Nobel Centennial Essays

A Century of Chemical Dynamics Traced through the Nobel Prizes

1995: Paul Crutzen, Sherwood Rowland, and Mario Molina

by J. Van Houten

Nobel Prize in Chemistry 1995
Paul J. Crutzen (1933–)
F. Sherwood Rowland (1927–)
Mario J. Molina (1943–)

for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone

This is the eleventh in a series of essays, written in commemoration of the centennial of the Nobel Prize, examining the history of chemical dynamics in the 20th century *(1)*.[W] Almost all the chemistry Nobel Prizes have recognized what is commonly considered "basic research." Although the work recognized by the 1995 Nobel Prize began as basic research into the properties of the atmosphere and into the fate of certain molecules in the atmosphere, that work eventually led to a most important, and unforeseen, environmental application—the discovery of the chemical mechanisms for the destruction of stratospheric ozone. This led, eventually, to international agreements to limit production and use of chlorofluorocarbons (CFCs). In addition to being leaders in their scientific fields, the 1995 Nobel Laureates were influential in the social and political debates on CFCs.

The second essay in this series *(1b)* mentioned that Svante Arrhenius, the 1903 Nobel Laureate, warned of potential damage to the atmosphere from industrial pollution. A recent article in *Science* by Crutzen and Ramanathan *(2)* tracing "The Ascent of Atmospheric Sciences" from the first quantitative measurements of temperature and pressure by Galileo and Torricelli to the present describes how in 1896 Arrhenius utilized Samuel Langley's observation of atmospheric CO_2 and H_2O absorption bands in solar and lunar spectra to develop a detailed model for the earth's radiation budget and to discuss how atmospheric CO_2 and H_2O could affect surface temperatures. In 1908 Arrhenius wrote *(3)* that CO_2 from the combustion of coal and petroleum was warming the globe, describing what is now known as the "greenhouse effect."

Paul Crutzen's Research on NO_x and Ozone

In 1965 Crutzen chose to study the mechanisms of stratospheric ozone creation and destruction as the subject for his *Filosofie Licentiat* thesis at the University of Stockholm.[1] He had already worked for several years on early computer models for meteorological research at the Meteorology Institute of Stockholm University (MISU) *(4)*. He said in his Nobel lecture *(5)*: "I wanted to do pure science related to natural processes and therefore I picked stratospheric ozone as my subject without the slightest anticipation of what lay ahead." Crutzen's background was in engineering, computer programming, and meteorology; he had little formal training in chemistry. Nevertheless he said that in 1965 when "I was given the task of helping a scientist from the United States develop a model of the oxygen allotrope distribution in the [atmosphere, it] got me highly interested in the photochemistry of atmospheric ozone, and I started an intensive study of the scientific literature."

Crutzen found that knowledge of stratospheric chemistry in the mid-1960s was sparse, and that the existing theory of the chemistry of stratospheric ozone was flawed. That theory, based on a proposal published in 1930 by the British scientist, Sidney Chapman *(6)*, is summarized in reactions 1–4.

$$O_2 + h\nu \rightarrow 2\ O\ (\lambda \leq 240\ \text{nm}) \quad (1)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (2)$$

$$O_3 + h\nu \rightarrow O + O_2\ (\lambda \leq 1180\ \text{nm}) \quad (3)$$

$$O + O_3 \rightarrow 2\ O_2 \quad (4)$$

As any student of chemical dynamics should recognize, for ozone to remain at a "steady state" in the atmosphere its rate of production by reactions 1 and 2 must equal its rate of destruction by reactions 3 and 4. Crutzen was aware that results published in 1965 Benson and Axworthy *(7)* showed "that reaction 4 was much too slow to balance the production of odd oxygen [ozone] by reaction 1." Thus the application of chemical dynamics to the problem of stratospheric ozone was born.

In his Nobel lecture *(5)* Crutzen described how, in the mid-1960s, various mechanisms for ozone production and destruction were considered, mechanisms involving reactions catalyzed by HO and HO_2 radicals. Being a theoretician, he relied on the laboratory studies of others, including Ronald Norrish *(1f)*. At the time, rate constants for some of the proposed reactions had not been measured in the laboratory, but had simply been postulated by proponents of a particular theory. Crutzen realized that the chosen rate constants "could not explain the vertical distribution of ozone in the photochemically dominated stratosphere" and that they would "lead to an unrealistically rapid loss of ozone (on a timescale of a few days) in the troposphere."

Crutzen said *(5)* he "discarded the theory" of HO and HO_2 catalysis and concluded that "at least part of the solution to the problem of ozone distribution might be [due to


photo courtesy Paul Crutzen

Paul Crutzen


photo by Morton Z. Hoffman

Sherwood Rowland


photo by Luisa Molina

Mario Molina

other] photochemical processes. The influence of nitrogen compounds on the photochemistry of the ozone layer should be investigated." He went on to say "Unfortunately no measurements of stratospheric NO_x (NO and NO_2) were available to confirm my thoughts about their potential role in stratospheric chemistry." By 1970 Crutzen had moved to Oxford University as a postdoctoral fellow of the European Space Research Organization. This gave him access to data on stratospheric HNO_3 which he said "gave me enough confidence to submit my paper on catalytic ozone destruction by NO and NO_2." In "The Influence of Nitrogen Oxides on Atmospheric Ozone Content" *(8)* Crutzen described the following catalytic cycle:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (5)$$

$$NO_2 + O \rightarrow NO + O_2 \quad (6)$$

$$\text{Net: } O + O_3 \rightarrow 2\ O_2 \quad (7)$$

When Crutzen learned that NO could also be produced from the oxidation of nitrous oxide by excited oxygen atoms (reaction 8)

$$N_2O + O(^1D) \rightarrow 2\ NO \quad (8)$$

he said "it became clear that enough NO is produced in reaction 8 to make reactions 5 and 6 the most important ozone loss reactions in the stratosphere in the altitude region between 25 and 45 km." The steady state abundance of "odd oxygen" (O and O_3) in the atmosphere was maintained through a delicate balance between its photochemical formation (reactions 1 and 2) and its destruction through the NO_x catalytic cycle (reactions 5 and 6) from *natural* sources of NO_x.

In the early 1970s Crutzen continued his study of stratospheric chemistry, saying *(5)*, "After it became clear to me that I had stumbled onto a hot topic, I decided to extend my study" by investigating the atmospheric chemistry of NO_x and HO_x compounds in greater detail. But, he continued, "I soon got into big difficulties" because some of the available laboratory data were incorrect. He said, "This was a terribly nervous period for me. At that time no critical reviews and recommendations of rate coefficients were available. With no formal background in chemistry I basically had to compile and comprehend much of the needed chemistry myself from available publications."

At about this time Crutzen recognized a new potential threat to the stratospheric ozone layer. Several countries (Britain, France, the U.S., and the U.S.S.R.) were proposing to build fleets of supersonic transport planes (SSTs). Being very concerned about the potential impact of large NO_x emissions into the stratosphere from these SST fleets, Crutzen wrote *(9)*: "Clearly, serious decreases in total atmospheric ozone level…can result from such activity." His concern was shared by Harold Johnston[2]; Crutzen *(5)* was "really happy to have support for my own ideas from such an eminent scientist." Not only did Johnston share Crutzen's concern about the environmental impact of the proposed SST fleets, but Crutzen also found that experimental data from Johnston's lab "removed several of the major kinetic problems I had encountered in my 1971 study."

Upon Johnston's recommendation, major research programs into the stratospheric chemistry of NO_x and ozone were set up in the U.S., Britain, and France. Although only a few Concorde SSTs were ultimately built, the data from the research programs "greatly enhanced knowledge about stratospheric chemistry [and] confirmed the catalytic role of NO_x in stratospheric ozone chemistry"*(5)*.

Rowland and Molina's Research on Chlorofluorocarbons and Ozone

At the time Crutzen was developing his theories regarding NO_x and ozone, Mario Molina joined Sherwood Rowland's group at the University of California, Irvine, as a postdoctoral fellow. Rowland was already an established leader in "hot atom" chemistry, investigating reactions of atoms produced by nuclear processes with excess translational energy *(4)*. For many years, Rowland's work had been supported by the Atomic Energy Commission (AEC, now the U.S. Department of Energy) and he had moved his research into the area of radioactive tracer photochemistry using ^{38}Cl and ^{18}F. When he decided to "retire" from the chairmanship of the chemistry department in 1970, Rowland was looking

for a "new challenging aspect of chemistry" to work on in order "to instill some freshness" into his research program *(4)*. At an AEC-sponsored conference in 1972 he learned of measurements by James Lovelock[3] showing the presence of CCl_3F and CCl_2F_2 in the atmosphere over Lovelock's home in Ireland and in air samples collected aboard the British research vessel, R. V. Shackleton, near Antarctica. However, when Lovelock later published his findings in *Nature (10)* he stated that those chlorofluorocarbons "are unusually stable chemically and only slightly soluble in water and might therefore persist and accumulate in the atmosphere…The presence of these compounds constitutes no conceivable hazard."

In commenting in his Nobel lecture *(11)* on Lovelock's findings, Rowland said: "The appearance in the atmosphere of a new, man-made molecule provided a scientific chemical challenge: Was enough known about the physicochemical behavior under atmospheric conditions of molecules such as CCl_3F to allow prediction of its fate, once released into the environment?" Because of his excellent "track record" as a productive scientist, Rowland was allowed to shift some of his AEC funding to an investigation of the atmospheric chemistry of CFCs. There was the possibility that CFCs could serve as tracers for air mass flows by taking advantage of their presumed chemical inertness and the fact that they did not occur naturally; however Rowland was not interested in exploring the use of CFCs as tracers *(12)*.

When Molina joined his group in 1973, Rowland said *(4)*, "Mario chose [to work on the CFC research, a project that was] furthest from his previous experience and from my own experience as well, and we began studying the atmospheric fate of chlorofluorocarbon molecules. Within three months Mario and I realized that this was not just a scientific question, challenging and interesting to us, but a potentially grave environmental problem, involving substantial depletion of the stratospheric ozone layer."

Initially they investigated mechanisms for removal of CFCs from the troposphere. Rowland reported *(11, 12)* that they recognized that all of the usual "well established tropospheric sinks" (photodecomposition, dissolution in raindrops, and chemical oxidation) would be ineffective for removing CFCs. Rowland asked "When all of these usual decomposition routes are closed, what happens to such survivor molecules?" They found the answer to that question when they realized *(11)* that CCl_3F had been observed in the laboratory to decompose upon exposure to ultraviolet radiation, releasing a chlorine atom,

$$CCl_3F + h\nu \rightarrow CCl_2F + Cl \ (\lambda \leq 220 \text{ nm}) \qquad (9)$$

but that such short wavelengths do not penetrate very far into the atmosphere due to absorption by O_2 and O_3. They went on to calculate vertical profiles for CCl_3F in the atmosphere and found that the maximum release of chlorine atoms by solar UV photolysis would occur in the stratosphere at altitudes of 25–30 km, and that the average lifetime for CCl_3F in the atmosphere was 40–55 years; similar treatment for CCl_2F_2 gave an average lifetime of 75–150 years. They reported their results in *Nature (13)* and sent a preprint of that paper to Crutzen in Sweden. Crutzen said *(5)* that when he received that preprint "I knew immediately that this was a very important paper." He mentioned it at a presentation on ozone at the Royal Swedish Academy of Sciences in Stockholm, where the press picked it up and it "quickly attracted worldwide attention."

As research into CFC and ozone chemistry continued, Rowland reported *(11)*: "The greatest surprise in the CFC-ozone story was revealed in the spring of 1985 with the discovery by Joseph Farman of…the British Antarctic Survey of massive springtime losses of ozone over their station at Halley Bay, Antarctica." This report of what has come to be known as the "ozone hole" gave new urgency to the problem. It also provided an important clue to the underlying chemistry.

Initially Molina and Rowland *(13)* and other workers *(14)* postulated that the mechanism for catalytic destruction of ozone by chlorine involved the simple reaction sequence:

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (10)$$

$$ClO + O \rightarrow Cl + O_2 \qquad (11)$$

$$\text{Net: } O_3 + O \rightarrow 2O_2 \qquad (12)$$

which is analogous to the catalytic NO_x (reactions 5 + 6 = 7) described previously. That sequence does, in fact, occur in temperate and tropical regions, and it accounts for the observed ozone loss in the 30–40 km altitude range everywhere *(12)*. However, that sequence ultimately had to be discounted as a possibility for polar stratospheric ozone loss because the amount of available O atoms (from the photolysis of O_2 or O_3) at polar latitudes would be too small (due to low sunlight intensities) to sustain reaction 11 at a reasonable rate. Several other reaction mechanisms were proposed, but each had problems in its chemical dynamics.

In 1987 Molina (then working at the Jet Propulsion Lab) found a solution *(15)* that made sense. In his Nobel lecture *(16)* Molina reported, "We proposed a mechanism involving the self-reaction of ClO to form chlorine peroxide, a compound not previously characterized." In somewhat simplified form, the sequence proposed by Molina is summarized in reactions 13–16.

$$ClO + ClO + M \rightarrow Cl_2O_2 + M \qquad (13)$$

$$Cl_2O_2 + h\nu \rightarrow 2Cl + O_2 \qquad (14)$$

$$Cl + O_3 \rightarrow ClO + O_2 \quad (2x) \qquad (15)$$

$$\text{Net: } 2O_3 + h\nu \rightarrow 3O_2 \qquad (16)$$

Molina recognized *(16)* that reaction 13, leading to the formation of chlorine peroxide, "can occur efficiently in the lower stratosphere at high latitudes, as it is facilitated by the lower temperatures and higher pressures prevailing at those regions."

In competition with the above reaction sequence, ClO can be deactivated by reaction with NO_2 to form relatively inert $ClONO_2$ thereby terminating the above cycle. However, Molina found *(16, 17)* in 1987 through a series of laboratory measurements that $ClONO_2$ would react efficiently with HCl on the surface of ice particles in polar

stratospheric clouds (PSCs) to form Cl_2. That Cl_2 would then undergo photolysis to yield Cl, which could then reenter the catalytic cycle in reaction 15. In his Nobel lecture *(16)* Molina discussed in detail how, in the end, it was found that the PSCs played a number of important roles in the mechanisms of ozone destruction by Cl from CFCs.

Lives of the Nobel Laureates

Although the careers of the three recipients of the 1995 Nobel Prize have been intimately intertwined over the last three decades, their early backgrounds could not be more different. Crutzen came from a working-class family in Amsterdam, Rowland was the precocious son of an American college professor, and Molina had an upper-class upbringing in Mexico.

Paul Crutzen was born in Amsterdam a few years before the outbreak of World War II in Europe. His father was a waiter from the southeastern corner of the Netherlands, near the border with Germany and Belgium. His mother, of mixed German–Polish ancestry, worked as a housekeeper and in a hospital kitchen. Crutzen's early education was disrupted by the hardships of living under the German occupation. He reported *(5)* that several of his schoolmates died of hunger and disease. Although he sometimes had only a few hours of school each week, he completed elementary school on time with special help from one of his teachers. In 1946 he entered a five-year program intended to prepare students for university admission. His favorite subjects were mathematics and physics, and he became proficient in French, English, and German. However, "chemistry was definitely not one of my favorite subjects."*(5)* He also "spent considerable time at sport: football [soccer], cycling, and my greatest passion—long distance skating on the Dutch canals and lakes."

Due to a fever, he did not score well enough on his final exams to qualify for a university stipend, so he chose to attend technical school and train as a civil engineer. This led to his first career—beginning in 1954 as an engineer in the Bridge Construction Bureau of the City of Amsterdam, with a 21-month interruption for compulsory military service. In 1958 he married a Finnish woman and they moved to the town of Gävle, on the east coast of Sweden about 200 km north of Stockholm, where he obtained a position in a building construction bureau. Shortly after moving to Sweden, Crutzen saw an advertisement for a computer programmer at the Department of Meteorology of Stockholm Högskola (since 1961 Stockholm University). Crutzen reported *(5)* "Although I had not the slightest experience in such work, I applied for the job and had the great luck to be chosen from among many candidates" thus he began his second career. His responsibilities included developing computer programs (which at that time had to be written in "machine language") to model meteorological process and for weather prediction. He was also able to take university courses, and he completed the requirements for the *Filosofie Kandidat* in 1963, the *Filosofie Licentiat* in 1968, and the *Filosofie Doctor* in 1973.[1] His dissertation topic was stratospheric ozone. He held a postdoctoral position at Oxford University, sponsored by the European Space Research Organization from 1969 to 1971.

In 1974 Crutzen moved to Boulder, Colorado, where he worked at the National Center for Atmospheric Research (NCAR) and at the National Oceanic and Atmospheric Administration (NOAA), rising to the position of Senior Scientist and Director of the Air Quality Division at NCAR by 1977. In 1980 he returned to Europe as Director of the Atmospheric Chemistry Division of the Max Planck Institute for Chemistry in Mainz, Germany. He was named Executive Director of the Institute (a rotating position) in 1983, and he retired from the Institute in 2000. During his career he also held secondary appointments at Colorado State University, the University of Chicago, and Scripps Institute of Oceanography at the University of California, San Diego. Since 1993 he has held the position of Honorary Professor at the University of Mainz. Crutzen has retained his Dutch citizenship despite the fact that he has worked in several countries outside the Netherlands since 1958.

Sherwood Rowland was born in Delaware, Ohio, where his father had just moved to become chairman of the mathematics department at Ohio Wesleyan University. He entered first grade at age five, skipped the fourth grade, and graduated from high school before turning 16. He said *(4)* his "first exposure to systematic experimentation and data collection" came as he operated an auxiliary U.S. weather service weather station with his high school science teacher. He played tennis and basketball in high school. When he entered college at Ohio Wesleyan at age 16 in 1943 in the middle of World War II, most of the older males were in the military. He attended college year-round while also playing on the varsity basketball and baseball teams and writing the sports page for the university newspaper. In 1945, after completing the equivalent of three years of college work, he enlisted in a Navy program to train radar operators. However, the war ended while he was in boot camp and the radar operator training program was scaled back, so much of Rowland's 14-month military service was spent playing competitive athletics for Navy base teams *(12)*. He said *(4)* that upon returning to college "This year away from academic life convinced me that, at age 19, there was little reason to seek a quick finish to my undergraduate education. I therefore arranged my schedule to take two more years rather than one to graduate and continued to play basketball on the university team." He said he "really enjoyed the academic side of university life" taking "more or less equal amounts of chemistry, physics, and mathematics" within Ohio Wesleyan's liberal arts curriculum.

Rowland entered graduate school at the University of Chicago in 1948 with support from the GI Bill. His randomly assigned mentor was Willard F. Libby[4], who had just finished developing the ^{14}C dating technique for which he received the 1960 Nobel Prize. Although the initial assignment with Libby was random, Rowland said *(12)* that Libby "was such a charismatic person that I never considered anyone else as an adviser—I asked him to accept me as a graduate student, and he said yes." Rowland had high praise for

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Libby's skill as a mentor *(4)*, saying "I settled automatically and happily into his research group and became a radiochemist…Almost everything I learned about how to be a research scientist came from listening to and observing Bill Libby." While at Chicago, Rowland took courses from five current or future Nobel Laureates: Libby taught radiochemistry, Harold Urey taught physical chemistry (along with Edward Teller), Henry Taube *(1h)* taught inorganic, and Maria Goeppert Mayer and Enrico Fermi taught nuclear physics. Rowland also remained active in athletics while in graduate school, playing baseball and basketball for the university teams, semi-pro baseball in Canada in the summer and basketball for several Chicago-area teams in the winter. In 1952 he completed his Ph.D. on the chemistry of highly energetic radioactive bromine atoms produced in Chicago's cyclotron.

Rowland's first position was as an Instructor at Princeton University. He spent his summers at Brookhaven National Lab where he developed a one-step synthesis of tritium-labeled glucose using the neutron flux from Brookhaven's nuclear reactor. In 1956 he accepted an Assistant Professorship at the University of Kansas, which had just constructed new facilities for radiochemistry. His new research group was very productive and he moved up quickly to the rank of professor in eight years. In 1964 he was hired as the first chairman of the department of chemistry at the new campus of the University of California, Irvine. While continuing "hot atom" research, Rowland said *(4)* he "deliberately followed a policy of trying to instill some freshness into [his] research efforts by every few years extending [his] work into some new, challenging aspects of chemistry." This led him to move into radioactive tracer photochemistry using ^{3}H and ^{14}C, then into chlorine and fluorine chemistry using radioactive ^{38}Cl and ^{18}F and, ultimately to the CFC–ozone problem.

Mario Molina was born in Mexico City. His father was an attorney who also taught at the National University of Mexico (*Universidad Nacional Autonoma de Mexico,* UNAM) and who was later the Mexican ambassador to Ethiopia, Australia, and the Philippines. Molina said *(16)* he "was already fascinated by science before entering high school." Aware of his interest in chemistry, his parents sent him to study in Switzerland at age 11 so he could learn German. He converted a spare bathroom in his home into a laboratory and, with the assistance of an aunt who was a chemist, he conducted college-level experiments.

Molina entered the chemical engineering program at UNAM in 1960 saying *(4)* that "this was then the closest way to become a physical chemist, taking math-oriented courses not available to chemistry majors." After completing his undergraduate degree in Mexico he decided to obtain a Ph.D. in physical chemistry. However he said "This was not an easy task; although my training in chemical engineering was good, it was weak in mathematics, physics, as well as in various areas of physical chemistry—subjects such as quantum mechanics were totally alien to me in those days." He went first to the University of Freiburg in Germany where he did research on polymerization kinetics. However, he said "I wanted to have time to study basic subjects in order to broaden my background and to explore other research areas." He spent a few months in Paris studying mathematics on his own and "discussing all sorts of topics, ranging from politics, philosophy, to the arts." He then returned to Mexico as an assistant professor at UNAM where he set up the first graduate program in chemical engineering.

In 1968 Molina entered the graduate program at the University of California, Berkeley where he joined the research group of George Pimentel. He wished to study molecular dynamics with chemical lasers *(1i)*, which Pimentel had discovered a few years earlier. Molina said *(4)* that Pimentel "was an excellent teacher and a wonderful mentor; his warmth, enthusiasm, and encouragement provided me with inspiration to pursue important scientific questions." Molina also enjoyed the intellectually stimulating environment in Berkeley at the beginning of the free-speech era. He said that at this time he also had his "first experience dealing with the impact of science and technology on society" as he felt dismay at seeing the high-powered chemical lasers that he used as a research tool also being developed for use as weapons. He said he "wanted to be involved in research that was useful to society, but not for potentially harmful purposes."

After receiving his Ph.D. in 1972, Molina stayed at Berkeley for a year continuing his research in chemical dynamics. Then he moved to Rowland's group in Irvine where he was intrigued with the opportunity to investigate the environmental fate of CFCs—although at the time CFCs were thought to have no significant environmental impact. He said *(4)* "This project offered me the opportunity to learn a new field—atmospheric chemistry—about which I knew very little." Within three months Rowland and Molina developed the "CFC–ozone depletion theory" but, he said, "the research did not seem very interesting [initially, because] nothing appeared to affect [CFCs in the troposphere]." Things became much more interesting following publication of their *Nature* paper *(13)* in 1974, as they attempted to communicate their concerns about the CFC–ozone issue to policy makers and the news media, because they "realized this was the only way to insure society would take measures to alleviate the problem."

Molina received a faculty appointment at UC–Irvine in 1975. Although he and Rowland continued to collaborate, Molina felt it was necessary to set up an independent research program. He began studying the chemical and spectroscopic properties of compounds of atmospheric importance that were difficult to handle in the laboratory. Among those compounds were HOCl and $ClONO_2$, which were later found to be important parts of Molina's detailed analysis of the chlorine-ozone reaction scheme. Molina said *(4)* that during his years on the faculty at UCI he "missed not doing experiments myself [sic]" and in 1982 he joined the Molecular Physics and Chemistry Section at Jet Propulsion Laboratory where he "had the luxury of conducting experiments with my own hands, which I enjoyed very much." While at JPL, Molina and his wife, Luisa, also a

chemist, characterized chlorine peroxide, which had not been reported previously but "which turned out to be important in providing the explanation for the rapid loss of ozone in the polar stratosphere."

In 1989 Molina returned to academia when he accepted an appointment at the Massachusetts Institute of Technology, where he remains to this day. He no longer spends much time in the laboratory, but takes intellectual stimulation from working with his students. He concluded his Nobel lecture *(16)* echoing the sentiments of earlier Nobel Laureates, Roald Hoffmann *(1g)* and Henry Taube *(1h),* on the relationship between teaching and research, saying: "I have also benefited from teaching; as I try to explain my views to students with critical open minds, I find myself continually challenged to go back and rethink ideas. I know teaching and research as complementary, mutually reinforcing activities."

An earlier essay *(1i)* noted that in 1986 Yuan Lee concluded his Nobel lecture *(18)* by observing: "In the remaining years of the 20th century, there is no doubt that the experimental investigation of dynamics and mechanisms of elementary chemical reactions will play a very important role in bridging the gap between the basic laws of mechanism and the real world of chemistry." Taken together, the work of the 1995 Nobel Laureates is an excellent illustration of Lee's visionary statement. The work of Crutzen, Rowland and Molina also shows how scientists initially investigating what they considered to be interesting basic research problems can make important discoveries which ultimately have a profound impact on society.

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.*

Notes

1. In Sweden, the *Filosofie Kandidat* corresponds to the M.Sc.; the *Filosofie Licentiat* is comparable to a Ph.D.; the *Filosofie Doctor* corresponds to the D.Sc.

2. Harold Johnston, University of California, Berkeley, first published his concerns about the impact of NO_x from SSTs on ozone in *Science* in 1971 *(19)*. Readers may recall that Johnston (who moved from Berkeley to Stanford late in his career) was the undergraduate mentor of the 1986 Nobel Laureate, Dudley Herschbach *(1i)*. In 1997 President Bill Clinton awarded Johnston the National Medal of Science in recognition of his contributions to the study of atmospheric chemistry.

3. Lovelock invented the electron-capture detector for gas chromatography. EC-GC remains the preferred technique for trace measurements of halocarbons. Crutzen *(5)* characterized the EC-GC as "a major advance in environmental sciences."

4. Rowland has told me (personal communication) that he believes Libby could well be included in the group of Nobel Laureates in chemical dynamics. Although Libby's Nobel Prize for ^{14}C dating techniques could not be considered to be chemical dynamics in the sense of the other Nobel Laureates covered in this series, he certainly made significant contributions to that field. For example, Libby's attempts to rationalize electron transfer reaction rates in transition metal complexes led to the development of the Marcus theory of electron transfer, as was discussed in some detail in the essay on Marcus' 1992 Nobel Prize *(1j).*

Further Reading

The Nobel e-museum Web site *(4)* contains a useful list of background sources.

Crutzen's 2000 *Science* article *(2)* provides an excellent short history of the development of atmospheric science with tie-ins to the work of many important figures in the history of chemistry. It then leads into an overview of current understanding of the threats posed by the greenhouse effect and the destruction of stratospheric ozone.

Several articles relating to the threats to the ozone layer have appeared in this *Journal* during the last three decades. The May 1987 issue featured an article "Chlorofluorocarbons and Stratospheric Ozone" by S. Elliott and F. S. Rowland (*J. Chem. Educ.* **1987,** *64*, 387–391) in which they cover the various aspects of the physical chemistry of the CFC issue in some detail. That issue featured satellite images of the Antarctic "ozone-hole" on its cover.

As early as 1972, J. P. Chesick (*J. Chem. Educ.* **1972,** *49*, 722–725) wrote on using Johnston's just-published (Ref. 18) results on the threat to the ozone layer from NO_x emissions from SSTs. Chesick's article discusses in detail using this as a practical application in teaching chemical dynamics.

F. Leh (*J. Chem. Educ.* **1973,** *50*, 404–405) discussed threats posed by ozone near the earth's surface. Although he mentioned that NO_2 is involved in ozone production, he did not refer to stratospheric ozone.

A brief note by J. A. Driscoll (*J. Chem. Educ.* **1977,** *54*, 675) described a laboratory exercise to demonstrate the spectroscopic properties of ozone. He concluded by pointing out that the ozone layer would be only 0.3 cm thick at 1 atm pressure and concluding "it can be appreciated how fragile the layer is."

E. Koubeck and J. O. Glanville (*J. Chem. Educ.* **1989,** *66*, 338) described a demonstration of the UV absorption of ozone.

J. Larson (*J. Chem. Educ.* **1990,** *67*, 943) wrote on error analysis in spectrophotometric determinations and the environmental consequences of a reduction in the ozone layer. That article discussed how the standard mathematics of spectroscopy (appearing in any standard instrumental analysis text) could be used to show that a large increase in UV radiation reaching the surface of the earth could result from a much smaller relative decrease in the ozone layer.

L. N. Kasperov and V. Stepanov (*J. Chem. Educ.* **1999,** *76*, 1182) described a laser photolysis experiment using transient spectroscopy to investigate the kinetics of ozone formation.

Two recent articles by E. Harvey and R. Sweeny (*J. Chem. Educ.* **1999,** *76,* 1309 and 1310) discussed a teaching

exercise using Mathcad to model stratospheric ozone kinetics.

K. R. Williams (*J. Chem. Educ.*, **2000,** *77*, 1540–1541) described the history of the use of CFCs in refrigeration and she made a brief reference to the ozone-hole.

E. T. Williams (*J. Chem. Educ.* **2002,** *79*, 433) reviewed a book "Stratospheric Ozone Depletion" by A. M. Middlebrook and M. A. Tolbert, University Science Books: Sausolito, CA 2000.

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