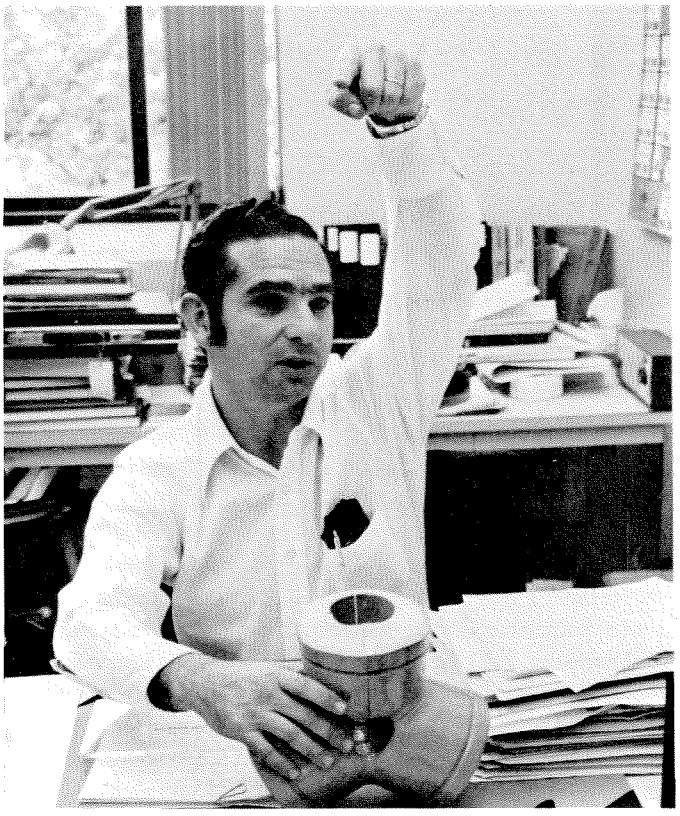
An Insight into Chemical Reactions



Historically, chemists have been interested in two fundamental concepts: chemical structure (the arrangement of atoms in molecules) and chemical dynamics (how molecules change due to chemical reactions). In terms of understanding the structure of molecules, chemistry is now a fairly mature field, but the understanding of chemical reactions is still in its infancy. Now research in that field too has begun to boom.

With the aid of theoretical models, Aron Kuppermann, professor of chemical physics, and his co-workers have revealed some new and important aspects of chemical reactions, including the existence of resonances. (Simply defined, a resonance in a chemical reaction is a short-lived intermediate, formed when two molecules in the process of reaction stick together.) The work may have a profound influence on our understanding of chemistry.

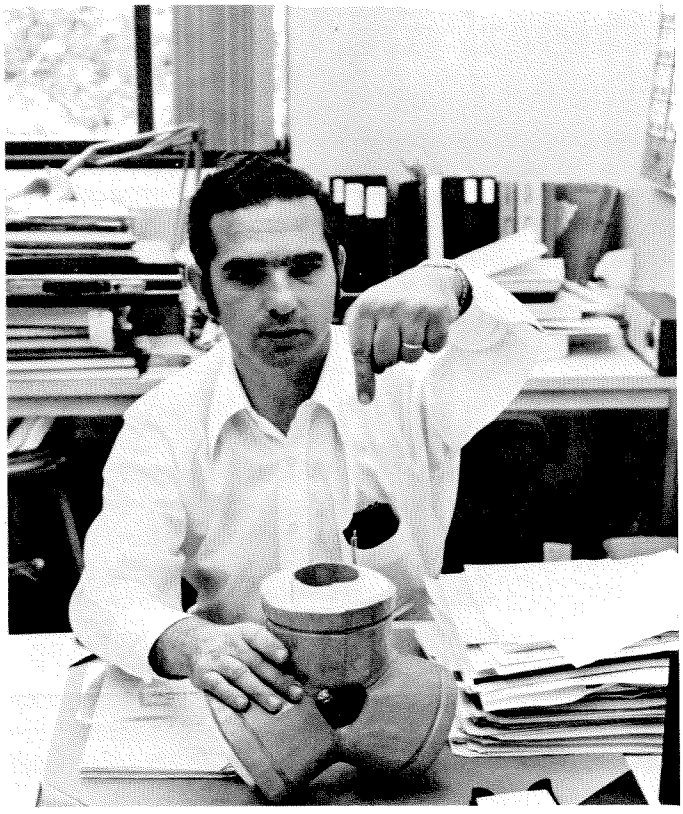
In the past, chemists have been handicapped for lack of sufficiently powerful experimental and theoretical techniques to answer vital questions concerning chemical reactions—questions that deal, for example, with the effectiveness of reactions. How is chemical change most efficiently brought about? What happens to the energy following a reaction? Does it appear in the vibration or in the translation of the resultant products of reaction?

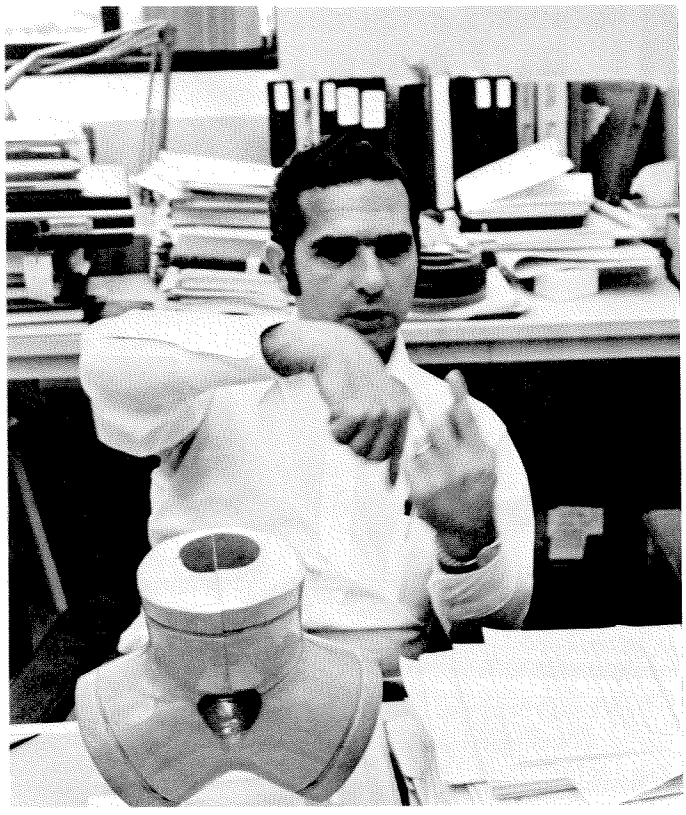
What makes this research important now is that there are new techniques that make the solving of these problems possible. "We can take a ride on top of a molecule and watch what's really going on," Kuppermann says.

The way Kuppermann looks at molecules is to employ a crossed molecular beam apparatus to study molecular collisions. This kind of apparatus was first used successfully 15 years ago at Oak Ridge National Laboratory and has since been markedly improved by investigators at Caltech and elsewhere. The device has the advantage over earlier experimental techniques of permitting a high degree of selectivity of the kind and energy of the molecules which are made to collide. When this energy is made sufficiently high, attention can be focused on reactive events that normally account for an extremely small fraction of the collisions between reactants.

Kuppermann's apparatus, known as "the beast," consists of two sources of molecules enclosed in a vacuum and set at right angles to one another. The molecules are propelled as a beam from each source toward a point of intersection. A mass spectrometer then detects the molecules scattered into different directions of space. The resultant information is fed through cables into a small computer where it is stored and processed. This billiard-ball technique is the most direct way to measure the forces between molecules. These forces determine the bulk properties of gaseous molecular mixtures, including viscosity and heat conduction.

To help his theoretical efforts, Kuppermann recently began building representative models of the potential energy in chemical reactions. The inspiration for his models, which was generated by a particular system of





Aron Kuppermann, professor of chemical physics, conceived, designed, and built this deceptively simple-looking balsa wood model of the potential energy in a chemical reaction. His gestures only hint at its inner complexities—a labyrinth of channels through which the tracks of colliding molecules and their reaction products can be traced.

mathematical coordinates, he says, "came in a flash, but only after many months of intensive work. I have in my briefcase about 250 pages of notes—and on page 250 there's a big 'Eureka'."

The models illustrate to scale all the translational, vibrational, and rotational motions of the colliding molecules and of their reaction products. The internal anatomy of the models determines what chemistry is going on.

Two of the models have proved particularly useful. The first describes geometrically the simplest chemical reaction occurring in nature—the exchange of an atom between a hydrogen molecule and a hydrogen atom. The other model represents a similar process between a hydrogen molecule and a fluorine atom to produce hydrogen fluoride. This product is formed with a large amount of vibrational energy and is one of the key processes in the hydrogen-fluorine chemical laser—one of the most powerful chemical lasers in existence.

Both models are equipped with hinges that allow partial disassembly, thus affording a view of their interiors. The intricate topological structure reveals, through the size and shapes of the holes and passageways, the prominent features of chemical events—giving clues to the probability of the occurrence of various reactions. By simply looking at the hydrogen-fluorine model, Kuppermann has suggested that the deactivation of vibrationally excited hydrogen fluoride molecules by

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hydrogen atoms may be a very efficient process. Events of this kind are of importance for the understanding and improvement of lasers.

With the aid of the models, he is making an extension from a simplified world of collinear collisions between atoms and diatomic molecules (used in preliminary theoretical studies) to the real three-dimensional world. This transition is the crux of his current theoretical research.

On the experimental side, Kuppermann initially used the crossed molecular beam apparatus but at purposely lower energies than requisite for reaction in order to study exactly how molecules bounce off one another. This work was designed to measure the intermolecular forces first postulated by the Dutch physicist J. D. van der Waals a century ago.

The van der Waals force is a long-range force due to the attraction of the electrons of one molecule by the nuclei of another. When two molecules approach each other, they feel the weak attraction due to this force. For a reaction to occur, the molecules must get much nearer, and a substantially larger degree of energy must be supplied to overcome the strong repulsions that frequently exist between molecules at close distances. Van der Waals forces, which are of crucial importance in nature, are a thousand times weaker than the chemical forces at play during reactions.

The van der Waals force esentially determines the physical state of matter—liquid, solid, or gaseous. It all depends on whether the molecules stay close enough to fall into the little van der Waals traps, corresponding to a minimum in the potential energy. In liquids and solids the molecules have fallen into and remained in these traps. At higher temperatures the molecules get excited and escape to form a gas. The van der Waals force is always present, but whether or not its effect is important depends on the molecular energies.

Before the first experiments were done, the Kuppermann group feared that the molecules' cigar-like shape and wild spinning motions would obscure tiny quantum mechanical oscillations predicted by theory. Instead, they found that the molecules bounced off in such a way that the fact that they were molecules rather than atoms (which are spherical) didn't make much of a difference. They also found that the quantum mechanical diffraction oscillations were, indeed, visible. From these oscillations, which showed that molecules behave like waves, the forces between molecules were precisely measured for the first time.

Kuppermann's study of van der Waals forces was an important milestone in studying molecular collisions. Using the cross-beam technique, he is now planning to shoot molecules at each other with much higher energies. The molecules will be energized to temperatures of about 20,000 degrees Fahrenheit—greater than the surface temperature of the sun—in a device called an arc-heated hypersonic beam source, built with the assistance of graduate student Mike Coggiola, who has also been a major contributor to the intermolecular force work. These very high energies are necessary to overcome strong repulsions and to permit the molecules to get near enough to react chemically.

Perhaps Kuppermann's most significant discovery from his recent calculations, done in collaboration with graduate student George Schatz, is the prediction of high-energy resonances in a chemical reaction—a phenomenon he hopes to find in the laboratory eventually. Theoretical particle physicists have found similar resonances at a billion times greater energies, but chemical resonances have never been observed and should prove technically very difficult to locate.

The implications of the current research are very encouraging. Potentially, it could make a host of related chemical systems better understood. "Chemistry is the source of chemical change," Kuppermann says. "The question we're asking about what happens when two very simple molecules collide and react are questions that pertain to what's happening in the chemical reactions that make you see and smile and breathe. But right now we're only trying to understand what happens when two little molecules bang into one another."

—Gary Prohaska '73