

# BETWEEN EARTH AND SKY

HOW CFCs CHANGED OUR  
WORLD AND ENDANGERED  
THE OZONE LAYER



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# PURE SCIENCE

**W**HEN THE SST CONTROVERSY was finally resolved, atmospheric scientists were left to ponder the troubling implication that human activities could introduce enough additional quantities of a trace gas into the atmosphere to significantly alter the natural processes whereby stratospheric ozone is created and destroyed. The Department of Transportation's official response to this worry had been to fund a \$21 million study of the SST's potential to modify climate, weather, and the chemistry of the upper air. Utilizing a thousand scientists from ten nations over a three-year period beginning in 1971, the Climatic Impact Assessment Program (CIAP) focused scientific interest on the stratosphere and pumped millions of research dollars into the atmospheric sciences. The SST controversy also gave wide publicity, for the first time, to the harsh consequences that any significant thinning of the ozone layer could have for life on earth. Depleted ozone, the public was told, would allow increased levels of ultraviolet light to enter the troposphere, where it could inhibit photosynthesis, harm essential sea plankton, and cause a host of medical problems for human beings, including various forms of skin cancer. But since the SSTs were not built in the large numbers once envisioned (the French and British ultimately produced only thirteen Concorde), as of the early 1970s the threat to the ozone layer remained largely hypothetical.



Twentieth-century atmospheric chemistry was something of an orphan of science, falling in between the more mainstream disciplines of meteorology, which concentrated on outdoor phenomena, and chemistry, primarily a laboratory pursuit. It had been invigorated, however, by the tremendous investment in nuclear-weapons research during the 1940s and 1950s. Atom- and hydrogen-bomb tests introduced radioactive elements into the atmosphere, and accurately measuring the by-products of nuclear detonations was essential so that the United States might know the full impact of its own weapons experiments and might monitor the Soviet competition. Samples of nuclear fallout could tell scientists precisely what a bomb was made of. But after atmospheric bomb testing was banned by international treaty in 1963, financial support for atmospheric chemistry was cut and interest in the field began to wane. In 1971 the Atomic Energy Commission, mindful, perhaps, that the test ban might not last forever, sponsored the first in a series of annual workshops bringing meteorologists and chemists together in an effort to reinvigorate the discipline.

One of the first hints that the issue of ozone depletion would once again become a matter of serious concern came in a presentation given by Lester Machta of the National Oceanic and Atmospheric Administration (NOAA) during one of the AEC workshops held in Fort Lauderdale, Florida, in January 1972. Among the participants at the conference was F. Sherwood "Sherry" Rowland, professor of chemistry at the University of California at Irvine. In the talk Machta revealed that, thanks to sensitive new instruments, measurable amounts of chlorofluorocarbons had been detected in the atmosphere. This announcement itself was not unusual, for atmospheric chemistry was still a young enough discipline that new discoveries about trace gases and the chemical interactions that take place in the atmosphere occurred with some frequency.

In 1972, CFCs were widely used as coolants in refrigerators and air conditioners, as a propellant in aerosol sprays, as a blowing agent in the manufacture of styrofoam and other plastics, and it had just been introduced as a solvent in the manufacture of computer chips—an industry expected to boom in the coming decades. Perhaps no industrial chemical compound more fully represented the slogan—"Better Living Through Chemistry"—that the Du Pont corporation had adopted in the midst of the Great Depression to suggest the power modern chemistry had to transform everyday life. (By 1970 the connotations associated with the word "chemistry" had changed, and the company had seen fit to drop its classic slogan and substitute a new one: "There's a World of Things We're Doing Something About.") Since their arrival as miracle refriger-



ants in the thirties and their adoption by the aerosol industry in the late forties, CFCs had retained their reputation as being among the most versatile and benign of all industrial compounds, posing no known danger to man or the environment. And due to their massive commercial proliferation they were quite literally everywhere on earth: in factories and in countless homes, cars, and places of work, in the air and in the oceans.

Lester Machta's presentation about CFCs at the 1972 conference discussed the as-yet-unpublished results of work by the maverick British scientist James Lovelock, who had succeeded in measuring CFC-11 in the atmosphere in concentrations roughly equal to the quantities that had been produced since its invention. Lovelock, who worked as a freelance scientist out of his home in Wiltshire, England, had been responsible for a major breakthrough in the atmospheric sciences, the invention of the electron-capture detector for gas chromatography, which made it possible for the first time for scientists to measure gases in the atmosphere in minute concentrations as small as 1 part per trillion. Before Lovelock's invention, chemists had barely been able to detect 1 part in a million. It was in the process of making observations with this instrument that Lovelock found CFC-11—in concentrations of approximately 70 parts per trillion in the northern hemisphere and 40 parts per trillion in the southern hemisphere. Machta reported Lovelock's suggestion that CFCs could be a potentially useful "tracer" of air motions in the atmosphere.

Following Machta's formal presentation, Rowland found himself in an informal discussion with several of the other workshop participants. He agreed that CFCs could be used as tracers, but he wondered aloud what eventually became of them. One of Rowland's specialties was photochemistry, or the study of how various molecules react when they are exposed to light or ultraviolet radiation. A decade before, when he was at the University of Kansas, he had worked with both fluorine and chlorine, constituent elements of CFC compounds, and one of his graduate students had conducted experiments with CFCs. Rowland knew enough about the photochemistry of the elements involved to deduce that while the CFC molecules Lovelock had measured in the atmosphere were stable in the lower atmosphere, they would almost certainly decompose if and when they drifted up as far as the stratosphere, where they would be exposed to short-wavelength ultraviolet light. Rowland also knew that chlorine had been shown in laboratory experiments to destroy ozone. And, having twice invited Harold Johnston to present seminars on the hydrogen-oxide and nitrogen-oxide chains, he recognized that catalytic reactions involving ozone were important.



To many of the scientists who attended the Fort Lauderdale workshop, CFC molecules were terribly complex. To a physical chemist like Sherry Rowland, however, CFCs, which in most forms contain only five atoms, are simple compounds. And while it was easy for the meteorologists to accept that CFCs were chemically inert and let it go at that, Rowland recognized what this assumption missed: that "there had to be chemistry involved" in their lingering presence in the environment.

Rowland felt strongly that the most interesting breakthroughs in science occurred "on the fringe," in places others might not be looking, and he was always alert to intriguing new research possibilities, but his wondering about the chemistry of CFCs in the atmosphere was at the time more a chemist's curiosity than a necessarily promising line of investigation. He knew Lovelock was wrong to assume that CFCs remained inert in the atmosphere, but thought it unlikely that they were present in sufficient concentrations to pose any serious environmental hazard.

Born in Delaware, Ohio, in June 1927, the second son of a mathematics professor at Ohio Wesleyan University, Sherry Rowland knew the name of Thomas Midgley, Jr., as a child. Midgley's home was only fourteen miles down the road in Worthington. Although Rowland's father, Sidney, was an academic, he had worked for General Electric before Rowland was born, and had a deep respect for the scientist-inventors of the early twentieth century and their life-enhancing achievements.

When Sherry Rowland graduated from Delaware High School in the summer of 1943 at the age of sixteen—too young to enlist in the service—he enrolled at Ohio Wesleyan, whose campus was only four blocks from his home, because as the son of a tenured professor, he could attend tuition-free. The war effort had decimated the university, leaving it particularly bereft of men. With normal college life so attenuated and a somber mood dominating the campus, Rowland attended classes year-round, studying diligently and with few distractions, gravitating toward a career in chemistry. Just before his eighteenth birthday, in 1945, he enlisted in the Navy, and was in boot camp when the war ended.

The break from academia may have been propitious. When he returned to Ohio Wesleyan after a year away, Rowland abruptly slowed the pace of his education. He had developed other interests, particularly in athletics. At six feet five, he proved to be a natural on the basketball court. He started at forward and was a star performer with the school's varsity team during his senior year in 1947–48. In 1948, Rowland graduated from Ohio Wesleyan and entered graduate school at the University



of Chicago, where he was assigned at random, like all new graduate students, to two advisors; one was the renowned radiochemist Willard Libby.

Like most eminent chemists and physicists of his generation, Libby was an alumnus of the Manhattan Project. While working at Oak Ridge, Tennessee, in the early 1940s, he had helped develop a method for separating uranium isotopes, a critical step in the development of the atom bomb. After the war, at the Institute for Nuclear Studies at the University of Chicago, his continuing work in radiation and "hot atom" chemistry led to a major scientific breakthrough, one with surprising applications to the seemingly unrelated discipline of archeology. Libby speculated that although the amount of energy received by the earth from cosmic radiation is minute, it must alter the earth's atmosphere in detectable ways. Based on laboratory observations, he surmised that the neutrons formed by cosmic radiation would interact with the abundant nitrogen in the air to produce radiocarbon, or carbon-14, and tritium. A search for radiocarbon and tritium in the atmosphere found them in roughly the amounts and concentrations Libby expected.

Libby calculated that the half-life of radiocarbon—or the length of time it would take for it to deteriorate by half—was 5,568 years, plus or minus thirty years (calculations that have since been refined), sufficient time for the radiocarbon produced by cosmic radiation to become distributed through the reservoir of all the carbon on earth, including the carbon contained in carbon dioxide. Since plants ingest carbon dioxide, and animals live off plants, Libby predicted that all living things would be rendered radioactive by cosmic radiation.

Living things ingest radiocarbon at a steady rate, just as radiocarbon decays at a steady rate. When a plant or an animal dies, however, it ceases to ingest radiocarbon, while the radiocarbon it contains in its tissues continues to decay. In other words, once living things die, they lose their radioactivity at a fixed rate. Libby had conceived of a way to accurately date organic material by measuring its radioactivity, a hypothesis he tested by carrying out experiments with organic samples of a known age. A panel of archeologists supplied Libby with samples such as wood from the deck of a funerary ship from the tomb of the Egyptian pharaoh Sesostris III; linen wrappings from the Dead Sea Scrolls; charcoal from the caves of Lascaux near Montignac in the Dordogne region of France; and a lump of beeswax associated with a smith's hoard of late Bronze Age objects found in England.

The samples were processed to remove the carbon from them, which then had to be converted to carbon dioxide, purified, reduced, and col-



lected. The resulting carbon's radioactivity was so weak that it was enormously difficult to measure. Libby was forced to invent a sensitive new instrument, a type of Geiger counter that could block out ubiquitous background radiation and detect minute amounts of radioactivity. The results were conclusive. By 1955 some two thousand samples had been tested. The ages of many samples were corroborated by Libby's method; others were discovered to have been incorrectly dated by archeologists who had relied upon far less precise and indirect methods—such as the rate of accumulation of sediments—to determine their age. Libby's carbon-14 dating method forced the reexamination of many accepted ideas about archeological and geological chronology. He later won the Nobel Prize for his efforts.

Libby's approach to science made a lasting impression on his young graduate student, Sherry Rowland. Libby had started out by asking basic questions about cosmic radiation, questions of purely scientific interest, with no obvious or practical end in mind. He had applied knowledge gleaned from laboratory work with radiation to natural, if previously undetected, phenomena. When necessary, Libby had invented equipment or techniques to test his theories. The eventual outcome was a major scientific development with tremendous implications far beyond the confines in which the work had originally been conceived.

Libby's freedom from orthodoxy extended to his personal relationships with students who worked under him. Throughout graduate school, Rowland devoted himself more to sports than to chemistry, a distraction other advisors might not have tolerated. Since he had come to athletics late as an undergraduate, Rowland had several years of eligibility left in both basketball and baseball and he played with the University of Chicago's varsity teams in both sports. In 1949, Rowland was named Most Valuable Player in the AAU Chicago city basketball championship game. He was a good enough basketball player to toy briefly with the idea of accepting an invitation to tour with the Harlem Globetrotters.

To Rowland, Libby's easy acceptance of his sports career was consistent with Libby's gifts as a research scientist, the expression of a relaxed temperament and a willingness to allow the world to impinge upon one's life and work. Inspiration could come to a scientist from the most unexpected places, and it was the whole person, with a full range of enthusiasms, who did the most creative work in the lab.

In the summer of 1952, Rowland married, earned his Ph.D. from the University of Chicago, and took an instructorship at Princeton. He was hired to teach undergraduates, but also continued the research work he



had begun with Libby, investigating the chemical reactions of radioactive atoms. Where Libby worked with carbon-14 and bromine, however, Rowland focused on tritium, the second isotope produced by the interaction of cosmic rays and nitrogen.

Rowland's work involved tritium produced in nuclear reactors under controlled circumstances in the lab. Many experiments involved the use of tritium as a tracer because tritium atoms are relatively easy to detect. An example with practical applications might be putting tritium tracers into a drug, then testing the drug on an animal and analyzing where the tritium tracers, and the drug, end up in the animal's body.

During the summers, Rowland's tritium studies took him to the Brookhaven National Laboratory on Long Island. In 1953, Rowland and a colleague at Brookhaven were attempting to measure the natural tritium content in atmospheric hydrogen when they found an unexpectedly high concentration of the isotope. After submitting their results for publication, they were asked by their superiors at Brookhaven to withdraw the paper. When the two scientists questioned the request, they were told that if they didn't withdraw the paper, it would be classified as secret government information. For an ambitious research scientist, the implications of having one's work classified are entirely negative. Such an action stifles all possible dissemination of specific scientific ideas, and thoroughly removes a scientist's data and conclusions from the larger discourse by which science progresses, thwarting the sharing of information and the give-and-take by which reputations are made and careers advance. Tritium is an essential component of hydrogen bombs, and Rowland later learned there had been a tritium spill at the Hanford plant in Washington State, which his measurements on Long Island had detected. It was eight years before the paper could be published. Such an experience, Rowland later recalled, "tends to discourage you from doing atmospheric chemistry."

Of course, the history of both radiochemistry and atmospheric chemistry was inextricably bound up with nuclear-weapons research and development, regardless of how purely scientific the motives behind the work of any individual scientist may have been. The political and military interest in turn generated money for research in particular areas, such as radiochemistry and high-energy physics. Those areas, nurtured by cash, tended to be where the most exciting scientific advances were made. Even scientists who were not interested in building bombs were attracted both to the excitement of the work being done in those particular fields and to the government money available for "pure" research in those same areas. Sherry Rowland was no exception. Beginning in 1956, the same year he



left Princeton for a job at the University of Kansas, his work was funded by the Atomic Energy Commission.

Within the small community of radiochemists, Rowland was well known for his continuing work with tritium, but the course of his career was not remarkable. In 1962 he branched out into photochemistry, and two years later, at the age of thirty-six, was hired to found the chemistry department at the brand-new University of California campus at Irvine.

The planned community of Irvine, in Orange County, sixty miles south of Los Angeles, stood at the frontier of the booming Sunbelt. Most of the future campus was a muddy construction site carved out of pastureland, and the challenge for the twenty or so newly hired faculty members was to build a sound academic institution from the ground up. Boasting no tradition of scientific excellence, no community of Nobel laureates, it hardly seemed a promising home for an ambitious scientist. But Irvine gratified Sherry Rowland's disposition for "the fringe," for "getting away from the crowd." While attending to his teaching and administrative duties, Rowland quietly pursued his interests in gas-phase kinetics, radiochemistry, and photochemistry.

Rowland's daughter, Ingrid, was a high-school senior and his son, Jeff, a freshman when Earth Day, April 22, 1970, came to the Irvine campus. Ingrid, in particular, was caught up in the Earth Day movement, helping to organize a protest march at her school. The Rowlands talked about the issues of the day at dinner; friends and family would cheerfully join in what they called "the Saturday night fights," which were often instigated by the outspoken Joan Rowland. Joan loved her new home in Corona del Mar, on a hill with a spectacular view of the Pacific, just a few miles from the Irvine campus. Sherry had bought the house before she saw it, on his second trip to California from Kansas. All she had asked, when he called to say he had found a house he wanted to buy, was that he make certain the kitchen was sunlit and bright. It had since become a family joke. At odd times Sherry would look at Joan and ask if the kitchen was bright enough. It was. But since moving to Corona del Mar in 1964, Joan had been disturbed that her view from the kitchen window was increasingly occluded by the smog that had begun to creep down the Orange County coast from Los Angeles. As environmental issues topped the national agenda in the 1970s and the Rowland family and friends debated them over supper, Joan would look across the table to her husband and his colleagues and say, "You guys are 'superscientists'! Why don't you do something?"



Rowland took the challenge seriously. He had always acknowledged that his own scientific inclinations were symptomatic of a larger social problem: that "good" scientists were attracted to theoretical challenges and shunned mere technical problems. That was why, he believed, nuclear power had not been developed to function satisfactorily—because prestigious scientists had not been willing to work with "garbage" such as nuclear waste. Perhaps he was even guilty, to some degree, he couldn't help but think, of perpetuating environmental problems by remaining complacently in an ivory tower. Rowland resolved to apply his skills to a practical problem. He chose, for his first venture, one of the leading environmental scares of the day: the possibility of widespread mercury contamination, particularly in fish.

Although mercury had been known for centuries to cause serious neurological disorders, even death, when ingested, it was thought to be harmless when it was released into the environment because it is heavy, insoluble, and inert. Inorganic compounds of mercury were confidently used in industry, and in agriculture as pesticides. The first suggestion that this practice might be harmful was a sensational case of mercury poisoning that occurred among people residing on the shores of Minimata Bay in Japan. Between 1953 and 1960, more than a hundred people died or were disabled after eating fish taken from the bay, and twenty-two children were born severely retarded and suffering from convulsive seizures to mothers who had eaten contaminated fish. A Minimata plastics and chemical factory had, since 1953, discharged inorganic mercury into the bay, yet the fish of Minimata Bay were found to be contaminated not with inorganic mercury but with the organic compound methylmercury, which was even more toxic. The riddle of the Minimata fish was solved by Swedish scientists who, in the mid-sixties, were concerned about elevated levels of methylmercury in Swedish wild bird populations and in eggs, fish, and meat. The Swedes discovered that inorganic mercury could be converted by microorganisms in mud into methylmercury, which then entered the food chain, becoming highly concentrated in fish.

In early 1970 a Canadian scientist reported finding dangerous levels of methylmercury in fish caught in the Great Lakes, and during the summer and fall of that year, fishing was banned or restricted in parts of seventeen states in the Great Lakes region, New England, and the South. In December 1970 a chemist at the State University of New York at Binghamton reported that he had tested a can of tuna and had found it to contain .75 part per million of mercury, well above the Food and Drug Administration's maximum allowable concentration of .5 ppm in a daily diet. Eleven days later the FDA began a recall of tuna from grocers'



shelves, and within weeks announced that up to 89 percent of swordfish on sale in the United States also contained impermissible levels of mercury. Pregnant women were advised to be especially careful about the fish they ate. Tuna and swordfish were believed to be particularly risky because they were large and predatory, higher on the food chain, and so more of the contaminant was concentrated in their flesh.

The insidiousness of mercury poisoning was profoundly disturbing. The possibility that man had polluted the entire globe to the extent that even deep-sea fishes were contaminated raised the prospect of one of the first truly global ecological crises. Peter and Katherine Montague, writing in the *Saturday Review*, went so far as to suggest that increased human exposure to mercury might even be responsible for modern man's "growing nervousness, irritability, skin ailments, insomnia, memory lapses, and emotional derangements."

Although the evidence was strong that some freshwater fish, and the fish taken from an identifiably polluted arm of the sea like Minimata Bay, were contaminated by man-made sources of mercury, it was less clear how wide-ranging, deep-water species like tuna and swordfish could have been contaminated, despite their place high in the food chain. Was it really possible that human beings had poisoned the vast oceans? In 1971, Rowland, along with two other Irvine faculty members and three students, decided to investigate this question by measuring the mercury content in fish that had been caught when the oceans were presumably far less contaminated. Seven tuna samples, caught between 1878 and 1909 and preserved in formaldehyde and alcohol, were obtained from the Smithsonian Institution. A swordfish specimen was found at the Museum of the California Academy of Sciences in San Francisco. The swordfish had been caught off the west coast of Baja California in 1946, and its head had been preserved due to a peculiar abnormality: the bill was deformed in such a way that it curved around and pierced the fish's own head. It turned out that there was no significant difference in the average levels of mercury contamination in the archival samples and samples of recently caught tuna and swordfish, which the scientists tested using the same methods. Rowland and his team had not proved that tuna and swordfish were safe to eat, but they had shown that the mercury these fishes contained was natural.

The results of the fish analysis were publicized, and although Vince Guinn, a forensic chemist, was the lead spokesman for the group, Rowland was nonetheless baptized into the highly emotional politics of environmental science when he and his colleagues were decried as apologists for polluters. One faculty colleague from another department sought



Rowland out to tell him he deplored his group's publicizing its results. It was wrong to minimize the overall danger of toxic pollutants, he told Rowland, by removing one from the list. To Rowland this was nonsense. In science, he replied, you have to let the chips fall where they may.

The episode, in any case, did nothing to discourage Rowland's curiosity about the environmental destiny of chlorofluorocarbons. He did not act on the matter immediately after the Fort Lauderdale conference, but he didn't forget it either, and in the summer of 1973, in his annual budget proposal to the Atomic Energy Commission, Rowland included a request for additional funding to study CFCs. The additional money was denied, but Rowland was granted permission to redirect some of his allotment for the study of radio- and photochemistry to CFCs if he wanted to. The CFC question thus remained marginal, potentially interesting, but far from urgent. Rowland might have let it go for another year or two if not for the arrival at Irvine that October of a postgraduate student named Mario Molina.

Mario Molina was born in Mexico City, and at the age of eleven had informed his family of his intention to become a research scientist. Recognizing that the Mexican educational system had little to offer their precocious and determined son, the Molinas sent him to a Swiss boarding school on the theory that since German was the international language of science, Mario would be well served by learning to speak it.

"I was very excited," Molina recalled later, "and then very disappointed, because the children in the boarding school were the same as those in Mexico. They had no particular interest in science."

Back home Molina still sometimes felt hopelessly out of step. In the privileged world of the Mexican upper class, a talent for science could almost feel like a curse. He had every opportunity, after all, people assured him, with his brains and family connections (his father served Mexico in a number of diplomatic posts, including that of ambassador to Australia), to pursue a lucrative career in law, business, or government. At the University of Mexico he studied chemical engineering—a field of applied technology that was the closest he could come to his true interest of conducting pure scientific research.

As a graduate student at the University of California at Berkeley, which he entered in 1968, Molina finally had the opportunity to pursue basic physical chemistry. His advisor, George Pimentel, was known for his work with chemical reactions that produce laser light without the addition of any other source of energy. The scientific motive behind



Pimentel's work with chemical lasers was to develop a new tool with which to observe the microscopic distribution of energy in elemental reactions, but the Air Force, which had provided Pimentel's funding, quickly recognized the potential defense applications of chemical lasers in hydrogen bombs and started classifying the research. For Pimentel and most of his research assistants, including Mario Molina, the military applications of chemical lasers were of little or no interest, and Pimentel's funding, although it was provided by the Defense Department, had been "clean," which is to say it was intended for pure research. Yet, at Berkeley in the sixties, he and Molina still had to be concerned that radical students might target them for protest, perhaps even by vandalizing the laboratory or destroying experiments and equipment.

Molina completed his Ph.D. thesis in 1973 on aspects of his and Pimentel's work with chemical lasers, then decided to pursue another area of physical chemistry. He opted for radiochemistry. Molina had met Sherry Rowland at a conference at Lake Arrowhead, California, in February 1973. A short time later Pimentel wrote to Rowland to recommend Molina for a job as Rowland's postdoc, and Rowland responded with an offer. When Molina arrived at the Irvine campus in early October 1973, Rowland asked him if he was interested in working on one of his established, ongoing projects in radiochemistry or photochemistry, or on something new. The something new that Rowland had in mind was the question of what happened to CFCs in the atmosphere.

For Molina the safe choice would have been to work in an area where Rowland's reputation was well known. Molina's immediate career objective was rather conservative, to add areas of expertise to his résumé, ideally by doing respected work whose results would be published and subsequently cited by other scientists in their own future work. Such citations, which are indexed by the *Science Citation Index*, provide a precise measure of a scientist's influence and the importance of his work. A large number of citations translates directly into prestige. The gamble in choosing the CFC option was that it could lead nowhere, or nowhere interesting, and Molina would have wasted his time. Worse, Rowland had little background in atmospheric chemistry, which meant that if the work turned tricky and Molina got stuck, Rowland might not be of much help. But Molina shared Rowland's intuition that the CFC question could prove interesting. He understood instantly, as Rowland had, that CFC molecules, while inert in the troposphere, would dissociate under the influence of ultraviolet light in the stratosphere, which meant that *something* would happen to their constituent atoms, something a chemist could understand. Like Rowland, he had kept abreast of the science that



had emerged from the SST controversy, and he didn't mind the possibility of moving into the reinvigorated field of atmospheric chemistry.

"If there was anything about chlorofluorocarbons that caught my attention," Molina later said, "it was simply that it seemed like 'bad manners' for men to put a chemical into the atmosphere without knowing exactly what happens to it."

Rowland and Molina discussed methodology. Before they examined whether CFCs were broken down by sunlight in the stratosphere, as they had theorized, they decided they first needed to demonstrate that there were no other significant CFC "sinks"—other processes by which CFCs were being removed from the atmosphere.

For Molina this was the "boring" part of his work, his basic education in the natural processes of the atmosphere. Because chlorofluorocarbons are chemically inert, Rowland and Molina knew it was highly unlikely there would be any sinks. The intellectual exercise for Molina was to dream up possible sinks in order to discount them. He concluded, among other things, that CFCs—even though they might enter the oceans—did not dissolve there, nor were they washed out of the atmosphere by rain; and CFCs neither interacted with nor were they absorbed by plants or other living things. Within two months he and Rowland felt confident in concluding that the only significant CFC sink was the stratosphere, as they originally had surmised.

The next step was to measure the rates at which CFCs break down under the influence of ultraviolet light. Similar work had been done the previous year, by scientists funded by Du Pont. In 1972, in response to James Lovelock's discovery that CFCs were present in the atmosphere, Du Pont had sent out a notice that it would finance the study of CFCs. Some of the money went to Lovelock to fund further measurements, some to pollution studies, and the rest to physicists at the University of Montreal, who measured light-absorption cross sections for CFCs. Not being atmospheric scientists, however, they were unconcerned with whether CFCs dissociated when they absorbed ultraviolet light, much less whether CFCs actually came into contact with ultraviolet light in the environment. Rowland and Molina confirmed the Montreal scientists' basic measurements showing the rates at which CFCs absorb ultraviolet light; they then did additional work to show that CFC molecules would eventually drift up into the stratosphere, with their average lifetime growing shorter the higher they drifted, as short as fifteen hours at the upper levels of the stratosphere.

Rowland and Molina had answered the basic questions they originally set out to ask. They had determined that chlorofluorocarbons have



a long life in the atmosphere—between 40 and 150 years—before they eventually drift into the stratosphere, where they are broken down by ultraviolet light. They had also determined that when CFC molecules do break down, a free chlorine atom is produced. They discussed publishing their findings, but then decided to ask one more question: what happened to the free chlorine atoms released by CFCs in the stratosphere? This was, for Rowland and Molina, a relatively easy question to tackle, a matter of the gas-phase chemistry they knew intimately. It entailed, for Molina, going back to his office and simply writing down a sequence of chemical reactions.

From that point, Rowland later recalled, it was only about seventy-two hours before “the bottom fell out.”

The day after he started work on the calculations, Molina reported to Rowland that he had come upon something unexpected. Chlorine atoms freed from CFCs by ultraviolet dissociation readily interact with ozone molecules ( $O_3$ ), breaking the ozone apart and producing oxygen ( $O_2$ ) and chlorine monoxide (ClO). The chlorine compound in turn breaks down, freeing its chlorine atom, which finds another ozone molecule to break apart, and the process begins all over again. *Thus, a single chlorine atom in the stratosphere would destroy not just one ozone molecule, but tens or hundreds of thousands, in a catalytic chain.*

The implication of Molina's discovery of this chlorine catalysis, what chemists refer to as a “chlorine chain,” was so alarming that his first reaction was to assume he had made some kind of mistake. Rowland's response was also to wonder if Molina might have erred. They agreed to do the calculations over, separately and using different methods, to see if they would come up with the same finding. Quickly, they both confirmed Molina's original results. The chlorine chain was irrefutable. Rowland still felt shaken when he returned home from the lab that evening. When Joan casually inquired how the work was going, Rowland heard himself reply, “The work is going very well, but it looks like the end of the world.”

There was one final step Rowland and Molina took to determine the extent of the problem they had uncovered. The real question was not how much chlorine there was in the stratosphere then, in 1973, but how much there would be in the future, after sufficient time had elapsed for CFCs to drift up and reach the stratosphere at a rate that equaled their rate of production. This calculation would ascertain the eventual degree of ozone depletion at steady state. Assuming a constant rate of production at the industry figures for 1972 (a deliberately conservative figure, since the rates of production were in fact rising annually), Rowland and



Molina calculated that the ozone layer might be diminished by as much as 20 to 40 percent within about a hundred years.

*Twenty to 40 percent.* It was a far more frightening estimate than the relatively small 1 percent or 3.8 percent losses projected during the SST debate. Even if, by a miracle, CFC production were halted immediately, there were already enough CFCs in existence, by Rowland and Molina's reckoning, to shatter the ozone layer.

"The feeling was of an abyss opening up," Rowland later said. "We weren't sure where the bottom was. We only knew it was down there somewhere—out of sight."

Once he realized that he and Mario Molina had found a major removal process of stratospheric ozone, Sherry Rowland called Harold Johnston at Berkeley. There were important parallels between Johnston's work with SST exhaust and nitrogen oxides and Rowland and Molina's work with CFCs and chlorine. As Paul Crutzen had shown and Johnston had confirmed, nitrogen oxides at naturally occurring concentrations contribute to the processes that maintain ozone at steady state. There is a nitrogen oxide chain similar to the chlorine chain Rowland and Molina discovered—that is, molecules of nitrogen oxides destroy stratospheric ozone without themselves being destroyed in the process. The absorption cross sections for nitrous oxide and CFCs are similar, and the nitrogen chain is analogous, chemically, to the chlorine chain. For anyone who understood nitrogen-ozone chemistry, chlorine-ozone chemistry was instantly comprehensible.

For Johnston and other scientists who attempted to calculate the potential impact of the SST in the early 1970s, the key question had not been whether nitrogen oxides were ozone scavengers, but whether the planes' exhaust would introduce enough additional nitrogen oxides to significantly deplete ozone levels at steady state. For Rowland and Molina, the question about the chlorine chain, once they had found it, was not really whether the chlorine chain itself would stand up to scrutiny—that, to them, was a matter of basic chemistry. The more pressing question was whether the amount of chlorine introduced by CFCs was enough to compete with the natural processes of ozone removal. Their conclusion of a 20 to 40 percent ozone reduction was so incredible that it only seemed prudent—before they did anything else—to run it by one of the few scientists knowledgeable enough about the subject to tell them they weren't crazy. After all, Molina reminded Rowland, the problem they had uncovered was so enormous, it seemed inconceivable no one else had noticed it.



Rowland called Johnston in early December 1973. "We've found a chlorine chain and a source of chlorine," he said.

"Do you know about Cicerone and Stolarski?" Johnston asked.

"No."

"They talked about the chlorine chain at Kyoto."

Ralph Cicerone, an electrical engineer, and Richard Stolarski, a physicist, both at the University of Michigan, had been awarded a contract to study the potential stratospheric effect of space-shuttle exhaust. NASA's 1972 final environmental impact statement for the space shuttle had revealed that the shuttle's rockets would spew, among other effluents, significant quantities of hydrogen chloride—containing chlorine—into the atmosphere.

Shortly after Cicerone and Stolarski started work on the NASA assignment, a Michigan colleague told them that Michael Clyne, a British chemist, had measured the rate constants of the reaction between chlorine atoms and ozone. Cicerone wrote to Clyne, and Clyne provided Cicerone and Stolarski with the results of his work. A brilliant laboratory chemist, Clyne had halted his efforts in chlorine-ozone chemistry, possibly because he was handicapped with a severe stutter, when he realized there were likely to be environmental and public implications to the work.

Cicerone and Stolarski had quickly determined that hydrogen chloride was totally foreign to the stratosphere. Clearly, then, something might go awry by introducing it in space-shuttle exhaust. Although, thanks to Clyne, they knew that chlorine destroyed ozone, it took several months—since neither of them was a chemist—for them to discover that it did so in a catalytic chain reaction. Even then the chlorine effluent in shuttle exhaust did not seem to pose an immediate environmental threat because, by Cicerone and Stolarski's calculations, the space shuttle—the only source of stratospheric chlorine they knew about—would deplete the ozone layer by only .3 percent at a rate of fifty shuttle flights a year.

In June 1973, Cicerone and Stolarski submitted their findings to NASA. Space-agency officials strongly suggested to the two researchers that much more work needed to be done in the area before experimental data potentially damaging to the space-shuttle program would be published. Consequently, when Stolarski presented the results of his and Cicerone's work on the photochemistry of chlorine at a scientific meeting in Kyoto, Japan, in September 1973, he did not mention the space shuttle. Instead, he talked about trace amounts of hydrogen chloride released into the atmosphere by volcanic eruptions.

Stolarski and Cicerone were interlopers in stratospheric chemistry. At Kyoto their paper was immediately attacked by a scientist who was far more established in the field, Mike McElroy of Harvard, who said he and



his colleague Steve Wofsy had looked into the impact of hydrogen chloride released by volcanoes, and did not believe volcanoes were a significant source of chlorine in the stratosphere. As it happened, McElroy and Wofsy had also found the chlorine chain and were about to publish a paper on their discovery. Neither Stolarski nor McElroy revealed, however, either to each other or to any of the other participants at the Kyoto conference, what both of them knew: that the real chlorine source they were talking about was NASA's proposed space shuttle.

Thus, the chlorine chain, while of academic interest, did not seem to be of overwhelming importance, since there was no significant natural source of chlorine in the stratosphere, and the potential man-made source—NASA's space shuttle—was not yet flying. There would be time for Cicerone and Stolarski and McElroy and Wofsy, and for NASA itself, to fully explore the problem before the shuttle's maiden flight, which was scheduled for the early 1980s. Alternative propellants could be devised for the shuttle booster rockets if necessary. For Cicerone and Stolarski the study of chlorine chemistry in the stratosphere had proven to be just the tonic they had sought for their careers: apart from a little professional sparring with McElroy and Wofsy and moderate unease on the part of their NASA sponsors, they had found a quiet corner of the stratosphere to investigate.

Even though the chlorine sources Stolarski and Cicerone were studying were small, Stolarski recognized that the potential importance of their work was that there could conceivably be larger sources they didn't know about. Yet Stolarski did not pick up on a clue he received in November 1973, when a young physical chemist named Chuck Kolb approached him at a NASA conference in Houston and asked if he had given any consideration to CFCs as a potential chlorine source. Kolb was a recent Ph.D. graduate of Princeton who had done his 1971 doctoral thesis on fluorine-atom reactions with Freon and other halocarbons. He had read the paper Lovelock published in *Nature* in 1973 reporting his finding that CFCs were ubiquitous in the atmosphere. Having worked with CFCs, Kolb, like Sherry Rowland, knew that Lovelock's contention that CFCs would have no conceivable environmental impact was ill founded. To the contrary, he knew CFCs would photodissociate in the stratosphere when they were exposed to ultraviolet radiation. After his graduation Kolb had been hired by a small, struggling research-and-development company outside Boston called Aerodyne Research, Inc. There his professional orbit crossed that of Harvard professor Mike McElroy—the guru of planetary atmospheres. Through that association Kolb learned that research was underway suggesting that chlorine emitted in space-shuttle exhaust might pose a threat to the ozone layer. He



realized instantly that the amount of chlorine introduced into the atmosphere by the space shuttle was "like a pimple on an elephant" compared to the chlorine that would be introduced by CFCs.

Kolb mentioned his insight to a number of people, including McElroy and his boss at Aerodyne. He later said he thought McElroy may not have paid much attention because McElroy still thought of him as a grad student. Similarly, in Houston, Kolb mentioned CFCs to Stolarski, but the comment, Stolarski later recalled, "sailed over my head.

"I was naive about chemistry," he later explained. "I guess I figured if they gave it a name like 'chlorofluorocarbons,' it must be something horrible. I didn't know it was actually a very simple molecule."

Kolb attempted to follow up on his hunch by writing a proposal to NASA for Aerodyne to study the CFC question, but the proposal was not funded. In the face of so much discouragement, Kolb was instructed by his employer to drop the question of CFCs and go back to the work the firm paid him to do.

Thus, by late 1973, although there were several researchers who knew about the chlorine chain, or who had concerned themselves with the long lifetimes of CFCs in the atmosphere, and at least one scientist, Chuck Kolb, who had speculated that CFCs were a potential source of chlorine in the stratosphere, only Rowland and Molina had put the complete picture together.

The two Irvine scientists flew to Berkeley to meet with Harold Johnston during the week between Christmas and New Year's, 1973. Johnston quickly confirmed their basic premise. There were, at least, no *obvious* mistakes in their reasoning. Johnston told Rowland and Molina that Michael Clyne's latest laboratory measurements had demonstrated that at stratospheric temperatures chlorine atoms would destroy ozone six times more efficiently than the nitrogen oxides associated with the SST.

Rowland asked Johnston if he would take the lead in helping to publicize this new danger to the ozone layer. Johnston was, after all, already a respected figure in atmospheric chemistry, and could, perhaps, better communicate the urgency of the problem. But Johnston recognized that both the burdens and the glories ahead belonged rightfully to Rowland and Molina. Publicly suggesting a ban on the production of CFCs would be controversial; it was, after all, the sheer size of the CFC business, and the modern world's dependence on the chemicals, that made Rowland and Molina's own calculations so disturbing.

"Are you ready for the heat?" Johnston asked them. The CFC industry, fat and prosperous, had thrived for more than four decades without question or interference. If this contented giant was disturbed, who could tell for certain what it would do?



\* \* \*

Sherry Rowland was scheduled to begin a long-planned sabbatical in Vienna just after New Year's, 1974. At first, he thought he would have to change his plans; however, as he and Molina discussed how they should proceed, they recognized that there was nothing to be gained by dramatically rearranging their affairs. They were in possession of the scientific scoop of the century, but if they were to be believed, they would have to assume a nonalarmist posture and publish their findings in an authoritative scientific paper subject to peer review. Shouting the news from the nearest rooftop, while certainly warranted, would only make them less credible, and the premature disclosure of the ozone-depletion theory could subject it to attack before its authors were fully armed for its defense.

With publication of the theory their obvious and best next step, Rowland and Molina agreed that despite their sense of urgency there was really no reason for Rowland to cancel his plans. He could write the paper in Europe and submit it for publication from there. Until it was published, there was little that either one of them could do and Rowland might as well enjoy his sabbatical. Molina, meanwhile, could handle anything unexpected that might come up back home in Irvine. Both of them could use the time to continue thinking about the CFC-ozone problem, conferring with selected colleagues to reassure themselves they had not overlooked anything significant.

Rowland wrote the paper his first week in Vienna, and sent it in early January to the prestigious British journal *Nature*. He chose *Nature* not only because it is held in high esteem, but also because it had a reputation for promptness in responding to submissions, a reputation Rowland seriously began to question after several weeks went by and he received no word from the editors. Impatiently awaiting the journal's decision on whether it would publish the paper, he phoned *Nature's* editorial offices repeatedly to inquire about the delay. When he finally did speak with someone from the journal's staff on the phone, he heard a number of excuses for the delay, chiefly having to do with the peer review process. Before a scientific paper is published, it is sent to "referees" in the field to verify its basic scientific merit. *Nature* informed Rowland that it was not having an easy time finding qualified referees in the field of stratospheric chemistry; in addition, the journal was between editors; the former editor, it seemed, had left for a long weekend and had simply failed to return.

The anticipation made it difficult for Sherry or Joan Rowland to be



at ease. They talked constantly about the terrifying implications of his discovery and about how their own lives would change when the word got out. Rowland was in constant touch with scientific colleagues around the world, scientists who appreciated what he was going through and who for the most part reassured him that they saw no significant or obvious errors in his theory. Rowland reflected on his relatively obscure past career. "You work hard," he told Joan, "and you find the work fascinating, and you publish it, and maybe two dozen people will read it." Now he had to anticipate that his work would be received with far greater interest and consternation.

In the meantime, within the small community of atmospheric scientists, word of the Rowland-Molina theory was slowly filtering out. In January 1974, Ralph Cicerone wrote Rowland in Vienna. Cicerone told Rowland about his and Stolarski's work on the chlorine chain and suggested an exchange of information. In response, Rowland sent Cicerone a copy of his paper. Having come up with the same chemical reactions independently of Rowland and Molina, Cicerone and Stolarski could fully grasp the theory's significance. CFCs were a further example of a phenomenon Rachel Carson had first observed—that inertness in chemistry, traditionally associated with safety, could instead portend long-term environmental problems with the potential to gather quiet strength before exploding. Carson had demonstrated how a man-made chemical found in trace quantities in the environment could become concentrated in the tissues of animals. Now, Rowland and Molina had shown how, by means of catalysis, a synthetic gas at trace concentrations could endanger humanity by affecting the chemistry of the stratosphere, a region long defined by its inaccessibility and very remoteness from man.

Slowly, the Rowland-Molina theory began to gain advocates and a hearing in scientific quarters. Harold Johnston couldn't resist mentioning it in January 1974 at a scientific workshop sponsored by NASA. In February the theory was outlined in a speech to the Swedish Academy of Sciences by meteorologist Paul Crutzen, who had seen a copy of Rowland and Molina's paper. The story was picked up by a Swedish newspaper, but went no further.

Rowland and Molina were in touch by mail throughout this difficult waiting period, keeping one another abreast of the work they were pursuing separately, especially refinements in their calculations and possible changes to the *Nature* manuscript, and exchanging news of their respective contacts with other scientists. In late January, Molina visited scientists at the University of California at Riverside who had been awarded Du Pont grants to study the "ecological effects" of CFCs. "But of



course," Molina wrote Rowland, "they had only worried about the troposphere." The important news, Molina continued, was that the Riverside scientists seemed to "corroborate strongly our conclusions about tropospheric stability." Moreover, Molina wrote, he had managed to glean this information from the Riverside scientists without divulging his and Rowland's discovery of the stratospheric problem. In February, Molina visited the National Center for Atmospheric Research in Boulder, where he met with atmospheric chemist Dieter Ehhalt to request stratospheric air samples from NCAR for future work he and Rowland wanted to carry out. Ehhalt had been at the Fort Lauderdale AEC conference with Rowland and understood their work implicitly. Molina told Ehhalt that he and Rowland had been working with CFCs, which were a source of stratospheric chlorine, that chlorine was a catalytic scavenger of ozone, and that they'd gone to steady state.

"Beautiful," Ehhalt responded, and agreed to assist the Irvine scientists in obtaining their air samples.

Rowland, meanwhile, gave a few talks on the CFC problem in Europe, outings that he intended to use to test his and Molina's work. The first presentations in West Berlin and Paris were easy because they were before chemistry colloquia, and Rowland was confident of his chemistry. The real test was a talk at the prestigious Institute of Meteorology in Stockholm, with Paul Crutzen and other notable meteorologists in the audience. Meteorology was Rowland's weakness. As it happened, Crutzen and Rowland hit it off well, although Crutzen did pose questions about the potential impact of a particular hydrogen chain species, HO<sub>2</sub>, on Rowland's calculations, enough to give Rowland cause for concern. That night, when he and Joan returned to their Stockholm hotel, he started work with his calculator to resolve the question. Lying in bed, Joan heard the "click, click" of Sherry's calculator all night long. The next morning he looked more refreshed than tired. "We're right," he told Joan. Crutzen, it turned out, had been up all night too, and had independently reached the same conclusion.

In March 1974, Rowland and Molina finally received word that *Nature* had accepted their paper. After several more weeks of delay they learned it had been scheduled for publication in June. "To use some Watergate language," Molina wrote Rowland in response to the news, "in retrospect we should have sent our letter to *Science*, not to (expletive deleted) *Nature*." A condition of publication was that news of the ozone-depletion theory had to be embargoed prior to the publication date. But the news had already begun to leak out. Harold Johnston told Molina that reporters had begun to call his Berkeley office, asking him about the possible connection between Freon and ozone depletion. Following an



American Chemical Society meeting in Los Angeles, a tiny item regarding the pending news appeared in an article in the *Chicago Tribune*. Molina was alarmed, while attending a scientific meeting in Berkeley in March, to overhear Raymond McCarthy, technical director of Du Pont's Freon Products Division, discussing rumors he had heard about a new ozone-depletion theory involving CFCs with another Du Pont researcher. Molina did not introduce himself. In response to the rumors, in May 1974, McCarthy expanded Du Pont's research program at UC-Riverside to analyze Freons in the stratosphere.

Rowland and Molina's seminal paper, entitled "Stratospheric Sink for Chlorofluoromethanes: Chlorine Atom-Catalyzed Destruction of Ozone," finally appeared in the June 28, 1974, issue of *Nature*. For all the anticipation, and Rowland and Molina's concern about a press leak and the public impact of the news, the article was greeted by a resounding silence. To the two scientists who had authored the paper, and to their colleagues who understood its implications, the silence was as ominous as it was unexpected. It was as if they had shouted "Fire!" in a crowded theater only to find their warning mistaken by the audience as part of the entertainment. A press release issued by the public-information office at the University of California at Irvine was ignored by the national media, with only a few articles appearing in California newspapers, including a page-three story in the *Los Angeles Times*.

Perhaps it should not have been surprising that even when it was spelled out, the ozone-depletion theory was difficult to recognize or accept at first. Like many epochal ideas, Rowland and Molina's theory was strikingly simple, so elegant that Rowland himself still sometimes suspected there must be something wrong with it. "From a physical point of view the theory was a neat idea," Rowland later said. "It was *too* clean and simple and it made you wonder if maybe nature isn't that clean and simple." In *Nature* the paper took up less than two pages. The most disturbing paragraph read:

It seems quite clear that the atmosphere has only a finite capacity for absorbing Cl [chlorine] atoms produced in the stratosphere, and that important consequences may result. This capacity is probably not sufficient in steady state even for the present rate of introduction of chlorofluoromethanes. More accurate estimates of this absorptive capacity need to be made in the immediate future in order to ascertain the levels of possible onset of environmental problems.

How easy it would be to read those words and fail to comprehend their meaning! The very language intended to convey a sense of scientific



detachment also tended to mask any sense of urgency. Rowland and Molina were probably right to launch the debate on this cautious note, but were still disappointed when their paper set off no fireworks. "We had been a little naive," Molina reflected later, "in thinking the press would immediately snatch the story up. Here we were concerned about a news leak. The problem seemed simple enough. It didn't occur to us that the whole subject was probably still too complicated for a nonscientist to understand." The inadequate response, however, charged them with a renewed sense of purpose. Too much was at stake to permit this debate to be hashed out in the pages of obscure scientific journals. If nobody else was going to bring the issue to public awareness, they would have to do it themselves.

"We realized there were no other spokesmen," Molina recalled. "As soon as that became clear, we never questioned the need to go public . . . we had a *responsibility* to go public."