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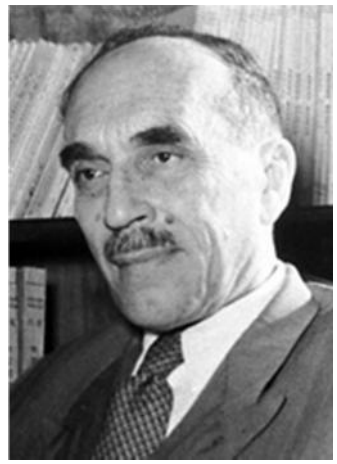
Nobel Prize in Chemistry 1956

Sir Cyril Norman Hinshelwood



Nikolay Nikolaevich Semenov

The Nobel Prize in Chemistry 1956 was awarded jointly to Sir Cyril Norman Hinshelwood and Nikolay Nikolaevich Semenov *"for their researches into the mechanism of chemical reactions"*

RESEARCH INFORMATION:

The Nobel Prize which is now to be given to Sir Cyril Norman Hinshelwood and Academician Nikolai Nikolaevic Semenov "for their researches into the mechanism of chemical reactions" reminds us of the very first Nobel Prize in Chemistry, which was awarded in 1901 to the Dutchman Jacobus Henricus van 't Hoff. He received his prize for "the discovery of the laws of chemical dynamics" i.e. the velocity of chemical reactions.

Van 't Hoff and the Swede Svante Arrhenius had already in the 1880's disclosed that when molecules of two substances collide, the collision must be sufficiently violent if the initial molecules are to break down and their atoms to rearrange into new molecules, that is, for a chemical reaction to take place.

Thirty years ago Hinshelwood studied a number of chemical reactions which allowed him to draw important conclusions concerning the collisions between molecules, which set them in such vibration that they became unstable.

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There are some chemical reactions which are extremely sensitive to light. In 1900 Max Planck had found that light was composed of discrete quanta. It was then natural to think that when a light quantum hits a molecule, it could be excited in such a way that it underwent a chemical reaction. But how could one possibly understand that a single absorbed light quantum could cause perhaps a million molecules to react?

In 1913 the German chemist Max Bodenstein put forth an idea which proved to be extremely fertile, the idea of chain reactions. This means, that if two molecules react, not only molecules of the final reaction products are formed, but also some unstable molecules, having the property of being able to react with the parent molecules without the collision being very violent. In this reaction, new unstable molecules are formed besides stable reaction products and so on. We thus obtain a chain of reactions, so when two molecules have reacted, they cause a great number of more molecules to react.

A Danish and a Dutch scientist, Christiansen and Kramers, in 1923 pointed out that such a chain reaction need not start with a molecule excited by light, but could also start with two molecules colliding violently in the way van 't Hoff had thought of.

Christiansen and Kramers also set forth another fruitful idea. If in one link of the reaction chain not only one, but two or more unstable molecules are produced, the reaction chain will branch. The result is that the reaction will spread over the whole mixture so it reacts in its entirety extremely rapidly, thus giving rise to an explosion. However, they did not elaborate the idea further, but pursued other researches.

The laws that were advanced by van 't Hoff do not always seem to be valid, a fact which he was well aware of himself An example: phosphorus glows in the dark, because it is oxidized by the oxygen of the air. We should then expect phosphorus to glow five times more intensely if we put it in pure oxygen, as air contains only 20% of oxygen. But already in the 18th century it was known that phosphorus did not glow at all when lying in pure oxygen. The oxidation also ceases suddenly when the oxygen content decreases below a certain limit.

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The combustion of phosphorus vapour and oxygen was studied in 1926 by two scientists in Leningrad, Chariton and Valta. The greatest authority of that time on chemical reaction velocities, Bodenstein, whom I just mentioned, said frankly that their results were incomprehensible and must be wrong. They *were* incomprehensible from the point of view of that time, but the essential results were *not* wrong. Semenov reinvestigated the matter and found that it really was so that a mixture of phosphorus vapour and oxygen did not react at all if the gas pressure was too small or too great, but that at intermediate pressures the mixture exploded. Semenov disclosed that the idea of Christiansen and Kramers gave the explanation of this behaviour. He and his team could show, that the pressures, at which the mixture exploded, were dependent on the proportion of gases and dimensions of vessel in a way which agreed completely with the assumption that this combustion was a chain reaction.

The mathematical relations in this case were rather simple. There are other combustions with far greater practical importance, but which are much more complicated. I will first mention the combustion of hydrogen with oxygen. This important reaction was studied both by Hinshelwood and his team in Oxford and by Semenov and his team in Leningrad. Of course also many other scientists have contributed to the final elucidation, but the present prize-winners have indicated the principles guiding the work. Another technically important chain reaction is the combustion of carbon monoxide, not to mention the combustion of hydrocarbons.

When it was found that a great number of reactions were chain reactions, many people in the first enthusiasm thought that almost all reactions were chain reactions and that the simpler mechanisms previously thought of were exceptions. But Hinshelwood put the matter in order. He found substances which could simultaneously react in two ways, one part reacting by a chain mechanism and at the same time the rest reacting in the old-fashioned way.

There are many reactions which do not start at once when the substances have been mixed, but after a while. A number of explosions behave that way and are therefore extremely unpleasant. Semenov showed that the concept of chain reaction could also explain this behaviour.

I shall conclude with an example showing how these researches have a direct bearing upon our daily life. I have just mentioned that the combustion of hydrocarbons is a chain reaction. When internal combustion engines were built with higher and higher compression in order to get more energy out of them, the result was that the air-gasoline mixture burned much more rapidly than was appropriate, it exploded. But the rapid combustion could be regulated by using gasoline containing suitable hydrocarbons or with suitable additions. Such gasoline is said to have a high octane number. The vast amount of work carried out in recent years to augment the effect of internal combustion engines in this way is founded, as far as its chemical aspects are concerned, on the fundaments laid down by these prize-winners.

<u>For more details please visit:</u>

http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1956/press.html