Cover Art Description[†,‡]

My research career is analogous to a two story house. The ground floor consists of fundamental experimental and theoretical physical chemistry. The upper floor is atmospheric chemistry concerning possible global ozone change caused by human activities, with emphasis on stratospheric aircraft. On both floors, the oxides of nitrogen play a major role. The word "NO" stands for "Don't pull the cat's tail", and also it is the chemical formula for nitric oxide. My professors and colleagues are represented by the wise owl. The distorted chimney above the roof states that some of my work was later found to be wrong.

A-1. Fast Gas-Phase Reactions among NO, NO_2Cl, NO_2, N_2O_5, HNO_3, O_3, F_2. I was a graduate student at Caltech, 1941−42, 1945−47, and Professor Don Yost was my research director. Professor Yost and I came up with the idea of a stopped-flow reactor for measuring fast chemical reaction rates in the gas phase. By light absorption, we followed a reactant or a product in a chemical kinetics system as a time-exposure photograph of the single sweep on an oscilloscope screen, thereby extending the lower limit time scale for direct measurement of gas-phase reaction rates from about 10 s down to 10 ms, a factor of a thousand. As an instructor at Stanford, my students and I measured the rate of several "fast" reactions. On hindsight, our studies appear to have been the first lap in the fast-reaction race. In 2000, kineticists using lasers directly measure reaction rates that are a million million (10^{12}) times faster than our "fast reactions" of 1947−1954 (Johnston and Yost, 1949). Image reproduced with permission of the American Institute of Physics. Copyright 1949.

A-2. Unimolecular Reactions. Using our fast reaction method and also large glass bulbs, Bob Mills and I followed the unimolecular decomposition of N_2O_5 from its first-order high-pressure limit down to its second-order low-pressure limit, a total pressure range of 10^5:

$$N_2O_5 \rightarrow NO_2 + NO_3$$

This study was the first to span high to low pressure limits at one temperature for a unimolecular reaction (Mills and Johnston, 1951).

Later students studied the unimolecular decomposition of HNO_3 and NO_2Cl. We compared our results with the RRK theory, which preceded the RRKM theory, and we followed the unimolecular decomposition, that is, thermal ionization rates, of Kr and Xe.

A-3. Kinetic Isotope Effects. We carried out extensive experimental and theoretical studies of kinetic isotope effects, especially reactions involving hydrogen-atom transfer. We calculated the full set of normal coordinates for reactants and for transition states. de Broglie wavelengths superimposed on standard potential energy surfaces of the transition state imply large degrees of multidimensional quantum mechanical tunneling for hydrogen transfer reactions (Johnston, 1960; Sharp and Johnston, 1962). Image reproduced with permission of the American Institute of Physics. Copyright 1962.

A-4. Photochemistry. Light absorption by NO_3 produces three different products, $NO_2 + O$, $NO + O_2$, or fluorescence. In collaboration with Floyd Davis and Yuan T. Lee (1996), we used Lee's universal molecular beam system directly to measure the quantum yield, Φ, as a function of wavelength for each of these channels.

B-1. Supersonic Transports As Planned in 1971. In their discussion of supersonic transports (SST), the MIT summer study (1970), Study of Critical Environmental Problems [SCEP, 1971] stated: "Both carbon monoxide and nitrogen in its various forms ... may be neglected."

Taking the stratospheric lifetimes and the amount of NO_x from 500 hypothetical SSTs as described by SCEP, I showed in 1971 that various assigned vertical distributions of exhaust gases in the stratosphere gave 3 to 23% calculated steady-state global ozone reduction (*Science* **1971**, *173*, 517−522). In the context of SSTs, this article proves that NO_x and vertical mixing of air are important variables. The SCEP hypothesis that NO_x may be neglected is false.

After this article was published in August 1971 and as a direct result of this article and publicity others gave it (*Annu. Rev. Phys. Chem.* **1992**, *43*, 1992, 23−25), the U.S. Congress in September 1971 set up a major program of stratospheric research, the Climatic Impact Assessment Program (CIAP), in the Department of Transportation, which ran from January 1972 through 1975. Its assignment was to assess effects of supersonic aircraft exhaust gases on the stratosphere, especially with respect to ozone. CIAP investigators made the first measurements of nitrogen oxides and other trace species in the stratosphere, discovered that chlorine radicals also destroy ozone, and calculated ozone reduction brought about by 500 hypothetical supersonic transports. In 1976 the Congress appointed NASA (National Aeronautics and Space Administration) to continue the study of the stratosphere, including possible global ozone changes by human activities. This article in 1971 launched the first of a series of major programs of stratospheric ozone research, which over the next 30 years supported scores of research projects.

B-2. History (1974−1988) of Calculated Ozone-Column Change to Steady State for Two Standard Assumed Perturbations: *(i) NO_x from 500 SSTs Cruising at 20 km (As Planned in 1971 by U.S.A.) and (ii) Chlorofluorocarbons (CFC-11 and -12) Emitted Continuously at 1974 Rate*. Scientists made these calculations using the Lawrence Livermore National Laboratory (LLNL) atmospheric model with only homogeneous gas chemistry. Over the years, this figure has appeared in various forms and in several reports. This figure is from Johnston (1994). The wide excursions in calculated values between 1975 and 1982 were caused by discoveries of new stratospheric species and from improved measurements of chemical rate parameters. From 1982 to 1988, the calculated global ozone reduction from SSTs was about 10%, and it was about 5% for CFCs. Image reproduced with permission from Blackwell Scientific Publications. Copyright 1994.

B-3. Heterogeneous Reactions Added to Atmospheric Models. Observations of the Antarctic ozone hole were announced in 1985, and its major features became understood by about 1989 in terms of newly discovered heterogeneous chemical reactions. This panel (Johnston, 1994) qualitatively shows the global effect of heterogeneous chemistry on observed CFC perturbations (Stolarski et al., 1991) and on calculated

[†] Part of the special issue "Harold Johnston Festschrift".
[‡] Artist, Barbara Schubert.

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supersonic stratospheric aircraft (Weisenstein et al., 1991). The calculated ozone reduction from supersonic aircraft fell almost to zero, and the observed global ozone reduction by CFC was much larger than that calculated by models, even those that included heterogeneous chemistry. Image reproduced with permission from Blackwell Scientific Publications. Copyright 1994.

B-4. Conclusion of NASA's Ten-Year Program, Atmospheric Effects Stratospheric Aircraft (AESA). A quotation from Kawa et al. in the AESA1998 final report: "Based on a combination of model calculations and expert judgment, the estimated column ozone change in the Northern Hemisphere is −0.4% for a fleet of 500 HSCTs [High-Speed Civil Transports, an alternate name for SSTs] flying Mach 2.4 with an NOx emission index (EINOx) of 5 g/kg, $EISO_2$ of 0.4 g/kg, and 10% of fuel sulfur converted to particles. Based on the same combination of model calculations and expert judgment for the uncertainty in component processes, the hemispheric ozone response will likely be in the range of −2.5 to +0.5%."

With respect to atmospheric observations, laboratory measurements, and atmospheric modeling, the AESA program produced scientific results of outstanding quality and pertinence. The discovery of the importance of heterogeneous chemical reactions in the stratosphere was a major contribution to atmospheric science.

B-5. What about the future? NAS/NRC, National Academy of Sciences/National Research Council, 1999 report on stratospheric aircraft states on page 39: "*Future Stratospheric Aircraft.* It must be stressed that the AESA assessment was restricted to studying the effects of only one type of aircraft (known as the Technology Concept Aircraft, TCA, Baughcum et al., 1998) that cruises at Mach 2.4 and has a NOx EI between 5 and 15. This restriction seems reasonable given the fact that the TCA was the only type of stratospheric aircraft that has been seriously considered for commercial production recently. It is quite possible, however, that other types of stratospheric aircraft may be considered in the future (for instance 'hypersonic' aircraft that cruise at higher speed and altitude). In such a case, it is imperative that the assessment calculations be redone to specifically test the effects of the appropriate mach numbers and emission indices. This is important because some very preliminary studies have shown that hypersonic aircraft could have quite devastating effects on ozone (Oliver, 1994)."

The NAS/NRC report supported the AESA findings with respect to the TCA concept, and I do too. Since Boeing withdrew from the High Speed Research Program in October 1998 and AESA was terminated in early 1999, the NAS report raised the question as to what "types of stratospheric aircraft may be considered in the future". Some evidence as to what other types might be introduced is given by the alternatives seriously discussed before the TCA concept was selected. During 1988−1990, NASA sponsored informal meetings including representatives from GE (engines), Pratt & Whitney (engines), Boeing (airframe), McDonnell-Douglas (airframe), NASA (Lewis, Langley, and Headquarters), and a small number of atmospheric scientists, including me. The group discussion included various types of supersonic aircraft that might be developed. I have saved notes, reports, and handouts from these meetings.

Boeing (1989) reported a sensitivity study of aircraft over a wide range of Mach numbers. "Hypersonic" aircraft (Mach 5 to 10) would use liquid methane or liquid hydrogen as fuel. "Supersonic" aircraft (Mach 1.6 to about 3.6) would use standard jet fuel or thermally stabilized jet fuel. As aircraft are considered with increasing Mach number, there are concurrent increases in the size, weight, fuel consumption, cruise altitude, NO_x emission index, and calculated ozone reduction (Boeing, 1989; Oliver, 1994). The Boeing report gave serious analyses for aircraft with Mach numbers 1.6, 2.4, and 3.2. NASA and aircraft engine representatives at the 1989 meetings pointed out that the expected nitrogen oxides emission index from engines for Mach 2.4 based on the efficient 1990s engine technology would be between 30 and 60 g/kg. In 1989, NASA announced its goal to reduce the NO_x emission index to 5. The average of seven modelers' calculations, including heterogeneous chemistry, indicated (i) Mach 1.6 aircraft with EI(NOx) of 5 or 15 would increase global ozone by 0.1 or 0.2%, (ii) Mach 2.4 aircraft with an NO_x emission indices of 5, 15, or 45 would reduce global ozone by 0.1, 0.4, or 2.4%, respectively, and (iii) Mach 3.2 aircraft with EI(NO_x) of 5 or 15 would reduce global ozone by 0.7 or 2.3% (NASA Reference Publication 1293, March 1993, p 92).

References and Notes

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