Nobel Centennial Essays

A Century of Chemical Dynamics Traced through the Nobel Prizes

1956: Hinshelwood and Semenov

by J. Van Houten

Nobel Prize in Chemistry 1956
Sir Cyril Norman Hinshelwood (1897–1967)
Nikolay Nikolaevich Semenov (1896–1986)

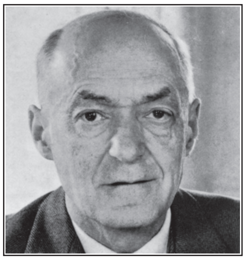
for their researches into the mechanism of chemical reactions

The post-World War II era saw a remarkable increase in interest in chemical dynamics and the mechanisms of fast chemical reactions. In part, that interest can be attributed to research on fuels and munitions in the years leading up to and during the war. There also were many peaceful applications derived from better understanding of combustion processes in internal combustion engines, jet engines, and high explosives. Furthermore, technological advances in the first half of the 20th century had made it possible to study ever-faster reactions in ever-more detail.

The 1956 Nobel Prize presentation speech for Hinshelwood and Semenov began by recalling the fact that in 1901 Jacobus van't Hoff had received the first Nobel Prize for "the discovery of the laws of chemical dynamics," and that van't Hoff and the 1903 Nobel Laureate, Svante Arrhenius, were responsible for the concept that molecules must collide with sufficient energy if they are to react (*1*). However, the dynamic behavior of many reactions could not be explained by the laws that van't Hoff had proposed. For example, phosphorus was known to glow in air (hence the term phosphorescence) but not in pure oxygen or in atmospheres with reduced oxygen partial pressure (*2*).

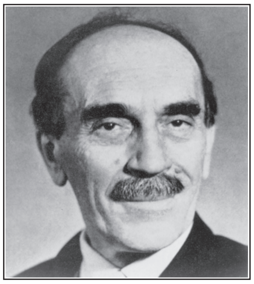
Photo-initiated reactions presented another paradox early in the 20th century—the concept that a single photon could initiate a reaction in a single molecule was accepted in accordance with Planck's theory, however the ability of a single photon to initiate the reaction of literally millions of molecules did not seem to make sense. In 1913 Max Bodenstein had first advanced the concept of reactive intermediates as part of a chain reaction mechanism. Bodenstein had managed to obtain an empirical fit to the kinetics of the reaction $H_2 + Br_2 \rightarrow 2HBr$, and he found that iodine hindered the reaction. However, he could not find a correlation between the free energy and the kinetics of the reaction (*3*). Ten years later Christiansen and Kramers postulated that chain reactions might be initiated thermally as well as by light and, furthermore, if two or more reactive intermediates were produced then the reaction could branch, resulting in an explosion.

Christiansen and Kramers did not pursue their research on chain reactions, and investigations of the reaction of phosphorus vapor with oxygen were taken up in 1926 by two scientists, Chariton and Valta, working at the Leningrad Physico-Technical Institute headed by Nikolay Semenov. They showed that the reaction of phosphorus vapor with oxygen did, indeed, depend on the pressure of the gases, with an explosion occurring only at intermediate pressures, and with no reaction at very high or very low pressures. Bodenstein, who was considered to be the world's authority on chemical dynamics at the time, stated that the results were incomprehensible and must be wrong. However, the simple fact that the experimental results were incomprehensible using the available models of the time did not mean that the results were wrong. Semenov explained the results by showing that chain reactions lead to explosions when the chain branches, thereby increasing the concentration of the reactive intermediates and, consequently, the rate of the reaction. Furthermore, Semenov developed the mathematical relations that showed why the rate of branching, and hence the rate of the reaction, was facilitated at intermediate pressures but not at higher or lower pressures (*1*).



Cyril Hinshelwood

Photo: Aaron Ihde collection



Nikolay Semenov

Photo: Aaron Ihde collection

Nikolay Nikolaevich Semenov

Nikolay Semenov spent his entire scientific career in Russia (U.S.S.R. during most of his life), and he was the first Russian to receive a Nobel Prize in chemistry or physics. He was educated at the University of Petrograd (later Leningrad and now again Saint Petersburg, the original name of that city when it was founded by Peter the Great), graduating in 1917. He became responsible for the electron phenomena laboratory of the Leningrad Physico-Technical Institute in 1920, and he was assistant director of this Institute from 1920 until 1931 when he became director of the Institute of Chemical Physics of the U.S.S.R. (*4*). In 1943 the Institute moved to Moscow, and Semenov was named a professor at Moscow State University. In 1960 he became chairman of the All-[Soviet]-Union Society for the Propagation of Political and Scientific Knowledge.

Semenov literally "wrote the book" on chain reactions. His first important book, *Chemical Kinetics and Chain Reactions*, published in Russian in 1934 and in English a year later, was the first book in his country to describe in detail the theory of branched and unbranched chemical chain reactions. His 1954 book, *Some Problems of Chemical Reactiv-*

ity, was first published in Russian and subsequently appeared in English, American, German and Chinese editions (*1*).

Cyril Norman Hinshelwood

Cyril Hinshelwood was doing his research on chain reaction mechanisms in England simultaneously with Semenov's work in the U.S.S.R. Both Semenov and Hinshelwood studied $2H_2 + O_2 \rightarrow 2H_2O$, one of the most important branching chain reactions now considered a textbook example, as well as the combustion reactions of carbon monoxide and of hydrocarbons. The research with hydrocarbon chain reactions provided a basis for understanding why some of the then new high-compression-ratio internal combustion engines "knocked." The knocking was shown to be the result of the fuel combustion reaction proceeding too rapidly at the higher pressures in those engines, leading to an explosion. The rate of branching (consequently the progress of the reaction) could be controlled by suitable additives, leading to the concept of octane number for gasoline.

Hinshelwood, like Semenov, spent his entire scientific career in his home country, England. He received his doctoral degree from Oxford University, and he held positions at Balliol, Trinity, and Exeter Colleges before being appointed Dr. Lee's Professor, University of Oxford in 1937 (*1*). His interests were not limited to the study of chain reactions, as evidenced by the titles of some of his important books: *Thermodynamics for Students of Chemistry* (1926), *The Kinetics of Chemical Change* (1926), *Kinetics of the Bacterial Cell* (1946), and *The Structure of Physical Chemistry* (1951). The Langmuir–Hinshelwood equation describing the rate of surface-catalyzed bimolecular reactions was discussed in this *Journal* in 1979 (*5*). Irving Langmuir won the Chemistry Nobel Prize in 1932 for "discoveries and investigations in surface chemistry" (*6*).

In 1950, three years before Watson and Crick proposed their model for DNA, Hinshelwood wrote that nucleic acids dictate the ordering of amino acids in protein synthesis. Crick later declared Hinshelwood's postulate to be the first serious suggestion of how DNA might function (*7*).

Hinshelwood was truly a "Renaissance man". He was fluent in many languages, was a classical scholar, and served as president both of the [British] Royal Society [of Science] (in 1955) and of the [British] Classical Association (in 1960) (*8*).

The concluding part of the 1956 Nobel Prize presentation speech for Hinshelwood and Semenov contains two remarkable observations. The first is an interesting reflection of the state of chemistry at that time. To place the science of this era in perspective, consider that in 1956 the Nobel Prize in physics went to the inventors of the transistor, and the Nobel Prize in medicine went to the developers of the heart catheter. The 1956 chemistry citation includes the statement: "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" (*1*).

Today, almost half a century after Hinshelwood and Semenov received the Nobel Prize, chain reactions are well understood. They are seen in many gas-phase reactions, and they have recently been recognized as being particularly important in atmospheric chemistry. The 1995 chemistry Nobel Prize (which will be discussed in a future essay in this series)$^{\mathrm{W}}$ was awarded for studies of atmospheric free-radical reactions (*6*). Free-radical reaction mechanisms are prominently featured in modern chemistry texts at all levels. In fact, radical chain reactions are frequently the first example of an intimate reaction mechanism that students encounter.

The second observation that I consider remarkable in the 1956 chemistry Nobel presentation speech is such by virtue of the facts surrounding the origin of the Nobel Prizes. "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" (*1*). Alfred Nobel derived some of the fortune that he bequeathed to support the Nobel Prizes from the invention of dynamite, which made handling high explosives much less hazardous. Inasmuch as Nobel lived in Russia as a youth and much of his fortune came from Russian oil fields that he inherited from his father (*9*), it seems appropriate that a Russian, Semenov, should be honored for elucidating the nature of chain reactions that are so important both to explosives and to the petroleum industry.

$^{\mathrm{W}}$Supplemental Material

A list of all recipients of the Nobel Prize in Chemistry, their affiliations, and the work for which the award was made, is available in this issue of *JCE Online*.

Literature Cited

1. Nobel e-Museum–Chemistry 1956 (with links to Prize Presentation and Biography pages). *http://www.nobel.se/chemistry/laureates/1956/index.html* (accessed Jan 2002).
2. See Keiter, R. L.; Gamage, C. P. *J. Chem. Educ.* **2001**, *78,* 908 for a discussion of this phenomenon and a demonstration involving the reaction between white phosphorus and oxygen.
3. Stock, J. T. ACS National Meeting, Chicago, August 2001, HIST 47.
4. Semenov entry. *http://www.biography.com* (accessed Jan 2002)
5. Glasser, L. *J. Chem. Educ.* **1979,** *56*, 22–23.
6. Van Houten, J. *J. Chem. Educ.* **2001,** *78*, 1570–1573; supplemental material (*http://jchemed.chem.wisc.edu/Journal/Issues/2001/Dec/abs1570.html*)
7. Hinshelwood entry. *A Dictionary of Scientists*, Oxford University Press, 1999. *http://www.xrefer.com/entry/494580* (accessed Jan 2002)
8. Hinshelwood entry. *http://www.biography.com* (accessed Jan 2002)
9. Nobel e-Museum—Alfred Nobel, The Man Behind the Prizes. *http://www.nobel.se/nobel/alfred-nobel/index.html* (accessed Jan 2002)

Josh Van Houten is a member of the Department of Chemistry, Saint Michael's College, Colchester, VT 05439; jvanhouten@smcvt.edu.