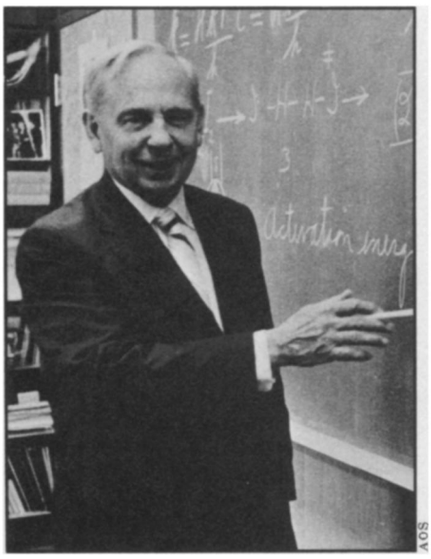
Eyring and His Theory of Reaction Rates

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



Eyring: "Like a clogged gas line."

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 succession, 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