

Nobel Centennial Essays

A Century of Chemical Dynamics Traced through the Nobel Prizes

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1967: Eigen, Norrish, and Porter

by J. Van Houten

Nobel Prize in Chemistry 1967
Manfred Eigen (1927–)
Ronald Norrish (1897–1978)
George Porter (1920–)

for studies of extremely fast chemical reactions, effected by disturbing the equilibrium by means of very short impulses of energy

This is the sixth in a series of thirteen essays, written in commemoration of the centennial of the Nobel Prize, examining the history of chemical dynamics in the 20th century.^W The first three essays described the three Nobel Prizes awarded in the first decade of the century for work in chemical dynamics—Jacobus van't Hoff in 1901 (1), Svante Arrhenius in 1903 (2), and Wilhelm Ostwald in 1909 (3). The next three essays focused on the middle decades of the century with the Nobel Prizes awarded to George de Hevesy in 1943 (4), to Nicolay Semenov and Cyril Hinshelwood in 1956 (5), and the subject of this essay—the 1967 Prize to Manfred Eigen, Ronald Norrish, and George Porter.

The techniques developed by Eigen, Norrish, and Porter represent a turning point in the study of chemical dynamics. Building on the work of earlier Nobel Laureates and others, Eigen, Norrish, and Porter developed valuable new techniques that enabled us to study reactions at the sub-millisecond timescale for the first time. Eigen, working in Germany, developed techniques that came to be known as temperature-jump and pressure-jump. Norrish and Porter, working together in England, developed the flash-photolysis technique.

The 1967 Nobel Prize presentation makes references to all three of the early Nobel Laureates in chemical dynamics. The 1967 presentation speech (6) begins by recalling that Jacobus van't Hoff received the first Prize in 1901 for summarizing the laws governing chemical reaction rates. It goes on to discuss how Svante Arrhenius had described the mathematical relationship between temperature and the rate of a chemical reaction. This is the first mention of the so-called Arrhenius equation in any Nobel presentation—Arrhenius received his 1903 Nobel Prize for other work (2, 7). Among the accomplishments mentioned in the Nobel biographical material for Manfred Eigen (6) is the experimental verification of the general theory of acid–base catalysis mechanism first proposed by Wilhelm Ostwald, the 1909 Nobel Laureate (3).

In discussing how Eigen, Norrish, and Porter had advanced chemists' ability to study chemical reactions into the

sub-millisecond time scale, the 1967 Nobel presentation speech states that “in the old days” (using manual timing) the fastest reactions that could be measured had half-lives on the order of seconds. Henry Taube, the 1983 Nobel Laureate (8), chose a reaction $t_{1/2}$ between one second and one minute as the arbitrary dividing line between what he termed “inert” and “labile” transition metal complexes. The technique known as “stopped flow,” developed by Hartridge and Roughton in 1923 (7), allowed reactions with half lives of tens of milliseconds to be studied, which represented the lower time limit prior to the developments of the 1967 Laureates. At the other end of the temporal scale, in a somewhat whimsical vein, Eigen is said to have stated that the slowest reactions one could study would be limited by the lifetime of a graduate student (7). The work of Eigen, in Germany, and Norrish and Porter, in England, moved our ability to study reactions into the nanosecond range, a limit primarily imposed by the speed of the existing electronic apparatus. In an interview published in *This Journal* in 1975, Porter speculated that “within five years we shall be doing experiments in the femtosecond region” (9). Although his timeline was a bit optimistic, femtosecond experiments are now possible, and Ahmed Zewail's 1999 Nobel Prize for femtochemistry (10, 11) will be the subject of the final essay in this series. In fact, the ultra-fast modern lasers that are now used to make picosecond and femtosecond measurements are a direct outgrowth of Norrish and Porter's flashlamps.

Given that the 1967 and 1999 Nobel Prizes recognize breaking the millisecond barrier and achieving the femtosecond limit respectively, it is interesting to consider that the ratio of a femtosecond to a millisecond is roughly the same as the ratio of a millisecond to the 32 years that elapsed between the 1967 and 1999.

The approaches to the study of fast reactions taken by Eigen in Germany and by Norrish and Porter in England were similar in some senses, but very different in others. All prior work, including stopped flow, relied on mixing reactants and following the course of the reaction as equilibrium was established after mixing. Therefore the prior work was limited by the rate that solutions could be mixed. Eigen, Norrish, and Porter took systems that were already homogeneously mixed and at equilibrium, then they perturbed the equilibrium and measured the rate at which the reacting system returned to equilibrium following the perturbation. However, the nature of the perturbations used by Eigen were very different from those of Norrish and Porter. Eigen used sound waves or electrical pulses to rapidly raise the pressure

or temperature of his samples by relatively small amounts. Norrish and Porter used intense flashes of ultraviolet light, which generally resulted in much larger perturbations than did Eigen's techniques. In each case, however, the underlying principles had been known for a long time.

Equilibrium shifts resulting from pressure or temperature changes were described by the van't Hoff–LeChâtelier Principle. In 1901, the year van't Hoff received the first Nobel Prize, a doctoral student of Walther Nernst (12) studied the propagation of sound waves through various gases, including nitrogen dioxide. The effect of pressure on the equilibrium between the brown monomer and the colorless dimer, $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$, can be easily observed with the color fading as the gas is compressed and returning as it expands. Since sound waves are, in fact, pressure waves, they will perturb the $\text{NO}_2/\text{N}_2\text{O}_4$ equilibrium as they propagate through the gas. Einstein described this behavior theoretically in 1920 (7). Manfred Eigen explored this phenomenon using ultrasound techniques developed by his colleagues at the *Max-Planck Institut für Physikalische Chemie* in Göttingen, Germany. In subsequent years Eigen developed techniques capable of measurements down into the nanosecond time scale. He utilized them to study a wide variety of reactions, including proton transfer reactions, multi-stage processes, and reactions of metal complexes. His interests have also ranged to biochemical processes such as hydrogen bonding in nucleic acids, code transfer dynamics, membranes, enzymes, information storage, and biological control and regulation (7).

In contrast to the relatively subtle changes induced by Eigen's experimental techniques, the flash photolysis techniques of Norrish and Porter were capable of much larger perturbations of the reacting system. Light flashes produce excited states whose chemical and physical properties can be very different from their ground state precursors. For

example, excited states may result in homolytic bond cleavage to produce free radicals, or they can undergo electron transfer. The fact that light could initiate chemical reactions was well known in phenomena such as solar bleaching of dyes and the photographic process. Norrish had begun studying photochemical reactions as a student at Cambridge in 1915 (13), but his undergraduate career was interrupted by service in the British Army during World War I. He returned to Cambridge after the war and remained there throughout his career, retiring in 1966 (7). Norrish described some of his early interest in photochemistry and free radical reactions in an interview published in *This Journal* in 1975 (13). Some of the free radical reactions that he studied were the same as those studied by Cyril Hinshelwood and Nicolay Semenov (5). Norrish used kinetic spectroscopy to study the ClO radical, which was later shown by the 1995 Nobel Laureates to be involved in the destruction of the ozone hole (14).

Norrish's photochemical research was interrupted by other projects during World War II, but was resumed in 1945 when George Porter, a student who had worked with radar in the Royal Navy during World War II (6), joined him. Porter's naval experience with electronics and short pulses proved invaluable in designing techniques to study fast reactions using pulses of light. In 1946 Porter conceived the idea of using pulses of light to generate free radicals and following their reactions spectroscopically; the first flash photolysis apparatus was constructed the following year. Norrish and Porter continued to collaborate until 1954 when Porter left Cambridge. He spent eleven years at the University of Sheffield until being named Director of the Royal Institution in 1966. He went on to become president of the [British] Royal Society [of Science] and is now at Imperial College, London. Throughout his career he has applied flash photolysis techniques to various problems in chemistry, physics,

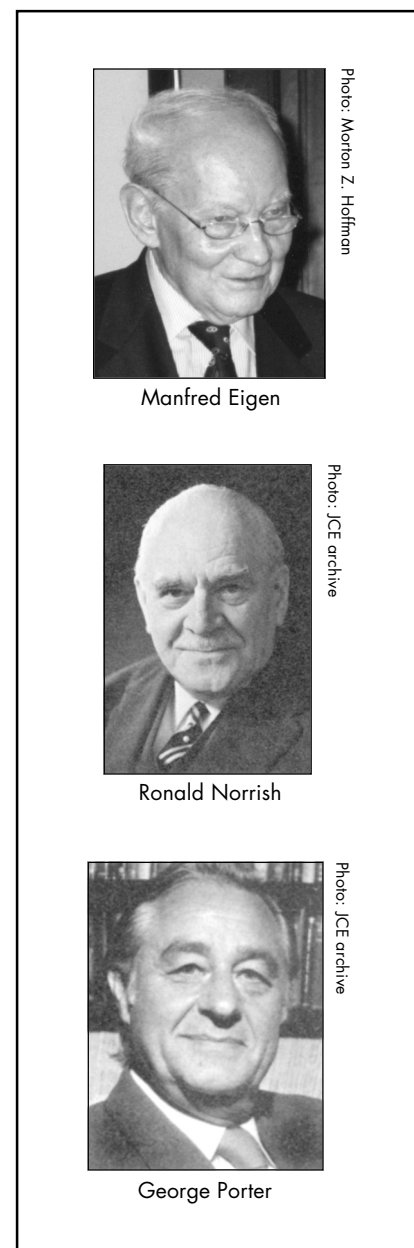


Photo: Morton Z. Hoffman

Manfred Eigen

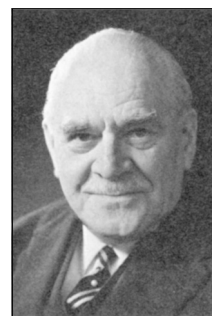


Photo: JCE archive

Ronald Norrish



Photo: JCE archive

George Porter

and biology and has also made contributions in other areas of chemical reaction dynamics including matrix isolation and radical trapping (6, 9).

Conclusion

This and the previous two essays (4, 5) have examined the life and times of the Nobel Laureates whose work led to

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significant advancements in chemical dynamics at the middle of the 20th century. The contributions of the six men who won the three Nobel Prizes in chemical dynamics during the mid-century years continue to be important now at the beginning of a new century. Isotope tracers developed by George de Hevesy remain routine tools in all branches of science including biology, geology, astrophysics, and atmospheric chemistry, not just in chemistry. Chain reactions first explained by Nicolay Semenov and Cyril Hinshelwood continue to be important in fundamental mechanistic studies as well as in biological and environmental applications—consider the 1995 chemistry Nobel Prize for “work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone” (14). Modern pulsed laser techniques, which have now been extended into the femtosecond regime and which were recognized with the 1999 Nobel Prize (10, 11), are essentially the same as the flash photolysis and temperature jump techniques of the 1967 Nobel Laureates, albeit with faster and more powerful energy pulses. Future essays in this series will examine the seven Nobel Prizes in the area of chemical dynamics awarded during concluding decades of the 20th century.

Supplemental Material

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

Literature Cited

1. Van Houten, J. J. *Chem. Educ.* **2001**, *78*, 1572–1573.
2. Van Houten, J. J. *Chem. Educ.* **2002**, *79*, 21–22.
3. Van Houten, J. J. *Chem. Educ.* **2002**, *79*, 146–148.
4. Van Houten, J. J. *Chem. Educ.* **2002**, *79*, 301–304.
5. Van Houten, J. J. *Chem. Educ.* **2002**, *79*, 414–416.
6. Nobel e-Museum—Chemistry 1967 (with links to Prize Presentation and Biography pages). <http://www.nobel.se/chemistry/laureates/1967/index.html> (accessed Feb 2002).
7. Nobel e-Museum—Chemistry 1903 (with links to Prize Presentation and Biography pages). <http://www.nobel.se/chemistry/laureates/1903/index.html> (accessed Feb 2002).
8. Nobel e-Museum—Chemistry 1983 (with links to Prize Presentation and Biography pages). <http://www.nobel.se/chemistry/laureates/1983/index.html> (accessed Feb 2002).
9. Farago, P. J. *Chem. Educ.* **1975**, *52*, 703–705.
10. Baskin, J. Spencer; Zewail, Ahmed H. J. *Chem. Educ.* **2001**, *78*, 737.
11. Nobel e-Museum—Chemistry 1999 (with links to Prize Presentation and Biography pages). <http://www.nobel.se/chemistry/laureates/1999/index.html> (accessed Feb 2002).
12. Nobel e-Museum—Chemistry 1920 (with links to Prize Presentation and Biography pages). <http://www.nobel.se/chemistry/laureates/1920/index.html> (accessed Feb 2002).
13. Farago, P. J. *Chem. Educ.* **1975**, *52*, 359–361.
14. Nobel e-Museum—Chemistry 1995 (with links to Prize Presentation and Biography pages). <http://www.nobel.se/chemistry/laureates/1995/index.html> (accessed Feb 2002).

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