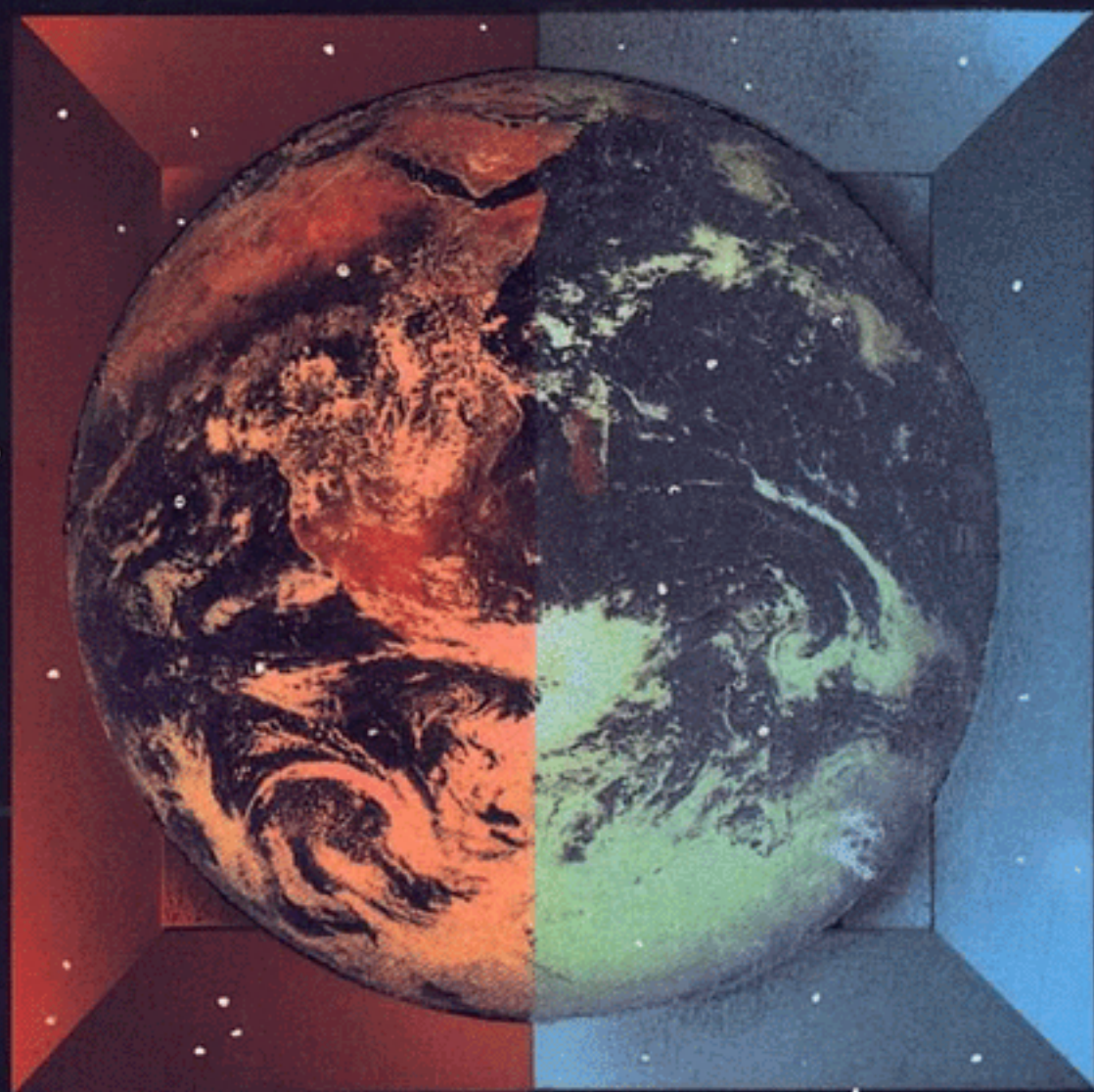


FIRE & ICE

THE GREENHOUSE EFFECT,
OZONE DEPLETION &
NUCLEAR WINTER



DAVID E. FISHER

A Planetary Time Bomb

The consequences could disrupt, and perhaps destroy, the biological systems of the earth.

—Paul Brodeur, in *The New Yorker*, 1986

In 1973 Mario J. Molina, now a senior researcher at the Jet Propulsion Laboratory, was a young Mexican who had just finished his Ph.D. work at the University of California at Berkeley. His thesis project had been in the field of laser chemistry, but he accepted a postdoctoral position with Professor F. Sherry Rowland at the Irvine campus of the UC even though Rowland's specialty was the quite different subject of radiochemistry.

As it turned out, Molina was not to learn much radiochemistry. Rowland had reached a point many scientists do in midlife. He was a good, solid researcher, well funded by federal agencies and respected by his colleagues, but not yet in the Nobel class and by this time in his life not likely ever to reach it. I remember meeting him once or twice at nuclear-chemistry conferences in the 1960s, a tall, broad-shouldered, athletic man with hair worn rather long and even then beginning to gray. He was one of the first to carry the new hand calculators around in a belt-slung holster, and was one of the leaders in radiochemistry.

But by the early 1970s he was beginning to look for something else to do, a different line of research to learn, something to stimulate him the way radiochemistry used to do. He planned a sabbatical for the second half of the coming year, to give him a chance to visit another laboratory and learn another subject, so that when Mario Molina came to Irvine to begin his postdoctoral year in October of 1973 Sherry Rowland was mentally packing up to leave.

This is a problem not infrequently encountered by postdocs. When I got my Ph.D. in nuclear chemistry I accepted a postdoctoral position at Brookhaven National Laboratory to work on nuclear reactions under one of the world's leaders, Gerhart Friedlander. But when I showed up a few months later I found he had left for the year to go to Switzerland, and I had to scrounge around to find someone else to work with.

In Molina's case it wasn't quite so bad. Rowland wouldn't be leaving till February, and so the two of them had time to talk about how Molina might spend his year. Rowland suggested that it might be worthwhile to take a look at the CFCs. A few years before, when he was just beginning to look for a new area of research, he had attended an International Atomic Energy Agency meeting in Salzburg, Austria, dealing with the applications of radioactivity to the environment. Nothing in particular clicked at that meeting, but after it he had a conversation with William Marlow of the United States Atomic Energy Commission, the agency that funded his research. During this conversation Rowland mentioned that he was looking for new areas to explore, and so in 1972, when Marlow was organizing a meeting in Fort Lauderdale that would deal with atmospheric problems, he invited Rowland.

Jim Lovelock's measurements of atmospheric CFCs had just been done, but weren't being formally presented at the meeting. Nevertheless, someone mentioned them during one of the informal coffee-break conversations. The scuttlebutt was, in fact, that the concentrations Lovelock had measured seemed to indicate an atmospheric load just about equal to the sum total of all the CFCs so far produced, which meant that the general consensus about them was correct: nothing interfered with them, nothing reacted with them, and once they got into the atmosphere they stayed there forever.

In the fall of 1973, when he was discussing with Molina what the young postdoc could be doing while he was away on sabbatical, Rowland brought up this topic and pointed out that nothing—neither diamonds nor love nor CFCs—are forever. Diamonds in fact slowly but irrevocably transform into graphite on this earth, and we all know about love, but what about the CFCs? *Something* has to happen to them. He suggested that Molina might investigate what their ultimate fate could be, while he (Rowland) was off on his sabbatical looking for something more interesting that they both

might do the following year. "Of course," he mentioned, "once they get up into the stratosphere they'll be dissociated by the ultraviolet, if nothing happens to them before."

And so Molina sat down and began to learn about atmospheric chemistry and about the chemistry of chlorofluorocarbons; he began to read books and to search through the more recent journal literature, and he began to compile a list of possible atmospheric sinks.

A "sink" is something that will absorb, eat up, or in some manner dispose of the subject under consideration. In the last chapter we mentioned a few possible sinks for the CFCs that turned out not to work: they wouldn't dissolve in rain water or the oceans, nor would they be oxidized or reduced or attacked by acids. Now Molina found that they also wouldn't be ingested and metabolized by any living creature, nor would they be deposited and buried in sediments. The longer he studied the literature, the longer became the list of sinks that simply weren't; and in the list of sinks that *were* he was able to write down just the one process already suggested by Rowland.

If nothing else happened to the CFCs, he agreed, they would float around in the atmosphere and gradually disperse both horizontally and vertically. Horizontally meant they would spread from the industrialized nations where they were being sprayed and leaked into the atmosphere, and in time they would be all over the globe; as Lovelock's work had shown, this was already happening.

Vertically meant they would migrate upward. Since they are heavy compounds relative to the nitrogen and oxygen molecules that comprise most of the atmosphere, their greatest concentration would remain close to the ground, but they would be driven inevitably higher as their lower concentrations increased, according to simple laws of diffusion. Eventually—if nothing else destroyed them—they would reach the stratosphere and mingle with the ozone there.

Ozone, although a reactive gas, is not reactive enough to react with such an inert molecule. But as the CFCs rose through the ozone they would be exposed to increasing fluxes of ultraviolet radiation—radiation that would be absent below the ozone layer but that was present in increasing doses as the molecules mounted higher and higher. The energy carried by the ultraviolet is enough to dissociate the CFC molecule, breaking it into its components and in particular

releasing chlorine atoms. The chlorine atoms are extremely reactive, and so is ozone; obviously the two will react, and the result will be the destruction of the ozone molecule.

When Molina reported this to Rowland, they immediately sat down to calculate the amount of destruction that might be done to the ozone layer if all the CFCs ever produced were to migrate up there, become dissociated by the ultraviolet flux, and produce chlorine, which would then eat up the ozone. The answer was reassuring to civilization, though it must have been a disappointment to Molina and Rowland, who were, after all, trying to find an important research problem. There was nowhere near enough of the CFCs to produce any noticeable effect, nor was there likely to be even if their production should increase, and so this reaction wasn't going to be important.

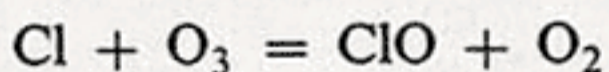
And somewhere, whatever gods may be must have been laughing.

Well, it happens all the time. The very nature of scientific research means that you're frequently trying to investigate a phenomenon that nobody knows anything about, which means that you can't tell in advance whether the problem you're attacking is solvable or, if it is, whether the solution will turn out to be interesting or not. During my postdoctoral at Brookhaven I became interested in meteoritics, one of the problems of which was the age of iron meteorites. A recent experiment had showed them to be about ten billion years old, but the age of the solar system was well established from stone meteorites at four and a half billion years. It might have been a bit older, when you throw in all possible errors; it might have been 4.6 billion, for example, but couldn't possibly have been any older than 5 billion. Ten billion was out of the question. Of course the iron meteorites could have come from beyond the solar system, which certainly would have been an interesting solution, but this was extremely unlikely on dynamic grounds. On the other hand, it was also extremely unlikely that anything originating within the solar system could possibly be ten billion years old, so it seemed like an interesting problem and I worked on it, off and on, for the next several years. Finally Lou Rancitelli, one of my Ph.D. students, and I discovered that the apparent age of the iron meteorites was due to a totally unexpected phenomenon. Potassium, which as the radioactive pro-

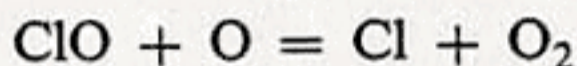
genitor of argon provided half of the age-measuring tool, was leached out of the meteorites during their time on earth, thus resetting the isotopic clock erroneously. The measured age had no real meaning: a totally uninteresting result.

And so Rowland and Molina prepared to write up their investigation of the atmospheric fate of the CFCs along with its totally uninteresting result: photodissociation in the stratosphere, period, end of story. But the gods must have chuckled a bit too loudly, and Molina must have heard them, for instead of writing *finis* to their paper he started to work out just exactly what would happen to the chlorine atoms released by the CFC photodissociation. And by late that night he was hearing the gods loud and clear.

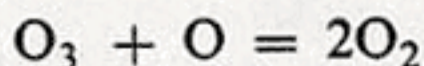
The next morning he discussed with Rowland what he had come up with. Molecules in the stratosphere are exposed to the ultraviolet flux and will dissociate, as they already knew. The CFCs will liberate, among other atoms, free chlorine (Cl); and also, Molina now pointed out, normal oxygen molecules (O_2) will dissociate into free oxygen atoms (O). The chlorine atoms will then react with the ozone (O_3) to form a chlorine-oxygen compound (ClO) plus molecular oxygen. But something else will also happen: the ClO is reactive enough to interact with the free atomic oxygen to form chlorine atoms and molecular oxygen. The sequence can be written in the shorthand notation that chemists use as:



and



It was now a simple matter of adding the equations together: the Cls and the ClOs cancel from opposite sides of the equations and Molina was left with the simple relation:



The astounding but inescapable conclusion was that, in the presence of free chlorine and oxygen atoms, the ozone would react with the oxygen to form normal molecular oxygen. The chlorine, although initiating the reaction, doesn't appear in the final equation and so doesn't react at all, in a very important sense. Another way of looking at it is that in the first reaction the atomic chlorine

disappears to form ClO, but in the next reaction the ClO gives back the original chlorine.

With either way of looking at it, the point is that the atomic chlorine (Cl) doesn't disappear, isn't chewed up; although it reacts it is also produced, and the net effect is that the single atom of chlorine is still there after the ozone molecule has been eaten up.

This is a well-known phenomenon in other areas of chemistry. It is known as a catalytic process inducing a chain reaction. The chlorine catalyzes the reaction of ozone with atomic oxygen, in which both of them are transformed into molecular oxygen, but the chlorine itself is not affected. This means that each atom of chlorine produced by the photodissociation of a CFC molecule will not only stimulate the destruction of an ozone molecule but will remain in the atmosphere to do the same thing all over again.

In fact it will do it over and over again, until finally the chlorine is eaten up by another reaction and disappears from the scene. Using reaction-rate kinetics, Rowland and Molina were able to calculate that each chlorine atom would aid in the destruction of 100,000 ozone molecules. This meant that their original conclusion was totally wrong. They had thought that there were not enough CFC molecules being produced and sprayed into the atmosphere to eat up any discernible amount of ozone, but now they found that each CFC molecule would destroy 100,000 times as many ozone molecules as they had previously calculated. Instead of being orders of magnitude too few, it now appeared that there were indeed enough CFCs around to affect the ozone layer by at least a few percent.

And suddenly it was a whole new ball game.

The catalytic chain reaction induced by chlorine atoms in the stratosphere had actually been known before Molina and Rowland "discovered" it. Other groups of atmospheric chemists, worrying about the effect of SSTs on the ozone, had known about it but had dismissed it from their calculations because they didn't think there was any source of chlorine that would make it important. Now, of course, there was.

Molina and Rowland wrote up their results and submitted them in a paper to *Nature*, the British scientific journal. (There is no significance to their submitting to a British instead of an American journal. Science is international in this respect, and the two leading

weekly journals of interdisciplinary science are the *American Science* and the British *Nature*. They probably sent their work off to *Nature* because *Science* is not really as interdisciplinary as it pretends, publishing almost entirely only biological reports.) They also sent an abstract to the American Chemical Society, indicating their intention of presenting the work orally at the society's Atlantic City meeting the following September. Then Rowland packed up and went off to Vienna for the spring semester.

The paper was published in *Nature* in June, but even before that, word began to circulate, as it often does in scientific circles. Rowland had heard about Lovelock's measurements before publication, in a coffee-break conversation, and in a similar manner word of the ozone problem began to leak around the world, worrying the people at E. I. du Pont de Nemours & Company.

The ozone layer, which shields us from ultraviolet, is not a constant thing, but is continually being produced and destroyed. It is produced naturally by the action of sunlight on normal oxygen molecules in the upper atmosphere, and is destroyed naturally through the action of nitrogen oxides (NO_x), which circulate upward upon being released by bacteria in the soil. The constant production and depletion lead to a steady-state situation in which the ozone is being produced at the same rate as it is being destroyed, and so the level in the atmosphere remains constant—at a concentration large enough to absorb all the UV-C and most of the UV-B. If anything should disturb this fragile equilibrium and deplete the ozone a bit faster, its steady-state concentration would drop.

In their *Nature* paper, Molina and Rowland were careful not to sound a precipitous alarm. They said only that "important consequences may result" and that "more accurate estimates . . . need to be made . . . in order to ascertain the levels of possible onset of environmental problems."

Mild enough. But as word of their work began to circulate through the scientific community, the CFC manufacturers began to feel the first touches of apprehension. They were sailing along on a many-billion-dollars-a-year boat, and they didn't appreciate its being rocked.

So even though the Molina-Rowland paper was mild enough, its implications were worrisome. In fact, there were rumors spreading that Harold Johnston, the Berkeley chemist who had first at-

tacked the NO_x problem in regard to the SSTs, had made some calculations based on the Molina-Rowland work that indicated that the effect on the ozone layer could be a depletion of as much as 20 to 40 percent. And in the April 5 issue of *Science*, Pythagoras Cutchis of the Institute for Defense Analyses in Arlington, Virginia (who was unaware of the Molina-Rowland idea but was still worried about the NO_x effects of a fleet of SSTs), calculated that a depletion at the upper end of that range would lead to nearly a tripling of the UV-B radiation at the surface of the earth. It had been calculated by several other workers that increases of only a few percent would lead to tens of thousands of skin cancers every year. Of course, skin cancer is not the worst kind of cancer; most cases are curable, but still . . . *Better things for better living through chemistry?*

When officials of the American Chemical Society prepicked the Molina-Rowland paper as one of the most newsworthy at the upcoming Atlantic City meeting, guaranteeing press attention, the industry thought it was time to take a hand. They had actually become involved in the problem several years previously. It's all too easy to blame all our problems on the rapacity and greed of big business, and though there's something to be said for the difficulty of overestimating these effects, there is usually something to be said on the other side.

The industry was in fact neither ignorant of nor uninterested in the possible environmental problems. In 1972 du Pont had organized a seminar on the ecological effect of CFCs, stating openly that the world was producing these things at an increasing rate and that it was time they found out if there were any harmful effects "now or in the future." The company had been instrumental in organizing a coalition of CFC producers to sponsor independent research on the problem, and by 1974 the results had indicated no detrimental ecological effects.

So what—they now asked—was all the fuss about?

An industry spokesman called Dorothy Smith, who as news manager for the ACS was arranging a press conference at which reporters could meet with Sherry Rowland, and he put the question to her. After all, he said, there was no proof of the Rowland calculations, no data at all that indicated a threat to the ozone. The whole idea was "just a theory." The phone call worried Smith; the last thing the ACS wanted was to get embroiled with a spectacular story that

might later prove to be nonsense. But after calling a few atmospheric scientists, who unanimously assured her that the "theory" was a good one, she went ahead with the press conference.

And, in a manner of speaking, the Flit hit the fan.

At the meeting and press conference Rowland told his audience that if the CFCs continued to grow at their present rate of 10 percent per year until 1990, and then remained constant, there would be a 5 to 7 percent destruction of the ozone by 1995, with an additional and unavoidable destruction of 30 to 50 percent by 2050. (This future destruction is an especially pernicious aspect of the problem. Because the CFCs are so inert, once introduced into the atmosphere they are not removed by any natural process; because they diffuse upward so slowly, it takes years for them to reach the stratosphere. Putting these two facts together, it follows that even if we were to cease all CFC production today, the CFCs already in the atmosphere would slowly but inexorably climb to the stratosphere and there do their damage. This means that even if we see no discernible ozone damage today the damage tomorrow *by the CFCs already in the atmosphere* will be greater and possibly significant. This, in turn, means that if we wait to cut back on production and use until we actually see a detrimental effect, it will be too late: a further drastic increase in the effect is mandatory. What we have here is a planetary time bomb.)

So the effects claimed by Sherry Rowland were not immediately verifiable, since they referred to the future; but they were immediately worrisome. Rowland went on to suggest that even a 5 percent reduction in ozone would cause forty thousand extra cases of skin cancer per year in the United States alone, with similar additional effects all over the world.

In that same month of September 1974, a group at the University of Michigan published computer calculations that supported the Molina-Rowland message, emphasizing that at the present rates the ozone equilibrium in the atmosphere would be displaced downward as early as 1985 or 1990. Another group, at Harvard, published similar work, arguing that "the reduction could be as large as 3 percent by 1980, or 16 percent by 2000, if Freon consumption were to grow at 10 percent per year. Even if Freon use were terminated as early as 1990, it could leave a significant (health, environmental) effect which might endure for several hundred years."

Although the Harvard paper wasn't published until February 1975, it was released to the press the previous September, and on the 26th of that month Walter Sullivan of the *New York Times* wrote a front-page story, and the media and the nation were off and running.

Within a month the National Academy of Sciences had convened an ad hoc panel to make recommendations. Included on the panel were several of the scientists who had rung the bell, including Rowland, Johnston, and Mike McElroy, one of the authors of the Harvard report. Meanwhile, du Pont announced that the industry was policing itself and had begun a comprehensive research program (to be overseen by its own Manufacturing Chemists Association) that would study the problem and all its implications, without fear or favoritism. Of course, doing responsible science does take time, as all men of good will would acknowledge, and the industry wanted to do it properly. Accordingly, they announced, it would take three years to complete the project, during which of course there would be profits as usual. It was to be hoped, they announced, that there would be no panicky reaction (or punitive legislation) before all the results were in.

It was not to be. By the end of that same month of October one of the ad hoc panel was quoted in the *Times* as urging the public to stop buying all spray cans with CFC propellants. The next month the *Washington Post* ran a story saying that the panel would soon be urging the banning of the spray cans. By the end of that month national sales had dropped by 7 percent.

In December the House Subcommittee on Public Health and the Environment opened a hearing, but nothing was done before Congress adjourned eight days later. In January of 1975 James Fletcher, the chief NASA administrator, saw the moving finger writing, and announced that his organization was prepared to act as the government's chief research agency (and pick up the biggest bundle of extra congressional funding) in this problem: "We have rather dramatically changed our emphasis within NASA to focus on stratospheric research."

In January the President's Council on Environmental Quality and the Federal Council for Science and Technology created a task force to conduct an "intensive study" of the situation. The panel included representatives of seven cabinet departments and five differ-

ent government agencies. In June they issued a report stating that CFCs were a legitimate cause for concern and should be restricted by 1978. At the same time the Senate Committee on Aeronautical and Space Sciences opened their own hearing but accomplished nothing.

The month before the task force met, Congressmen Paul Rogers of Florida and Marvin Esch of Michigan had introduced a bill authorizing the Environmental Protection Agency (EPA) to ban all CFCs if the National Academy of Sciences (NAS) decided the threat was real. Their bill died in committee. In February 1974, they reintroduced it; an even stricter bill was introduced by Les Aspin of Wisconsin. Neither bill passed.

Instead the public heard about a report in the du Pont *Management Bulletin*, which stated proudly that there were no adverse pollutant effects caused by the CFCs in the troposphere. (Well, of course there were none: the whole basis of the ozone problem was that the CFCs didn't react with anything in the troposphere, so how could they cause any problems there? The *Bulletin* didn't discuss the stratospheric problems.)

Still another committee was formed that February: the Ad Hoc Federal Interagency Task Force on the Inadvertent Modification of the Stratosphere (IMOS), sponsored by the President's Council on Environmental Quality, the Federal Council on Environmental Quality, and the Federal Council for Science and Technology. In March the National Academy of Sciences appointed a Panel on Atmospheric Chemistry, to report to its Climatic Impact Committee, which had been established originally to investigate the SST problem (which by now had gone away), and *New Times* quoted Sherry Rowland as saying to his wife when she asked how his day had been: "The work is going well, but it looks like the end of the world."

To which our government's reply was, as we have seen, the formation of more committees. To be fair, it wasn't simple; no one knew who had legal or scientific jurisdiction. Back in November the National Resources Defense Council had petitioned the Consumer Product Safety Commission to outlaw spray cans. There was a law in effect which said that upon such petition the commission must either comply or issue a written denial in four months. They did neither, because they couldn't decide if they had the legal power. The

CPSC general counsel, Michael Brown, suggested, "This may be something for the EPA." But the EPA responded that "We take care of the *lower* atmosphere, and this is an *upper* atmosphere problem." They suggested perhaps NOAA might be the right organization to take charge.

In April Congressman Robert Michel (Illinois) complained that he couldn't understand the whole thing.

Still, progress was made. In June 1975, came the first break in the industry's united front. (They had been reasonable, according to their own lights. They had never rejected the ozone-depletion argument, nor claimed that it was unimportant; they merely claimed that it needed more study. They were investigating it themselves, and in "three years" they could have the answer. This figure, "three years," never changed very much; you have to give them high marks for consistency. In 1974, in 1978, in 1984, they were still sure they would have the answer "in three or two or four years.") But now, in June 1975, the Johnson Wax Company announced it would not use any more CFCs. Since they really hadn't used them in any significant quantities for several years, their decision didn't have much economic impact, but the publicity of their announcement did. Other companies followed, and by that summer the production of aerosol valves had been cut in half.

That June Oregon banned the spray cans altogether, with an effective date of March 1977. New York State decided that by April 1977 all cans would have to carry a warning that the product "may harm the environment." In October the industry fought back, with du Pont taking out full-page newspaper ads saying that their research had turned up new evidence that made the ozone-depletion effect 300 percent less than Rowland and Molina had "estimated." Subsequent work proved that the industry evidence was erroneous; it was simply a case of rushing into print because they *wanted* to believe.

By December, measurements had shown that the CFCs had doubled their atmospheric concentration between 1968 and 1975. The industry now argued once again for a three-year delay for further studies. They claimed that such a delay wouldn't hurt anyone; depletion would be "an insignificant and undetectable effect of one half of one percent." (Even if this was true, and no one at the time knew what the depletion would be, the best estimates were that "one

half of one percent" depletion would mean an extra 6,000 cases of cancer per year, and this would continue for roughly a hundred years, so the "insignificant" effect would translate literally into 600,000 extra cases of cancer.)

The public was not fooled. Purchases of spray cans continued to drop, companies continued to desert the market, and by the end of the year Washington was abounding in rumors that legislation banning all nonessential uses of CFCs was just around the corner. The battle seemed to have been won.

The battle, yes; the war, no. For the always fickle attention of the public and the legislators now began to stray toward a new romance.