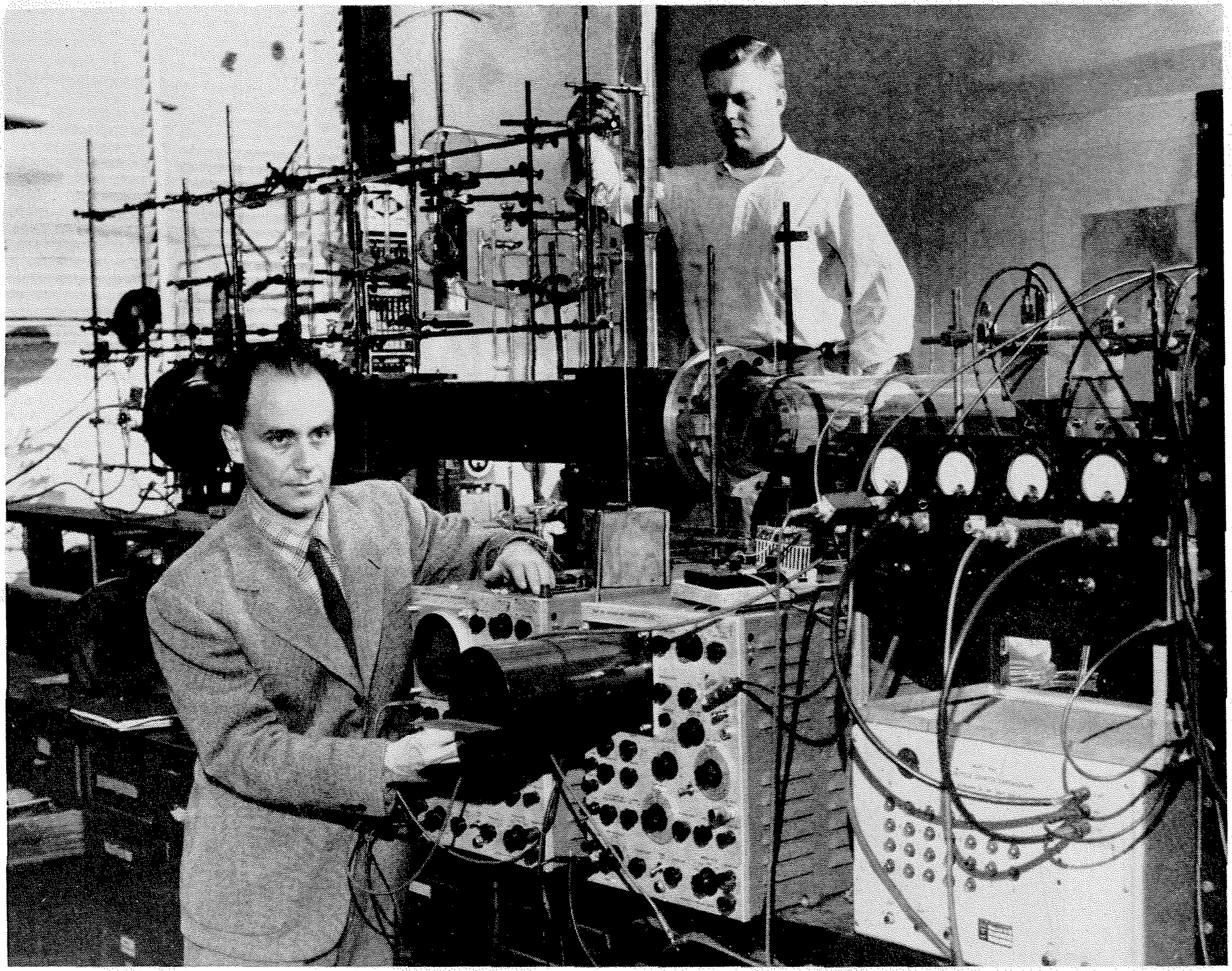


Dr. Norman Davidson, graduate student Garry Schott, and the shock tube used in their studies of very fast reactions.

MICROSECOND CHEMISTRY

A progress report on Caltech reseach into chemical reactions which take place in less than a thousandth of a second

by NORMAN R. DAVIDSON

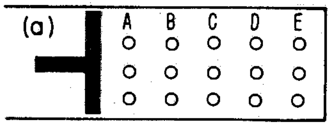
CHEMICAL KINETICS is the study of the rates of chemical reactions. The study is worth while for two reasons—one practical and one theoretical. The practical reason is that chemical reactions are used to make useful substances or to convert chemical energy into mechanical energy. Obviously such reactions must proceed at a suitable rate, neither too fast nor too slow, if they are to be useful. The theoretical reason is that an undersanding of the mechanism of a chemical reaction—a picture of how the molecules actually collide and rearrange—can be gained by measuring the reaction rate and its variation with the experimental conditions, such as temperature, pressure, or concentration of reactants.

It is relatively straightforward, in principle, to measure the rates of slow chemical reactions. One mixes the reactants and at a suitable time subjects the reacting mixture to a chemical analysis which indicates how much reaction has occurred. Alternately, one can measure some physical property of the reacting system—for example, its color, electrical conductivity, or pressure—which changes as the reaction takes place. In practice, of course, a great deal of skill and hard work is required for a successful measurement.

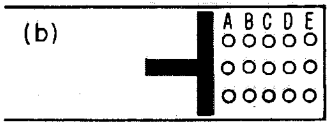
Chemical kinetics is a comfortably big subject. There are many slow reactions whose rates and mechanisms have not yet been properly studied. Why then should chemists set up elaborate apparatuses and go to a great deal of trouble to measure the rates of fast reactions? One reason is that some fast reactions are of considerable practical importance. A high explosive, for example, must react and liberate hot gases extremely rapidly if it is to perform its destructive function properly. On the other hand, a propellant charge in an artillery shell or a rocket must burn rather rapidly so that the hot gases generated can propel the shell or rocket forward—but it must not burn so fast that it acts as a high explosive and blows the cannon or rocket to pieces.

Acetylene is made by rapid heating and cooling of methane. If the cooling process is somewhat slower, carbon black is the main product. Both of these products are used in ton quantities in America, but acetylene sells for about one dollar per pound and carbon black for compounding rubber sells for about ten cents a pound. Thus, an understanding of the factors which control the relative rate of acetylene formation as against carbon formation may be of great commercial value.

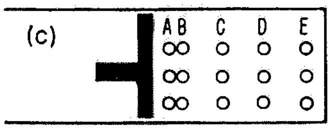
A second reason for interest in fast reactions is theoretical. A simple reaction such as the attack of a hydrogen atom on a bromine molecule, $H + Br_2 \rightarrow HBr + Br$ is very fast; it probably takes place on almost every collision. Part of the reason why the reaction occurs so readily is that the molecular rearrangement is so simple. The hydrogen atom comes up on one side of the bromine molecule and attaches itself to the nearest atom, simultaneously ejecting the other atom. This example is typical of a large class of reactions frequently encountered. Precise knowledge of these simple molecular rearrangements is necessary as a basis for a theory which will enable us to predict what happens in more complicated cases.



(a) Molecules inside cylinder will be compressed and heated by inward motion of piston.



(b) Piston has moved in slowly: molecules have been compressed into a smaller volume and have been heated.



(c) By rapid inward motion of piston, molecules A and B are compressed and heated before pressure disturbance reaches C, D, and E.

The two problems involved in measuring a fast rate are: (1) to prepare the reaction system so that there is a zero time when the reactants are mixed but have not yet reacted very much, and then (2) to measure the rate of reaction. The standard solution to the second problem, when one of the reactants or products absorbs visible or ultraviolet light, is to make rapid measurements of the change in light absorption by the system by means of a photoelectric cell and a cathode ray oscilloscope. This is a fast and sensitive method.

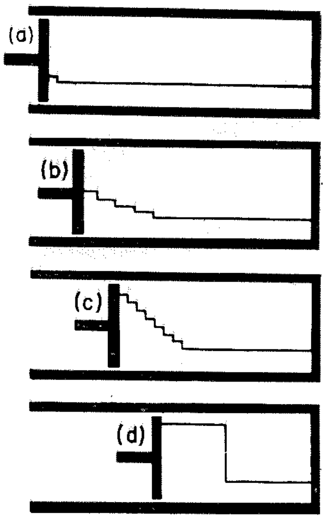
The most obvious solution to the first problem is to mix the reactants as fast as possible. This is fine. In fact, it is the only method for some reactions. But it takes a certain amount of time to mix two chemicals, and, if the reaction occurs as fast as the mixing, all one can measure is the rate of mixing.

Another general approach is to add energy, in some form or another, in a short period of time to a system which is not reacting. If this pulse of energy initiates a chemical reaction, the rate of this reaction can be followed by the method outlined above. There are several ways of realizing this energy pulse idea—by passing an electrical discharge through a gas; by shining a lot of light into a system in a short period of time by means of a high-speed flash lamp; or by heating a gas rapidly by compression.

Rapid compression

The rapid compression method is illustrated in the diagram at the left. The gas in the cylinder is rapidly compressed and heated by moving the piston inward. The molecules are depicted as being stationary; they are, of course, actually moving quite rapidly in all directions and their average velocity of random motion is a measure of the gas temperature. The inward-moving piston hits the gas molecules and thereby increases their velocity and temperature. This must be done so rapidly that the gas molecules are not cooled by collisions with the cooler walls of the cylinder. A small motion of the piston imparts additional motion to molecule A, which then moves over and hits molecule B, which then hits C, and so on. The heating is transmitted from A to E at a velocity that is approximately the velocity of the molecules.

If the piston is moving at a velocity considerably lower than this, then it does not move very far in the time required for its effect to be transmitted from A to E; the gas is being uniformly heated and compressed. This is depicted in (b). It is what happens in the normal operation of an automobile engine (with each piston going at about 4000 revolutions per minute); in the compression cycle preceding ignition by the spark, the



A shock wave is formed because the rearward pressure steps of a large pressure wave travel faster than the front ones and catch up with them. In this diagram the pressure steps are generated by the inward motion of the piston. The magnitude of the pressure is indicated by the height of the line inside the cylinder.

piston compresses the gasoline-air mixture in about 0.0075 second; the piston moves at a velocity of about 1000 centimeters per second, which is about 1/40 the velocity of the gas molecule; and with a compression ratio of 6, the gas is heated by about 300°C.

Suppose it is desired to heat the gas more rapidly and the experimenter manages to get the piston moving at a velocity comparable to or greater than that of molecules. Now he must worry about the fact that the piston moves an appreciable distance while the pressure and temperature are being transmitted from molecule A to molecule E. In effect, molecules A and B are heated as much as they are going to be before molecules D and E are heated at all, as depicted in (c). The compressional pressure wave which travels from left to right down the cylinder has interesting and surprising properties which we now consider.

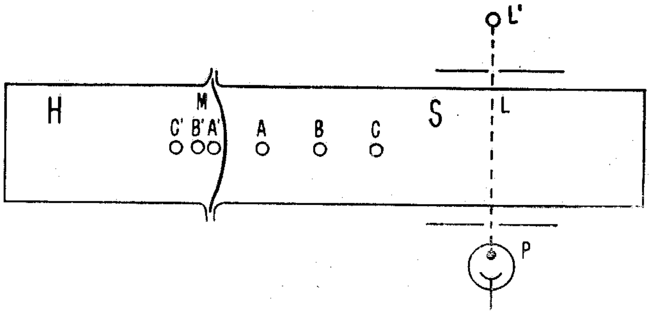
In (a) of the diagram at the top of this page, a small compressional pressure wave has been generated by a single inward jerk of the piston. This pressure wave travels from left to right along the tube at a velocity which is the velocity of sound in the gas—sound being a collection of such small pressure waves. This velocity is approximately the average velocity of the molecules, because the disturbance is transmitted by one molecule moving over and hitting the next one, etc. Obviously, this argument is not an exact one, so that the velocity of sound and the average molecular velocity are not exactly the same.

In (b) more pressure steps have been generated by further inward jerks of the piston. These travel along the tube, pursuing the preceding one. Each pressure step moves through gas which has been heated by all the previous compressions. Therefore, each step travels faster than the one in front of it, and catches up with it. The final result, therefore, is a single large step-shaped pressure wave. This is called a shock wave.

A shock wave is a wonderful way to heat a gas molecule in a hurry. Each molecule in its path is hit and heated as the wave moves down the tube. It takes only a few molecular collisions for each molecule to pass through the shock front—that is, to go from the unshocked, unheated condition to the shocked, heated condition. Therefore, at atmospheric pressure, where each molecule undergoes about 10^{10} collisions per second, it takes between 10^{-10} and 10^{-9} second to heat up a molecule of a gas by passage of a shock wave.

The only impractical feature of the rapid heating apparatus described so far is the piston. To move it at a velocity of 1.1 x 10^4 centimeters per second (2500 miles per hour)—which would be required to heat air from room temperature to 1000°C—would probably require that the piston be propelled by a cannon. It is practical, however, to push on one gas with another gas. The device for doing this, called a shock tube, is illustrated in the drawing below.

In this diagram, a membrane M separates the tube into two compartments. The one on the left, labelled H, contains high-pressure gas to push the piston, the compartment S on the right contains gas, at a lower pressure, which is to be compressed and heated. When the membrane M breaks (or is broken by touching a pin to it), Molecule A^1 from the high pressure side moves over and hits molecule A. A hits B. B hits C, and the compressional pressure wave travels down tube S. At the same time, B^1 pushes on A^1, C^1 pushes on B^1, etc. That is, the high-pressure gas in H expands and pushes on the low-pressure gas in S: it plays the role of a piston.



Schematic diagram of a shock tube. Molecules A^1, B^1, and C^1 are in the high-pressure (driving) section H, separated by the membrane M, from molecules A, B, and C in the low-pressure (driven) section S. L is a beam of light from the lamp L^1, shining through the tube S, on the photocell P.

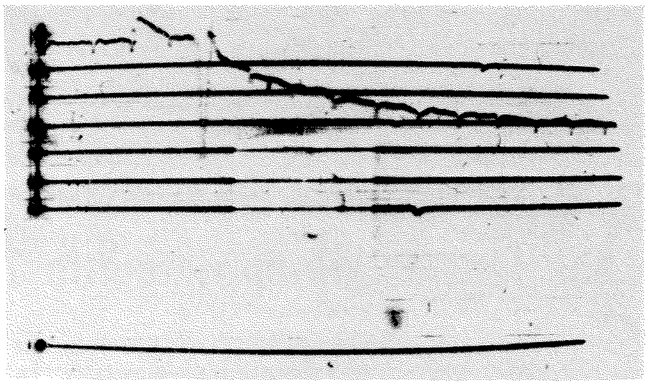
With this device it is comparatively easy (that is, just an ordinary difficult scientific job) to generate good shock waves. For example, with a pressure of about 1 pound gauge of air in S, a pressure of about 130 pounds of hydrogen in H produces a shock wave which travels through the air at a velocity of about four times the velocity of sound and heats the air up to 1000°C. (It is assumed here that the hydrogen does not mix with the air and react with it but simply pushes on it. Because of their low mass, hydrogen molecules have a high molecular velocity and are good pushers.)

Photo-electric measurement

One other feature is shown in this shock tube. There is a light beam, L, that shines through the tube. As already described, the rate of a chemical reaction in a color change can be measured by photo-electric measurement of the change in the light transmission of the system. An example of this sort of investigation was conducted in our laboratory by Dr. Tucker Carrington. The chemical reaction is

$$\underset{\text{colorless}}{N_2O_4} \rightarrow \underset{\text{brown}}{2\,NO_2}$$

Nitrogen dioxide, NO_2, is a brown gas—it absorbs blue light. Two NO_2 molecules stick together to form one N_2O_4 molecule, which is colorless. At low temperatures, the stable form is N_2O_4. When the temperature is raised, the molecules are broken apart into NO_2 molecules and the gas becomes more colored. The rate of this reaction has been measured by passing a shock wave through a gas containing N_2O_4 (nitrogen was present as an inert diluent gas). The shock wave heats up the N_2O_4 which then dissociates into NO_2 molecules. Depending on the temperature and nitrogen concentration, the reaction takes place in about 0.000010 to 0.000100 second. One of the measurements of the rate of this reaction is recorded below.



Oscilloscope record of rate of reaction $N_2O_4 \rightarrow 2NO_2$. Line starting at top left is photocurrent; bottom line is zero photocurrent. Other horizontal lines are calibration marks. Downward pips on photocurrent trace are timing markers 10 microseconds apart. The first small positive signal is a time marker from a delay circuit and is related to the measurement of the velocity of the shock wave. The large negative spike occurs as the shock wave intersects the light beam and is due to refraction of the light beam by the large refractive index gradient at the shock front. After this we are looking at heated gas in which the reaction $N_2O_4 \rightarrow 2NO_2$ is occurring. As NO_2 is formed over a period of 70 to 80 microseconds, light transmission and photocurrent decrease.

A shock wave, generated in a shock tube, can be used to heat up a gas either by a few degrees or by a few thousand degrees. It requires 1 to 3 microseconds for such a shock wave to pass through a light beam 1 millimeter thick. This method can be used to study any reaction which is caused by the heating by the shock wave and in which there is a change of color that affects the transmissions of the light beam, and which takes place in a time of from 10 microseconds to 1 millisecond.

Fast high-temperature reactions

We have been particularly interested in applying this technique to the study of fast high-temperature reactions. In intial investigations, we have chosen reactions which are simple both experimentally and theoretically.

An example from the work of Mr. Doyle Britton is the rate of dissociation of bromine molecules into the atoms, $Br_2 \rightarrow 2\,Br$. The diatomic molecules are brown—they absorb blue-green light—and the atoms are colorless. The reaction takes place at temperatures of the order of 1500-2000°.

The results show that the mechanism of the reaction is indicated by the equation, $A + Br_2 \rightarrow A + Br + Br$; that is, the dissociation reaction occurs when another gas molecule, such as the argon atom in the equation above, collides with a bromine molecule with great vigor and knocks it apart into atoms. These dissociation reactions are models for a class of reactions that occur in practically important high temperature processes, such as combustion reactions, and therefore their study is of some practical significance.

It would be particularly interesting to study the reactions that occur when air is rapidly heated. These phenomena are of importance for understanding the heating problem when a hypersonic projectile goes through the atmosphere. At high temperature, the nitrogen molecules (N_2) and oxygen molecules (O_2) will dissociate into atoms and will react to form NO.

None of these atoms or molecules absorb the right kind of light for the methods described above to be applicable. We are trying to think of a new idea—of a new technique—which will enable us to study this interesting system.