## LETTERS

### The Ozone Question

The 3 October issue of *Science* (pp. 8 and 9) carried a paid advertisement from the Du Pont Company on the fluorocarbon-ozone question. The same advertisement appeared also in many other newspapers and magazines. This advertisement stated that, "The ozone depletion theory, based on a computer model of the stratosphere, was reported in 1974 by two chemists at the University of California.... In order to estimate hypothetical reactions, and because little is actually known about the real ones, the modelers made a number of assumptions about the way the upper atmosphere behaves."

All of the major reactions included in our calculations had been observed and measured in the laboratory (*1–5*). The hypotheses involved estimates of present and future stratospheric consequences, reached by combining the measured reactions with known intensities of solar radiation, and with the known stratospheric concentrations of a number of species (for example, $CH_4$, $O_3$, and NO) (*6*) plus those of some (for example, O and OH) whose concentrations were then indirectly inferred from other stratospheric measurements and have since been measured directly (*7, 8*).

The statements about our assumptions were not made by us, but are apparently inferences drawn by the writers of the advertisement. The three supposed assumptions listed in the advertisement are as follows.

ASSUMPTION: The ozone-depleting reaction with chlorine from fluorocarbons takes place at a rate that demands an *immediate decision* on fluorocarbon use.

We made no such assumption.

ASSUMPTION: Fluorocarbons are the only significant source of chlorine available for interaction with ozone in the stratosphere.

We made no such assumption.

ASSUMPTION: There is *no other way to get fluorocarbons out* of the atmosphere except by the ozone-depleting reaction.

We made no such assumption in our actual research. Such a statement about models can easily be misinterpreted, since readers might assume that reactions not included in the model had not been considered. We searched for removal processes and found none of any importance except stratospheric decomposition processes (*1–5*). No important removal process has since been discovered which does not lead to the release of stratospheric chlorine species

capable of depleting ozone (*9*). The models simply reflect this situation.

The advertisement further states, "... the net effect of both reactions [ozone/chlorine and chlorine/methane] is to lessen the originally-calculated impact of fluorocarbons. In fact, the impact was overstated by 300%."

The quantitative statement is in error. The two reactions mentioned are among several which have been more accurately measured in the past 15 months (*10*). The concentrations of important species (for example, OH) have also been measured more accurately (*8*). When all corrections have been made, the current assessment of ozone depletion by models falls within the range of our original estimates made in August 1974 (*2, 3, 11, 12*).

The advertisement also stated, "One well-known class of chemical reactions not considered in this model is that of chlorine compounds in the atmosphere in heterogeneous reactions."

Heterogeneous reactions *were* considered, but they were not included because the evidence indicates that they are negligible in importance. The possible involvement of heterogeneous reactions with the chlorofluoromethanes was discussed in extensive detail on pages 22 and 23 of (*4*). We found no evidence that such reactions were occurring and some strong evidence that they were at most minor. We know of no evidence in the refereed scientific literature leading to a conclusion different from ours.

A further statement in the advertisement was, "Atmospheric chemistry involving ion molecule reactions has been described in recent months by several investigators.... ion molecules could react with fluorocarbons, allowing them to be removed from the atmosphere."

The only extensive description so far published in the scientific literature about the possible ion-molecule reactions for removal of chlorofluoromethanes is our own discussion on pages 20 and 21 of (*4*). We concluded there that ion-molecule reactions were not important for the removal of these compounds, and no conclusions to the contrary have been published in the scientific literature (*13*).

This further statement was also made in the advertisement, "*Many chlorine-containing materials are present in the atmosphere* in varying concentrations. Of particular significance, large amounts of methyl chloride and carbon tetrachloride have been discovered in the troposphere and stratosphere."

The pertinence of carbon tetrachloride for this problem is the chief topic discussed by us more than a year ago in (*14*). The importance of chlorine compounds of natural origin, such as $CH_3Cl$ (*15*), relative to the fluorocarbon-ozone problem is easily (and frequently) overstated. The concern is with *changes* from the natural situation caused by man. All calculations indicate a progressive effect of added stratospheric chlorine (*16*) such that the change from the natural situation is basically the same whatever the precise level of natural chlorine before the introduction of further stratospheric chlorine by man. Carbon tetrachloride released by man in quantities comparable to the current release rates for fluorocarbons 11 and 12 would also have important effects on ozone depletion, but its current atmospheric release is much less than that of the two molecules listed above.

Our original conclusion was that, at current rates of technological use, flurorocarbons 11 and 12 were the two most important man-made compounds, in terms of potential effects on the ozone layer. This conclusion still stands and has been amplified and supported by numerous studies, including direct stratospheric experiments (*17*) as well as more detailed calculations of ozone depletion (*11, 12, 18*).

We believe that sufficient facts are already available in the refereed scientific literature to establish that chlorine released by stratospheric photolysis of fluorocarbons 11 and 12 will indeed have a substantial effect on the average ozone level of the earth in the future if present usages are maintained. The possible consequences of such ozone depletion have been outlined in detail in (*12*) and (*19*), together with the uncertainties involved. The 3 October issue of *Science* also carried a report of the possibility of a "greenhouse" effect of accumulated chlorocompounds in the atmosphere (*20*).

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**References and Notes**

1. M. J. Molina and F. S. Rowland, *Nature (London)* **249**, 810 (1974); in *2nd International Conference on the Environmental Impact of Aerospace Operations in the High Atmosphere, 1974, San Diego, Calif., Preprint Volume* (American Meteorological Society, Boston, Mass., 1974), p. 99.
2. F. S. Rowland and M. J. Molina, "Chlorofluoromethanes in the environment" (Atomic Energy Commission report No. 1974-1, Univ. of California, Irvine, 1974).
3. ———, "$ClO_x$-chain-catalyzed removal of ozone from the earth's stratosphere following solar photodissociation of chlorofluoromethanes," paper presented at the 168th American Chemical Society meeting, Atlantic City, N.J., 1974.
4. ———, *Rev. Geophys. Space Phys.* **13**, 1 (1975).
5. F. S. Rowland, *New Sci.* **64**, 717 (1974).
6. A. J. Grobecker, Ed, "The natural stratosphere of 1974" [Climatic Impact Assessment Program (CIAP), Monograph 1, Department of Transportation, Washington, D.C., 1975]. See also earlier reports of the 2nd and 3rd CIAP conferences.
7. J. G. Anderson, *Geophys. Res. Lett.* **2**, 231 (1975).
8. ———, "The in situ measurement of atoms and

radicals important to the photochemistry of the stratosphere," paper presented at the 8th International Conference on Photochemistry, Edmonton, Alberta, 1975.
9. J. N. Pitts, Jr., H. L. Sandoval, R. Atkinson, *Chem. Phys. Lett.* **29**, 31 (1974); N. E. Hester, E. P. Stephens, O. C. Taylor, *Atmos. Environ.*, in press.
10. A summary of these effects has been given in F. S. Rowland, *New Sci.* **68**, 8 (1975). The revised rate constants for the reaction of OH with HCl are given in (*4*). Revised rate constants for the reactions of Cl with $O_3$ and $CH_4$, as well as other pertinent chlorine reactions, have been collected in R. F. Hampson, Jr., and D. Garvin, Eds., *Chemical Kinetic and Photochemical Data for Modelling Atmospheric Chemistry* [addenda to *Nat. Bur. Stand. (U.S.) Tech. Note 866* (1975)].
11. P. J. Crutzen, *Geophys. Res. Lett.* **1**, 205 (1974); ——— and I. Isaksen, in preparation.
12. Council on Environmental Quality, Federal Council for Science and Technology, *Fluorocarbons and the Environment: Report of the Federal Task Force on Inadvertent Modification of the Stratosphere* (Government Printing Office, Washington, D.C., 1975).
13. A much more complete description has been given of the ion-molecule problem by A. I. Schmeltekopf in a statement to the House Science and Technology Committee, subcommittee on environment and atmosphere, Washington, D.C., 31 July 1975; F. C. Fehsenfeld, P. J. Crutzen, A. L. Schmeltekopf, C. J. Howard, D. L. Albritton, E. E. Ferguson, in preparation.
14. M. J. Molina and F. S. Rowland, *Geophys. Res. Lett.* **1**, 309 (1974).
15. The measurement of $CH_3Cl$ and other halocarbon molecules has been reported in increasing detail and accuracy. See J. E. Lovelock, R. J. Maggs, R. J. Wade, *Nature (London)* **241**, 194 (1973); J. E. Lovelock, *ibid.* **252**, 292 (1974); *ibid.* **256**, 193 (1975); P. E. Wilkniss, J. W. Swinnerton, R. A. Lamontagne, D. J. Bressan, *Science* **187**, 832 (1975); E. P. Grimsrud and R. A. Rasmussen, *Atmos. Environ.*, in press. See also (*12*).
16. For an illustration of the additive nature of Cl reactions on ozone, see figure 6 in S. C. Wofsy and M. B. McElroy, *Can. J. Chem.* **52**, 1582 (1974).
17. A. L. Schmeltekopf, P. D. Goldan, W. R. Henderson, W. J. Harrop, T. L. Thompson, F. C. Fehsenfeld, H. I. Schiff, P. J. Crutzen, I. S. A. Isaksen, E. E. Ferguson, *Geophys. Res. Lett.* **2**, 393 (1975); L. E. Heidt, R. Lueb, W. Pollock, D. H. Ehhalt, *ibid.*, p. 445; D. G. Murcray *et al.*, *ibid.*, p. 109; A. L. Lazrus, B. W. Gandrud, R. N. Woodward, W. A. Sedlacek, *ibid.*, p. 439; C. B. Farmer, O. F. Raper, R. H. Norton, in preparation; M. Ackerman, private communication, October 1975. Ackerman has made spectroscopic measurements of the stratospheric concentrations of HCl between the altitudes of 18 and 34 kilometers.
18. R. S. Stolarski and R. J. Cicerone, *Can. J. Chem.* **52**, 1610 (1974); R. J. Cicerone, R. S. Stolarski, S. Walters, *Science* **185**, 1165 (1974); S. C. Wofsy, M. B. McElroy, N. D. Sze, *ibid.* **187**, 535 (1975); R. J. Cicerone, D. H. Stedman, R. S. Stolarski, *Geophys. Res. Lett.* **2**, 219 (1975); S. C. Wofsy, M. B. McElroy, Y. L. Yung, *ibid.*, p. 215; D. H. Stedman, W. L. Chameides, R. J. Cicerone, *ibid.*, p. 333; R. J. Cicerone, *J. Geophys. Res.* **80**, 3911 (1975); Y. L. Yung, M. B. McElroy, S. C. Wofsy, *Geophys. Res. Lett.* **2**, 397 (1975); R. C. Whitten, W. J. Borucki, I. G. Poppoff, R. P. Turco, *J. Atmos. Sci.* **32**, 613 (1975).
19. Climatic Impact Committee, National Research Council–National Academy of Sciences–National Academy of Engineering, *Environmental Impact of Stratospheric Flight* (National Academy of Sciences, Washington, D.C., 1975).
20. V. Ramanathan, *Science* **190**, 50 (1975).

Du Pont's advertisement was not intended to attack the published scientific work of Rowland and Molina on ozone depletion, which, as we have said before, we believe to have raised a significant point.

The principal source of misunderstanding appears to be that the authors interpret the advertisement to say they made certain assumptions in their "actual research." To the contrary, the assumptions lie in the products of their research—particularly in the public position taken by Rowland with regard to the implications of his research.

The stimulus for the advertisement was the many media articles discussing the issue, which have been presented with scare headlines and predictions of dire consequences that are at variance with scientific facts as they exist today. Insofar as differing viewpoints have not been adequately reported, our intent was to present a less technical description of the question to ensure that nonspecialists were informed on both sides of the issue.

That early model predictions were overstated by some 300 percent as mentioned in the advertisement is easily documented. An overstatement range of 280 percent has been calculated (*1*) for the two revised rate constants described in the advertisement. These two rate constants are the only significant revisions to the calculated depletions since the first time-dependent calculations of Wofsy *et al.* (*2*). Rowland and Molina make reference in their letter to OH, but any attempt to revise $HO_2$ reaction rates on the basis of a single measurement at a particular latitude, altitude, time of day, and season is premature. The $HO_2$ rate constants in question will be measured in the laboratory, and appropriate revisions to estimated depletions can then be made.

We are firmly of the impression that Rowland has been asking for immediate regulation of fluorocarbons, although not, of course, in his "refereed scientific articles." As early as December 1974, Rowland testified before the House subcommittee on public health and the environment that he believed the use of fluorocarbons as aerosol propellants should be banned now.

Additionally, Rowland and Molina state in their original article (*3*), "We have not included any estimates for other chlorinated aliphatic hydrocarbons also found in the atmosphere such as $CCl_4$ . . . for which there is no evidence for long residence times in the atmosphere." Six months later, an article (*4*) by the same authors was published treating $CCl_4$ in exactly the same manner that the fluorocarbons were treated in the first article. A month after that, $CH_3Cl$, a molecule not even mentioned in the first article, was shown (*5*) to be the largest single source of chlorine presently established in the atmosphere. Whether or not the authors assumed that fluorocarbons are the only significant source of chlorine available for interaction with ozone in the atmosphere, the fact remains that there are other significant sources than those mentioned in their original article and that they were only pointed out at a later date. There is thus an established record of things having been left out; one may reasonably ask what else has been left out.

This leads to a clear philosophical distinction which appears to be at the basis of the differences between Rowland and Molina and the fluorocarbon industry. There is, on the one hand, the review involved in the refereeing of published papers and, on the other hand, the much more stringent test of nature. Thus one hears statements to the effect that the theory has been around for a year and no one has seriously challenged it. This is somehow regarded as establishing its validity, which, of course, it does not. Similar reasoning is implicit in the statements in the Rowland-Molina letter concerning removal mechanisms and heterogeneous processes.

All of the above would indeed be academic if it were not for the fact that Rowland has asked for a fluorocarbon ban. This is the stage at which the implicit assumption of correctness of the conclusions enters the picture. If that is not the case, how is it that other eminent scientists, not related to industry, have said the evidence is not conclusive and a ban is premature?

It is clear that experiments can be performed to validate or invalidate the theoretical conclusions and that no undue risk is involved in taking the time to perform them. Large-scale government and industry programs are under way. Under these circumstances, reason would appear to dictate that we should permit science to pursue its normal course to enable public policy-makers to make informed judgments based on fact.


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#### References and Notes


1. A value of 280 percent has been calculated using the original (*2*) set of $HO_2$ rate constants (N. D. Sze, personal communication).
2. S. C. Wofsy, M. B. McElroy, N. D. Sze, *Science* **187**, 535 (1975).
3. M. J. Molina and F. S. Rowland, *Nature (London)* **249**, 810 (1974).
4. ———, *Geophys. Res. Lett.* **1**, 309 (1974).
5. This was originally detected by R. A. Rassmussen and first reported by J. E. Lovelock, *Nature (London)* **256**, 193 (1975).


### The "Greenhouse Effect"

The term "greenhouse effect" continues to be incorrectly applied to the effect of the atmosphere in warming the earth's surface by absorbing and reradiating infrared radiation. In fact, because of the importance of understanding climatic change (including man-induced change), use of the term is becoming part of "accepted knowledge" (*1*).

The facts as they relate to the atmo-