The Energy of a Chemical Reaction

Caltech chemists have made the first direct measurement of the minimum energy required for a chemical reaction, and it is expected to have far-reaching effects on chemical research. Aron Kuppermann, professor of chemical physics, directed the research, which was sponsored by the Atomic Energy Commission. He points out that the measurement will make it possible to gain new insight into chemical reactions, their rates, and the energies required for them. It may also make it possible to learn, at last, if bi-molecular chemical reactions can be described by the laws of classical mechanics or if it is necessary to use quantum mechanics.

Graduate student John M. White, working on his doctoral thesis under Dr. Kuppermann's direction, made the measurement. He showed that 0.33 of an electron volt of energy is required to initiate one of the simplest chemical reactions—that of splitting a hydrogen molecule and linking a deuterium atom with one of the hydrogens. If less than that amount of energy is applied, the reaction will not occur.

The chemical reaction was energized by light from a 200-watt mercury lamp. The light—in the ultraviolet spectrum—was made monochromatic, to standardize the photon energy, by a diffraction grating. Change in the angular orientation of the grating permitted the wavelength (and, consequently, the energy) to be varied.

The light beam was shone on a glass vessel containing a mixture of hydrogen gas and deuterium iodide (molecules made up of one atom of deuterium and one of iodine). The photons kicked apart the deuterium and iodine atoms but did not affect the linked hydrogens. The iodines, being heavy, moved sluggishly, while the deuteriums moved much more quickly.

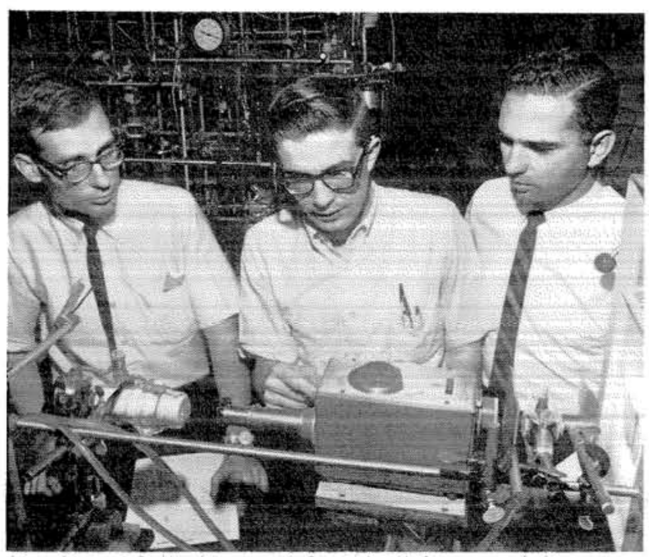
When a sufficiently energetic deuterium atom strikes a hydrogen molecule, it can split off one of the hydrogens and stick to the other one, forming a molecule of deuterium hydride. The freed hydrogen atoms later combine into other molecules, and the freed iodine atoms combine into pairs.

As the gases were irradiated, their chemical composition gradually changed. At the end of an hour or more the contents of the reaction vessel were examined in a mass spectrometer—built by Samuel Epstein, professor of geochemistry at Caltech, especially to analyze very small amounts of deuterium hydride in hydrogen.

The experiment was repeated with light of increasing wavelength (decreasing energy) until no deuterium hydride was formed. This provided a direct measurement of the minimum energy required for the reaction to occur.

Donald R. Davis, a National Science Foundation postdoctoral fellow and part-time instructor at Caltech, is now carrying on the research with Dr. Kuppermann. He is using a much more powerful light source—a 5,000-watt xenon high-pressure lamp similar to those in the projectors in drive-in theaters. This intense light, 25 times more powerful than the one used earlier, will provide a greater number of reaction events per time of exposure, thus permitting an even more precise figure for the minimum energy of the reaction. Minimum energies also will be measured for more complex chemical reactions.

This new technique should make it possible to resolve a major question in chemistry: How does the probability of a reaction between two molecules depend on the energy with which they collide?



Dr. Donald R. Davis, John M. White, and Dr. Aron Kuppermann find the minimum energy of a chemical reaction by decreasing the energy of light shining on a glass vessel until no reaction occurs.