it's true that these sciences are more useful than any other sciences once you have acquired such knowledge. I'd like to offer lectures in such a way as to make my students become aware that these sciences are indispensable for establishing the structure and systems of society.

◎ Just a word from . . . ◎

● **A student : In a single word, Dr. Ohmura is a man of knowledge. Not to mention his lectures, he has a wide range of topics to talk about, from history and culture as well as cooking, food ingredients, and wine. We are totally brought into his world before we know. He is also good at sports. I'm sure his physical strength is greater than ours!**

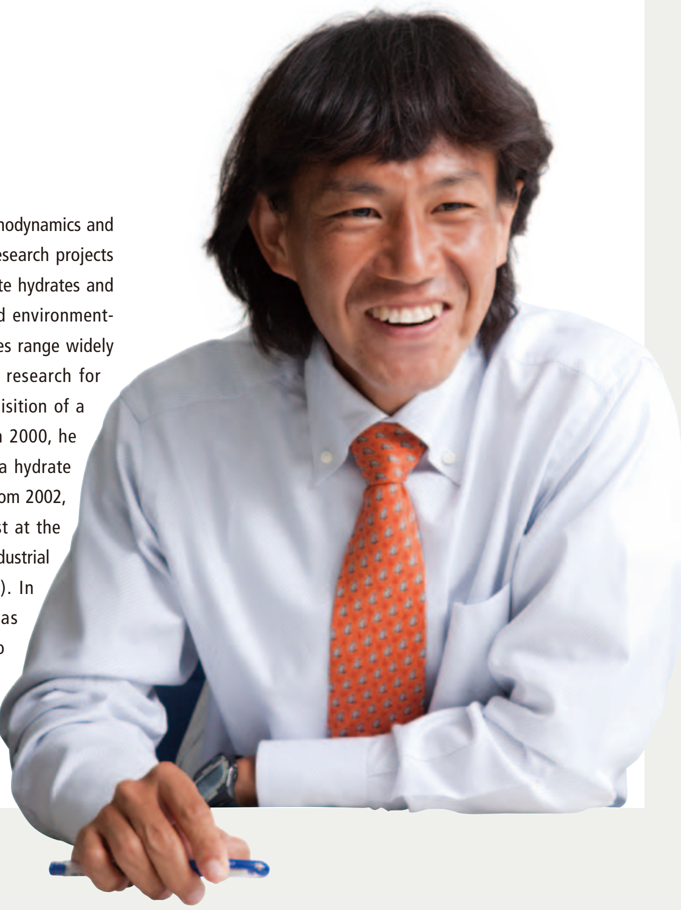
(Reporter & text writer: Kaoru Watanabe)

For the full text of this interview
http://www.st.keio.ac.jp/kyurizukai

I'd like my students to acquire the practical application ability based on the laws of physics, with which they can judge things correctly.

Ryo Ohmura

Dr. Ohmura's specialties are thermodynamics and physical chemistry. His current research projects are physical chemistry of clathrate hydrates and the development of energy- and environment-related technologies. His activities range widely from basic research to applied research for practical application. After acquisition of a doctor's degree (engineering) in 2000, he visited France to participate in a hydrate research project. For four years from 2002, he served as a research scientist at the National Institute of Advanced Industrial Science and Technology (AIST). In 2006, he arrived at his post as an assistant professor of Keio University Faculty of Science and Technology, and then he was promoted to his current post as an associate professor in 2009.



Gastronomique Omura Lab!

Cooking in the lab

"Food makes a man!" . . . We, Ohmura lab members, are partial to "eating." In the following, students report on our delightful lab dining party!

The Ohmura lab holds a dining party two to three times a month. We do not use ready-made food, but cook food ourselves by buying ingredients, such as ham, cheese, and sausage. This photo shows dishes we cooked to celebrate our colleague's article printed in an academic journal. Dishes on the menu were penne salad and ham and tomato French bread sandwiches.

This photo shows completed dishes neatly arranged on the table. Tidbits, such as cheese and crackers, can be seen along with bottles of wine brought by Dr. Ohmura. All lab members joined forces to prepare the dishes, which made them all the more delicious. We enjoyed the dishes while drinking wine and beer.

The dish shown here is calzone which we enjoyed at an Italian restaurant. The same base as that of pizza is folded into the shape of a crescent moon with ingredients in it, and then both sides are baked. It was very delicious. I recommend calzone to everyone. We are ready to visit any restaurant if it has a good reputation for its food. We also visit Oktoberfest and other beer festivals where German-style sausages and beer can be enjoyed.

My Favorite Wines and Beers

I (Ohmura) was influenced by French and other European cultures, especially by their dietary cultures. From day to day, I'm in pursuit of wines from various regions of France while also striving to appreciate the deep taste of Belgian beers.

Following the acquisition of my doctor's degree in March 2000, I studied in France for approximately nine months. Many Keio teachers advised me to go to the United States or England in expectation of good research achievement, but I didn't accept their advice (sorry!). I chose to study in France because of my admiration for its great culture, staying for five months in Toulouse and four months in Saint Étienne.

Gaillac, the wine on the right, is the most popular wine in the suburbs of Toulouse and is praised for its taste (the best among wines from southwestern France) and attractive color. The wine in the center is Saint-Joseph, one of the wines from the Rhone River basin. I got this information from Prof. Herri and Assistant Prof. Bonnefoy of Ecole Nationale Supérieure des Mines de Saint Étienne. Learning about high-quality wines like a sommelier may be one way, but commoner-like style of wining as suggested by my French friends suits me.

As for beers, Prof. Herri also suggested that I try Belgian beers. Belgian beers have their own deep world which is different from those of Germany and Czech, the two great beer countries. The bottle with a blue label, Blanche de Bruges, is a white beer from Brugge, and a glass next to it is one exclusively for Blanche de Bruges. Brugge is a beautiful town. If you have an opportunity to visit this town as a tourist, don't miss this white beer.

私の本棚

My favorite books

Clathrate Hydrates of Natural Gases

This volume is a technical book authored by Prof. Sloan (Colorado School of Mines), the world-leading authority on chemical engineering research on clathrate hydrates. This book contains almost every aspect of scientific and technological characteristics of natural gas hydrates – from crystallographic and physicochemical properties of hydrates to the history of R&D into hydrates, to related engineering technology, and even to geological research on distribution of natural gas hydrates. This book is a must for those concerned with research into hydrates – undergraduate and graduate students as well as researchers and engineers.

Shiga Naoya

Of the many master writers of modern Japan, I respect Shiga Naoya the most. In my parental home, my father had a complete collection of Shiga Naoya's works. I took advantage of this and read all of his works, from novels and essays even to diaries and letters. His works are characterized by vivid descriptions "as if you are on the scene" and compact, rhythmical sentences that minimize the use of punctuation. His finely-honed literary style is said to represent the culmination of Japanese expressions. Since clarity is an essential requirement of our scientific articles, I think we can learn a lot from Shiga Naoya.

Chemical and Engineering Thermodynamics

This textbook is a work by Prof. Sandler (University of Delaware, U.S.A.), the foremost researcher in the field of chemical and engineering thermodynamics. I chose this book from among the many thermodynamics textbooks mainly because Prof. Sandler is a teacher (thesis supervisor) for Dr. Sum (Associate Prof. of Colorado School of Mines), one of the few close friends of mine with whom I became acquainted through hydrate research activities. I refer to this book from time to time not only for preparing for a lecture but also for my own thermodynamic research on hydrates.

Thermodynamics (JSME textbook series – in Japanese)

As a publication from the Japan Society of Mechanical Engineers, this book mainly deals with engineering thermodynamics. At Keio University, it is used as a textbook for "The Introduction to Thermodynamics" – an obligatory subject for sophomores of the Department of Mechanical Engineering – and several other thermodynamics-related subjects. The fact is that thermodynamics is not a science of "mechanics," but a science of "energy." If you thoroughly study thermodynamics, you will come to understand many things that you formerly couldn't understand with knowledge of mechanics alone. This book is useful and easy to understand for both beginners and those concerned with the practical aspect of thermodynamics.

Transport Phenomena

If literally translated into Japanese, the title of this book may be something like "Transfer Kinetics." But it's not a book about means of transportation. The field of science dealing with transfer speeds of energy and materials and fluid dynamics is known as transport phenomena. Together with thermodynamics that deals with energy balance, transport phenomena is a field of physical science that plays a fundamental role for solving energy and environment-related issues. The concept of transport phenomena was initiated in the 1950s by the author of this book and several others. Over a half century has passed since then, but the importance of this science is increasing more and more today.

A gift from the Earth

While many people have come to know that the rise of carbon dioxide (CO_2) concentration in the atmosphere is a major culprit of the global warming and climatic changes, there seem to be few who know that CO_2 concentrations have repeated significant fluctuations at a cycle of tens of thousands years over the past 700,000 years. Clathrate hydrates, the research theme of Associate Prof. Ohmura, hold the key to the study of past climatic changes.

By now, CO_2 concentration data for the past 720,000 years have been databased, of which actually measured data are for only tens of years. The remainder has been obtained by boring and analyzing ice sheets in Antarctica and Greenland. Therefore, ice sheets from deep underground are necessary to investigate the composition of the atmosphere of ancient times.

Down to a depth of about 800 meters, air contained in ice sheets exists as bubbles floating with ice, but further down, air reacts with water in the ice to become crystals surrounded by water molecules. In other words, air becomes hydrated. This is because, in a low-temperature, high-pressure environment as seen in depths greater than 800 meters, air contained in ice can be stable as air hydrates rather than existing as bubbles. Furthermore, these air hydrates have the same structure as methane hydrates, making it possible to confine air within crystals just as it was like back then. It's interesting to know that ancient ice sheets became the ideal place to preserve air from 700,000 years ago.

Ice sheets in Antarctica are believed to have been formed by the coldness and snow that has fallen over tens of millions of years. The air back then first existed as bubbles in ice sheets for some time, and then went to sleep for countless years with air hydrates as its cradle. Given this, it's wondrous to assume that ice sheets bored from great depths are time capsules prepared by the Earth to convey the state of ancient times to our modern times.

Science and Technology **Information**

The 12th KLL Industry-Academia Collaboration Seminar "Resilient Community: the Ways to Realize It"

Date: October 28 (Fri.), 2011 15:00 ~ 17:30
Place: 1st floor symposium space, Raiosha Bldg. on Keio Hiyoshi Campus
Admission free; Prior applications required
http://www.kll.keio.ac.jp/seminar/index.html

Following the seminar, there will be an opinion exchange meeting. Please apply for participation via the above URL.

The 12th KEIO TECHNO-MALL 2011 "Let's get started"

Date: December 9 (Fri.), 2011 10:00 ~ 18:00
Tokyo International Forum (Exhibition Hall 2, E Block B2)
Admission free, no prior registration required
http://www.kll.keio.ac.jp/ktm/index.html

The KEIO TECHNO-MALL, organized by KLL, is an annual exhibition of science and technology. For this year, the closing time will be extended to 18:00. The exhibition hall to be used will be changed from the previous year.

Strategic Management Chair for Creating Innovations (a Sony-donated chair) Open Symposium 2011 "Toward a New Phase of Development of Humankind and the Future"

2nd seminar: "The Internet and the Future of Mankind" November 24, 2011 (Thur.)
3rd seminar: "How Far is the Future Predictable?" January 27, 2012 (Fri.)
http://www.koukai-sympo.net/portal/
Details of these evens will be uploaded successively on the above URL.

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Editor's postscript

On a certain day in August, Associate Prof. Ohmura appeared to make preliminary arrangements for the interview and data gathering for this issue, wearing an aloha shirt (which suited him very well). Judging from his appearance, I expected that he would accept our request open-mindedly. But I became upset when I heard him say, "I'm an old type of researcher who thinks that researchers should be okay only if they produce good results and publicize them through articles." In the actual interview, however, he was so cooperative as to talk a lot about the romantic side of research activities, and even demonstrated a 95kg bench press for us. By the way, we used "the color of the Mediterranean sky" for the front cover background in response to Dr. Ohmura's request (this indicates he is a great romanticist!).

What's more, he likes to wear a necktie featuring a design of a frog ("kaeru" in Japanese which also means "return home") when taking a business trip. His wife chose this tie expecting him to return home safely! Our interview was rewarded with one delightful surprise after another about his personality.

(Saori Taira)

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