Science News of the Week

Eyring and His Theory of Reaction Rates

For nearly half a century, the absolute reaction rate theory has been gospel in the field of chemistry and, to follow the metaphor, its founder, Henry Eyring, has been an apostle. He has won nearly every major American chemistry award, written eight books and 500 technical papers and taught 115 Ph.D. candidates. At this week's national meeting of the American Chemical Society in Philadelphia, Eyring collected that group's highest award, the Priestly Medal, and as testament to his continuing scientific activities he proposed a modification to his original reaction rate theory.

The absolute reaction rate theory explains the energy budget of colliding particles. When two molecules collide, it says, a short-lived activated complex of the colliding particles is formed. This can break down into the original molecules or can form new molecules. Sometimes such a reaction takes place spontaneously and gives off heat, and sometimes, a reaction won't take place unless heat is supplied. Usually, the more heat added, the faster the reaction.

The reaction rate theory calculates the energies required and released during the reaction of different combinations of molecules and the rate at which the reactions can occur at different temperatures. It is applied widely to both living and nonliving systems but it doesn't explain the behavior or reaction rates of all colliding particles. Eyring, a chemistry professor at the University of Utah, and others, have noticed that at very high temperatures the reaction

Eyring: "Like a clogged gas line."

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rate is often much slower than would be predicted on the basis of a large amount of heat present.

An example of this is seen during the detonation of certain types of explosives. Although the collision and rearrangement of molecules can take place in a fraction of a second, the reaction can be as much as 10,000 times slower than would be predicted on the basis of the very high temperatures present (1,000 degrees K. or more). Eyring's new theory attempts to explain why this enormous supply of energy does not drive the reactions at the expected rate, and what different sort of energy budget is observed at high temperatures.

During an explosion of a stick of TNT, for example, there are a series of chemical events. An initial spark causes the molecules to begin colliding with each other—in other words, to heat up. The energy from the collisions must be transferred in a second step to the chemical bonds holding the molecules together. These bonds can break apart very quickly—faster, in fact, than energy can be transferred to them from the colliding particles. Herein lies the rate limiting factor, Eyring says.

When two processes occur in succes-

sion, he says, the slower of the two regulates the rate of the entire reaction. "It's like having a car with a clogged gas line. You can push your foot down on the accelerator as hard as you like but the speed of the car will be determined by how quickly the gas can come through the clogged gas line." In the case of TNT, the jostling molecules form an energy reservoir that "stokes" the bond-breaking process. Since the bonds can break faster than energy can be "shoveled in," the reaction proceeds at this transfer rate and not at an idealized faster, bond-breaking rate.

This new theory has implications for fusion and explosives research, Eyring says. Laser-fusion experimenters will have to take account of this new theory, he says, and realize they can't make the fusion reaction occur more quickly by merely raising the temperature of the system. There will have to be new ways devised to transfer the energy more quickly to the hydrogen bonds in the fuel. The shape and circumference of the fuel pellet might influence this transfer. "This is going to be an obstacle for laser-fusion people, but I don't say that it can't be done." In fact, "I hope it can be done," he says, "because I hate to be cold."

Conducting electricity organically

The creation of a unique and fascinating chemical compound was announced by Johns Hopkins's chemists this week. It is a member of a relatively new class of synthetic compounds called organic metals, and this fact alone is enough to make the substance interesting. But this glossy, black crystalline material with the unmanageable name HMTSF-TCNQ is also the first organic material that acts like a metal (can conduct electricity) throughout a wide range of temperatures from room temperature almost all the way to absolute zero.

The first such organic metal, TTF-TCNQ, was created by Dupont chemists about 10 years ago. It is composed of stacked-up layers of the two components, TTF, an organic compound with two five-member rings each containing two sulfur atoms, and TCNQ, a six-membered ring with four carbon-nitrogen groups attached. TTF is positively charged and TCNQ is negatively charged, and together, they can propagate electric currents in one direction up the stacks of molecules. Since this first

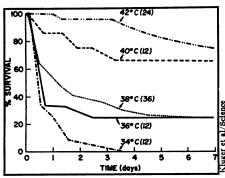
organic metal was synthesized, solid state chemists and physicists have been trying to create new compounds from which they hope to gain two things: useful basic information on the nature of conductance within solid material and useful products such as solid state batteries, solar collectors and magnetic organic materials.

Aaron N. Bloch, Dwaine O. Cowan and colleagues from the Johns Hopkins chemistry department reported their synthesis at an American Chemical Society symposium on organic metals. The positive component (HMTSF) is structurally different from TTF but the negative component is structurally identical. HMTSF has four five-membered rings and four selenium molecules replacing the sulfur molecules of TTF. The conductance properties of HMTSF-TCNQ are quite different from all other organic metals. Most of them will conduct electricity at room temperature (although not very well compared with metals such as copper), then exhibit an increased ability to conduct electricity as the material is cooled to about 100

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degrees K. The materials then exhibit a sharp decrease in ability to conduct electricity (that is become insulators) when cooled further. HMTSF-TCNQ, on the other hand, can continue conducting electricity from room temperature down to about .045 degrees K., nearly absolute zero. It is, therefore, the only organic material yet created that can act like a metal throughout a broad temperature range and does not become an insulator.

Fevers: A means for survival?



Infected lizards kept at higher temperatures were more likely to survive.

A burning fever may be the body's way of killing bacteria, a team of University of Michigan medical scientists report. In studying the effects temperature has in controlling disease in lizards, Matthew J. Kluger and his colleagues at the University of Michigan Medical School discovered that when lizards are inoculated with live bacteria, their body temperature rises, and their chances of survival increase.

Lizards have advantages over mammals in such a study. A lizard's body temperature fluctuates according to its surroundings, and the animal's temperature can be controlled under a wide variety of experimental situations.

The physiologists found that lizards, once exposed to fever-causing bacteria, survive significantly more often if their body temperature is maintained at an elevated level (40 to 42 degrees C.) for 24 hours. This leads them to conclude in the April 11 Science that "fever following a bacterial infection is beneficial to the host." Since lizards maintained at 40 degrees C. had more effective defense systems against bacteria than those in cooler environments, Kluger says a reduction in temperature may reduce the host's ability to fight infection. If fever evolved as a mechanism of defense, its function should be similar in mammals. If that is the case, then widespread use of antipyretics to lower the temperature of people with moderate fevers should be reevaluated, the researchers conclude.

Panel urges new wildlife management

A group of distinguished biologists and wildlife managers, meeting last weekend near Washington, has produced a new set of scientific guidelines for the management of wild resources. Specifically, they found that the concept of maximum sustained yield—harvesting as much of a wild species as possible on a continuing basis—needs updating and should not be codified as the last word in resource management by the current Law of the Sea Conference or in legislation pending before Congress.

Noting that past attempts to manage the exploitation of wild animal and fish resources had led to "gross depletion" of many species, the panel announced a new set of general conservation principles, which organizers hope will be incorporated into law and international agreements. Around 30 wildlife experts from universities and government laboratories in the United States and Canada came to the conference, sponsored by the World Wildlife Fund, the Council on Environmental Quality, the Ecological Society of America and the Smithsonian Institution. The official report will be made public next week.

Science News was present at the meeting and obtained a draft copy of the report, in which four general principles were laid out for future wild resource management: Rather than concentrating on just one species in setting hunting and fishing quotas, managers should concentrate on maintaining species balance within an ecosystem, the panel recommended, including minimizing the risk of irreversible change and keeping open as many options as possible to meet future needs. Decisions should include adequate safety factors, to allow for gaps in knowledge and inevitable institutional imperfections. Waste of other resources, including energy, should be avoided in determining how best to harvest wild species. Before exploitation begins, careful surveys should adequately determine the extent of a resource, and continuous, publicly available monitoring should accompany its use.

Most cases of overexploitation—such as that which caused the decline of the great whales—have resulted from institutional inadequacies, rather than lack of a good theoretical management base. But the scientists were concerned that in the current rush to create new commissions and reach new international agreements, the latest scientific knowledge about vast, though fragile ecosystems might be ignored. Conventional wisdom has held that maximum yield is produced when the population of a species is hunted or fished to a population level about half that originally present. The panel's report calls this concept of maximum sustained yield "simplistic," since it does not take into account age distribution of a catch, growth rates and social order of a species, or the effects of one species on another. Destruction of a predator, for example, may lead to an overabundance of its prey. But worse, the concept has too often been used as an "argument for brinkmanship," says Sidney J. Holt of the United Nations Food and Agricultural Organization. Instead, he said, it should be the "boundary of exploitation, rather than the goal."

Conference organizer Lee M. Talbot told conferees he hoped their meeting would help prevent out-dated management ideas from getting "set in concrete," through new legislation. He and Holt are working on a modified version of the panel's conclusions to be presented to the Law of the Sea Conference in Geneva. So far, however, that meeting has failed to solve the basic problem of how new management regimes would be enforced.

The Thin Edge

Public television has aired several programs in recent months that prove television can be educational, entertaining and popular at the same time. The Ascent of Man, Nova and Civilisation are prime examples. Last week the Public Broadcasting Service opened a new series, the overwhelming response to which suggests that certain forms of educational programming may have a much larger audience appeal than has generally been believed. The series, called The Thin Edge, deals with mental health problems.

The first hour-long program of the series discussed depression. It was well made, highly informative and interestingly presented by host and executive producer David Prowitt. It was shown on 253 stations, 136 of which had local follow-up programs during which viewers could call in and have questions answered on the air. At WNET in New York, where the series was produced, all available phone lines were tied up for several hours. The phone company there estimates that at least 150,000 people tried to get through. The program was so successful, in fact, that it has already been purchased by a commercial distributor (Medcom in New York) and will eventually be available as educational material for schools and doctors.

The remaining four programs in the series will be shown on alternate Monday nights. They will examine: Aggression, April 14; Guilt, April 28; Anxiety, May 12; Sexuality, May 26.

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