

## **Nobel Prize in Chemistry 1967**



**Manfred Eigen**



**Ronald George Wreyford Norrish**



**George Porter**

The Nobel Prize in Chemistry 1967 was divided, one half awarded to Manfred Eigen, the other half jointly to Ronald George Wreyford Norrish and George Porter *"for their studies of extremely fast chemical reactions, effected by disturbing the equilibrium by means of very short pulses of energy"*.

### **RESEARCH INFORMATION:**

The chemists of older times were chiefly interested in how to produce substances from natural products which might prove useful; for example, metals from ores and the like. As a matter of course, they were bound to notice that some chemical reactions took place rapidly, while others proceeded much more slowly. However, systematic studies of reaction velocities were hardly undertaken before the mid-19th century. Somewhat later, in 1884, the Dutch chemist, [Van 't Hoff](#), summarized the mathematic laws which chemical reactions often follow. This work, together with other achievements, earned for Van 't Hoff the first Nobel Prize for Chemistry in 1901.

Almost all chemical reactions will proceed more rapidly if the mixture is heated. Both Van 't Hoff and [Svante Arrhenius](#), who for other discoveries was awarded the third Nobel Prize for Chemistry in 1903, set up a mathematical formula which describes how the

velocity of a reaction increases with temperature. This formula could be interpreted by the assumption that when two molecules collide, they usually part again and nothing happens; but if the collision is sufficiently violent, the molecules disintegrate and their atoms recombine into new molecules. One could also envisage the possibility that the molecules moved towards each other at moderate velocity, but that the atoms in one molecule oscillated violently so that no severe impact would be required for that molecule to disintegrate. It was already then realized that higher temperature implied two things: the molecules moved faster, and the atoms oscillated more violently. It was also realized that when a reaction velocity could be measured, only the merest fraction of the collisions involved really resulted in a reaction.

How fast were the reactions that could be measured in the old days? Considering that the substances first had to be mixed, after which samples had to be removed at specified times and then analyzed, the speed of the procedure was necessarily limited. The best case was if one could observe the change in some physical property such as colour; then it was not necessary to remove samples. The chemists had to read off his clock and measuring instrument, and then to make entries in his laboratory journal. If he was quick, he could keep up with a reaction which had run half its course in a few seconds.

How slow were the reactions one could measure? Eigen has said that this is determined by how long a time a young man wants to devote to his doctoral dissertation. If as a practical maximum we say that half the reaction is completed after three years, that comes to around 100 million seconds. Naturally, there are even slower reactions.

Many reactions were of course known to proceed at velocities so great as to defy measurements. For example, no one had succeeded in measuring the velocity of the reaction between an acid and an alkali. In such cases it was understood that the molecules reacted without the collision being very violent. In the study of reactions where a large number of molecules take part, it turned out that the velocity often depended on the quantities of substances used in such a manner that a step-by-step sequence had to be assumed for the reaction: one of these steps was slow and hence determined the overall

course of the reaction, while the other steps were immeasurably fast. The German chemist, Max Bodenstein, studied many such reactions at the beginning of this century.

A major advance was achieved in 1923 by the Englishmen, Hartridge and Roughton, who let two solutions arriving through separate tubes meet and be mixed, and then caused the mixture to flow swiftly through an outlet tube, in which the reaction could be observed as it proceeded. This method permitted measurement of reaction times down to thousandths of a second. But there are still many reactions that proceed still more rapidly. They could not be studied by this method for the simple reason that the substances cannot be mixed fast enough

When nitric acid gets to react with a number of substances, a brown gas, nitrogen dioxide, formed. This gas has certain properties which were interpreted by assuming that the brown molecules could form pairs, thus doubling their size. This was a typical example of a high-velocity reaction that no one has succeeded in measuring.

In 1901 a student studying for the doctorate with Walter Nernst investigated the velocity of sound in several gases, among them nitrogen dioxide. He found that the equilibrium between the single and double molecules was accomplished much more rapidly than the sound oscillations. But he perceived that the speed of sound ought to be modified if one used sufficiently high-pitched tones - far beyond the capacity of the human ear to hear. No less a person than [Albert Einstein](#) carried out a theoretical study of this phenomenon in 1920. However, many years were to elapse before instruments could be devised to measure it. A complication was found to be involved here in that the sound is absorbed by the gas. None the less, the principle is important; the essential point here is that one is not going to mix two things, but rather to start off from a chemical system in equilibrium and to disturb this equilibrium, in this case by exposing the gas to the condensations and attenuations which constitute sound.

The fact that light produces chemical reactions has been known since time immemorial. Thus it bleaches colours and alters silver salts, which action is the very basis of photography. The ability of light to produce a chemical reaction depends on its

absorption by a molecule, which then becomes so excited that it can react. Investigations of the energy states thus acquired by molecules were begun some fifty years ago. One of the findings was that the atoms of a molecule oscillated at rates of the order of billionths of a second. Chemical reactions inevitably take longer, for time must be allowed for the atoms to dissociate and re-combine into new molecules. For these purposes the times required come to, say, one tenthousandth part of a millionth of a second. In other words, such are the times for the fastest chemical reactions. They amount to one-tenth of one-millionth of the times Hartridge and Roughton were able to measure with their method. To convey an idea of what one tenthousandth part of a millionth of a second means, it can be said to form the same part of one second as one second is of three hundred years.

The 1967 Nobel laureates in Chemistry have opened up the whole of this vast field of reaction kinetics for research. They did so by applying the principle I have just mentioned: to start from a system in equilibrium and to disturb this equilibrium suddenly by one means or another.

If a molecule has absorbed light so that it can react, it usually does this so fast that too few of these activated molecules are present at any one time to reveal their existence by any known method of analysis.

Ever since the 1920's, Professor Norrish has been studying reaction kinetics and he was one of the leading scientists in this field. A younger associate joined him in the late 1940's in the person of George Porter. They decided to make use of a flash lamp, the kind you have seen photographers use. The only difference was that they made their lamp thousands of times more powerful. Indeed, subsequent refinements have led to the construction of such lamps with an effect greater than the total effect which the whole city of Stockholm consumes on a winter afternoon with the lights turned on and the factories still humming before closing time - and that is 600000 kilowatts. There is just one catch, however; this enormous effect in the lamp lasts no more than onemillionth of a second or so. Still, in this way much if not most of a substance in a tube next to the flash lamp can be converted into an activated form, or the molecules broken up so as to yield atom groups

with a high reactivity. It then becomes possible to study these newly formed molecules spectroscopically, but since they react so readily, this must be made extremely fast. Thanks to modern electronic equipment, however, these rapid processes can be recorded.

The new method developed by Norrish and Porter enabled them to study at first hand many fast reactions which one had previously only guessed that they took place. I cannot begin to enumerate even a sample of the reactions which Norrish and Porter, not to mention a great many other scientists, have investigated with this method. Suffice it to say that, in an earlier day, the study of these short-lived high-energy molecules and their chemical characteristics could hardly even have been contemplated as a wild dream. The flash photolysis method of Norrish and Porter inflicts a drastic change of behaviour on molecules. By contrast, Eigen treats his molecules more leniently. In 1953 he and two associates published a study on the absorption of sound in a number of salt solutions. The theoretical part of their report demonstrated how this absorption could be used to estimate the velocity of fast reactions which take place in the solution. Thus a solution of magnesium sulphate contains ions of magnesium and sulphate, as well as undissociated salt molecules. Equilibrium sets in after about  $1/100000$  of a second. This causes that sound which oscillates 100000 times a second is absorbed by the solution.

Eigen has invented several methods, however. If, say, a solution of acetic acid is subjected to a high-tension electric pulse, more molecules of this substance are dissociated than else would be the case in an aqueous solution. That takes a certain length of time. When the electric pulse is turned off, the solution goes back to its former equilibrium; this also takes some time, and that relaxation can be recorded.

The shock current caused by the application of the high-tension pulse will heat the solution a few degrees. Most chemical equilibria are slightly displaced when the temperature is changed, and the rapid establishment of the new equilibrium after heating can be recorded.

Eigen has also specified other methods for starting fast reactions in a solution formerly in equilibrium. Whereas the study of electrolytic dissociation equilibria was

already commenced in the 1880's by [Svante Arrhenius](#), it is now possible to measure the reaction velocities at which these equilibria are established. A large number of extremely fast reactions can now be studied, involving all kinds of molecules ranging from the very simplest ones to the most complex that the biochemists work with.

Although Eigen starts his reactions in another way than that employed by Norrish and Porter, the instruments that record the fast reactions are largely identical for both research groups.

The chief importance to chemists of the methods worked out by Eigen, Norrish and Porter is their usefulness for the most widely diverse problems. A great many laboratories round the world are now obtaining hitherto undreamt-of results with these methods, which thereby fill what used to be a severely-felt gap in the means of advance available to Chemistry.

***For more details please visit:***

[http://www.nobelprize.org/nobel\\_prizes/chemistry/laureates/1967/press.html](http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1967/press.html)