SOVIET PHYSICS
JETP

SOVIET PHYSICS JETP VOLUME 3, NUMBER 4 NOVEMBER, 1956

Nikolai Nikolaevich Semenov

(On the sixtieth anniversary of his birth)

J. Exptl. Theoret. Phys. (U.S.S.R.) 30, 625-627 (April, 1956)

NIKOLAI Nikolaevich Semenov is one of the greatest Soviet physicists, noted for his works in many fields of physics, and chiefly in the new branch of science, created by him, on the borderline between physics and chemistry.

N. N. Semenov was born in Saratov, April 15, 1896. In 1913 he completed the course at the higher school in Samara and enrolled in the physical-mathematical faculty of the University of St. Petersburg. While still a university student, Nikolai Nikolaevich began to engage in scientific investigation. He took an active part in the work of the student physics circle founded by A. F. Ioffe, many of whose members have now become great scholars. In 1916, at the age of twenty, he published his first work on the collisions of electrons with molecules.

On graduating from the university in 1917, N. N. Semenov worked at the University of Tomsk as an assistant in the physics department. In 1920, at the invitation of A. F. Ioffe, he returned to Leningrad and began work in the State Physico-Technical Roentgenological Institute, where he was associate director and headed the laboratory of electron physics (since 1931 this has been the Institute of Chemical Physics of the U.S.S.R., with Nikolai Nikolaevich as permanent director down to the present time).

At the beginning of his scientific activity N. N Semenov studied mainly elementary processes (together with V. N. Kondrat'ev, A. I. Leipunskii and others). They investigated the ionization potentials of vapors of salts and of metallic vapors, and processes of dissociation and recombination. In these works there were discovered the phenomena of dissociation of diatomic molecules by electron impact and the direct recombination of a normal and an excited atom with the emission of a light quantum. The results of these works were published in the report "Chemistry and Electron Phenomena" (1924) and later, together with V. N. Kondrat'ev and Iu. B. Khariton, in the book "Electron Chemistry" (1927).

During this same time Nikolai Nikolaevich gave much attention to electrical phenomena in gases and solids. Together with A. F. Val' ter he carried out many investigations on electric fields, the passage of electric current through gases, breakdown of vacuum, and breakdown of solid dielectrics. As a result of his work on the breakdown of solid dielectrics he and V. A. Fock developed a theory of thermal breakdown.

A considerable number of N. N. Semenov's works at this time were devoted to molecular phenomena in the condensation of vapors on cold surfaces. Together with Iu. B. Khariton and A. I. Shal'nikov he investigated critical phenomena in the condensation of vapors and of molecular beams, and discovered the dependence of the critical condensation temperature on the vapor density. N. N. Semenov and Ia. I. Frenkel gave an exhaustive theory of these phenomena. Investigations were also made on the joint condensation from two molecular beams with formation of a molecularly dispersed mixture, which was of interest for the study of reactions in the solid phase.

The interest of N. N. Semenov in molecular beams was of long standing; as early as 1920 he and P. L. Kapitza projected the application of molecular beams in an inhomogeneous magnetic field to measure the magnetic moments of atoms and molecules. Later this work was successfully carried out by Stern and Gerlach.

The world-wide fame of N. N. Semenov is most of all connected with his works on chemical kinetics. He always displayed enormous interest in the investigation of chemical phenomena by physical methods, believing that physics is the key to the most interesting and at the same time the least studied problems of chemistry, and that a close union of physics and chemistry must lead to new achievements of science.

As is well known, the application of physics to chemistry led to the creation of a most important branch of chemistry--the theory of chemical equilibria. But the question of the speeds of chemical reactions remained almost completely undeveloped. A theory of the speeds of chemical reactions can be constructed only on the basis of a known mechanism of chemical changes. In the first attempts to construct a theory of the speeds of chemical reactions (van't Hoff) the transformation of individual molecules was represented as a single elementary act, expressed by the overall stoichiometric equation of the reaction, i.e., as a direct interaction between saturated molecules. It was also supposed that in the accomplishment of the reaction there must exist some sort of energetic barrier, connected with the breaking up and regrouping of the bonds. These ideas about the direct molecular interaction have been found to be applicable only in very rare cases.

It has been established that a chemical change takes place in several stages with the formation of a whole series of intermediate products. But this conception also failed to provide the key to an understanding of the mechanism of the progress of chemical reactions and to the calculation of their speeds. For the solution of this problem it was necessary to seek an essentially new mechanism of the progress of chemical reactions.

The fundamental accomplishment of N. N. Semenov and the school he founded lies in the fact that he was the first to construct a chain theory of chemical reactions. The basic role in the mechanism of a chain chemical reaction is played by free radicals. The initial formation of an individual free radical is regarded as an extremely rare and difficult event, but once having been formed, the radical enters into interaction with molecules of the system, is repeatedly regenerated, and thus produces a long chain of chemical changes up to the time when, through causes that are accidental from the point of view of the reaction (destruction at the wall of the vessel, interaction with some other sort of active center), it ends its existence.

Of particular importance was the discovery by Semenov of reactions with branched chains, in which the radicals in the course of their interactions with the molecules are not only regenerated, but also multiplied. If the multiplication predominates over the destruction of radicals, the reaction proceeds with an acceleration, which can lead to an explosion. The actual course of the reaction depends in an essential way on external conditions; for example, if the destruction of active radicals occurs at the walls of the vessel, then the acceleration of the reaction depends in a critical way on the dimensions of the vessel, the pressure, admixtures of inert gas, etc. For example, at a given temperature, pressure, composition of the mixture, and condition of the surface of the walls of the vessel, there exists a critical size of the vessel, beginning at which the multiplication of active centers predominates over their destruction. This size is also the critical one with regard to the chain reaction. This was first discovered in 1926 by Iu. B. Khariton and Z. Val'ta in experiments on the oxidation of phosphorous vapor. The correct interpretation of these experiments was also the initial link in the creation of the chain theory. A model example of a reaction with branching chain is the reaction of oxidation of hydrogen.

$$\begin{gathered} OH + H_2 = H_2O + H, \\ H + O_2 = OH + O, \\ O + H_2 = OH + H. \end{gathered}$$

The result of this chain is that from two molecules of hydrogen and one molecule of oxygen there are obtained, through the participation of an OH radical, one molecule of water and two new radicals OH and H. Thus in the course of the reaction the number of radicals increases sharply.

At the present time the nuclear chain reaction of uranium fission is well known to all. This reaction was predicted theoretically on the basis of the chain theory of chemical reactions. We note that in the case of the nuclear reaction the mechanism of the elementary act and the "active center", i.e., the neutron, were comparatively well known, whereas in the development of the theory of chemical chain reactions, on the other hand, it was necessary to draw the conclusion about the mechanism of the reaction and the nature of the active centers--the free radicals--from the behavior of the reaction itself.

The large amount of experimental and theoretical material accumulated at the Institute of Chemical Physics up to 1934 served as the foundation of N. N. Semenov's classic monograph "Chain Reactions", constantly used as a reference by all workers in the field of chemical physics both in the U. S. S. R. and abroad. The general theory of chain reactions worked out in this book was developed further by Semenov and his collaborators for various classes of chemical reactions: oxidations, polymerizations, thermal cracking, and so on, and is still being elaborated in the Institute of Chemical Physics.

The characteristic feature of the investigations being conducted at the present time is the study of the detailed chemical mechanism of chain reactions, and the determination of the nature of concrete active centers--the atoms and radicals responsible for the development of the process by the chain mechanism.

One of the important branches of chemical kinetics is the theory of combustion and explosion. The introduction of chain concepts has shown itself very fruitful here. The possibility of the occurrence of a chain explosion is readily understood in the case of branching chains. Besides chain explosion, Nikolai Nikolaevich also studied thermal explosion. The theory of thermal explosion which he originated is closely related in method to the theory of thermal breakdown of dielectrics which was mentioned earlier. Under certain conditions the heat produced in the course of a reaction does not have time to be conducted away from the reaction zone and raises the temperature of the system, accelerating the reaction and thus simultaneously speeding up the evolution of heat. These concepts are also essential for an understanding of thermonuclear reactions.

To N. N. Semenov, together with Ia. B. Zel'dovich, there also belongs the credit for important works on the mechanism of combustion and the propagation of flames.

At the present time the theory of the mechanism of chemical processes is still being developed on the basis of the chain theory. Nikolai Nikolaevich is taking the most active part in the development of this theory, penetrating exceptionally deeply into all the questions connected with chemical kinetics, and is the intellectual leader and inspirer of the school he has founded.

The range of Nikolai Nikolaevich's interests is extraordinarily wide. Together with the continuation of the work on the kinetics of various chemical processes, he gives great attention to scientific and methodical questions of nuclear physics. On his initiative and with his direct participation, a series of investigations of nuclear reactions with fast particles was set up in the Institute of Nuclear Problems of the Academy of Sciences of the U.S.S.R. In his study of fast particles, Semenov became interested in the problem of constructing a linear accelerator for the production of large currents. His splendid physical intuition, clearness of thought, and inventiveness enable him to lead the work of a whole association of workers both in this field and in a number of other branches of physics and technology.

N. N. Semenov reaches his sixtieth birthday in the full flower of his creative powers. His colleagues in the Institute of Chemical Physics and many other physicists and chemists of the Soviet Union, having known Nikolai Nikolaevich throughout several decades, have always admired his unusual theoretical activity. All who have ever had personal dealings with Nikolai Nikolaevich or who have made use of his work, wish with all their hearts that he may continue this creative activity for many years.

Translated by W. H. Furry
132