J. Phys. Chem. A **2001,** *105,* 1393−1410

Bibliography of Harold Johnston[†,‡]

1. Introduction

My complete bibliography, with articles from 1 to 166, is available from me, 132 Highland Blvd., Berkeley, CA 94708, or from the Department of Chemistry, University of California, Berkeley, CA 94720. I list these articles here, but they are grouped according to subject matter and have comments. The title of each article is preceded by a number that corresponds to the sequential listing.

2. Laboratory Chemical Kinetics

2.1. Fast Reactions Measured in the Laboratory Primarily by Absorption of Ultraviolet and Visible Light. 2.1.1. The "Fast" Reaction of Nitrogen Dioxide and Ozone. This study was based on my Ph.D. thesis at Caltech (1947). The method involved fast flow, fast mixing, and sudden cut off of the cell entrance and cell exit. The action of stopping the flow triggered a single sweep across the oscilloscope screen. A narrow beam of light went down the center of the cell, and a notched rotating circular plate chopped the light to give an ac signal on a photomultiplier tube (Figure 1). We recorded the course of a reaction by a time exposure photograph of a single sweep across the oscilloscope screen. By choosing the appropriate wavelength of light, we could follow a reactant or a product. This method extended the lower limit time scale for studying gas-phase chemical kinetics from 10 s to 0.01 s. (See panel A-1, on the cover.)

1. "The Kinetics of the Rapid Gas Reaction Between Ozone and Nitrogen Dioxide." Harold S. Johnston and Don M. Yost, *J. Chem. Phys.*, **17**, 386−392 (1949).

The Faraday Society had a "Discussion" of fast reaction kinetics in 1954. I presented a paper that reviewed our work over the five year period 1949−1954. We had developed systems that spanned a wide range of pressure and temperature.

21. "Photoelectric Methods for Following Fast Gas-Phase Reactions." Harold Johnston, *Faraday Soc. Discuss.*, **17**, 1−8 (1954).

2.1.2. Reinvestigation of Two Classic Reactions. We reinvestigated one of Bodenstein's classic reactions over a fairly wide pressure range, using two different reaction systems.

$$2NO + O_2 \rightarrow 2NO_2$$

Our results at one temperature gave the same rate constant over the entire pressure range, and our rate constant agreed with that of Bodenstein. After that, we used Bodenstein's reaction to calibrate each new reaction system. This reaction shows third-order kinetics, and the rate varies widely with reactant pressures. I became familiar with the rate of this reaction at both low and high reactant pressures.

5. "Oxidation of Nitric Oxide at High Pressures of Reactants." Harold S. Johnston and Loren W. Slentz, *J. Am. Chem. Soc.*, **73**, 2948 (1951).

The classic reaction, decomposition of N_2O_5, has a large activation energy, and we followed its rate from below room temperature to almost 100 °C. We found no surprises.

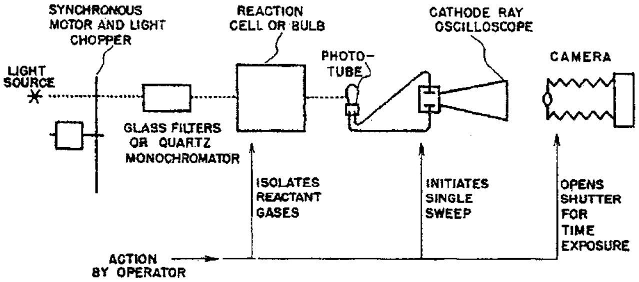

Figure 1. Schematic diagram of optical system for recording rate of fast reaction. Reproduced from ref 1 with permission from American Institute of Physics. Copyright 1949.

6. "Thermal Decomposition of Nitrogen Pentoxide at High Temperatures." Harold S. Johnston and Yu-Sheng Tao, *J. Am. Chem. Soc.*, **73**, 2948 (1951).

2.1.3. Bimolecular Fast Reactions by Methods Described in (2.1.1). In a "bimolecular" reaction, two molecules react with each other. We brought the reactants together by fast flow, fast mixing, and sudden stopping of the flow, and we followed the rate by its absorption of visible or ultraviolet light.

10. "Rapid Gas Phase Reaction Between Nitric Oxide and Ozone." Harold S. Johnston and Harvey Crosby, *J. Chem. Phys.*, **19**, 799 (1951).

11. "The Kinetics of the Fast Gas-Phase Reaction Between Nitryl Chloride and Nitric Oxide." Edward C. Freiling, Harold S. Johnston, and Richard C. Ogg, Jr., *J. Chem. Phys.*, **20**, 327−329 (1952).

We built a small electrolytic cell for production of fluorine and found that nitrogen dioxide and fluorine react more slowly than nitrogen dioxide and ozone.

17. "Kinetics of the Fast Reaction Between Nitrogen Dioxide and Fluorine." Richard Perrine and Harold S. Johnston, *J. Chem. Phys.*, **21**, 2202−2205 (1953).

57. "Reaction Rates of Xenon Fluorides with Oxides of Nitrogen." Harold S. Johnston and Robert Woolfolk, *J. Chem. Phys.*, **41**, 269−273 (1964).

2.2. Reactions Studied by a Variety of Methods.

96. "Kinetics of the Gas-phase Reaction Between Ozone and Nitrogen Dioxide." R.A. Graham and H. S. Johnston, *J. Chem. Phys.*, **60**, 4628−4629 (1974).

We used lasers that emitted fast pulses of radiation, and we used a "probe laser" to detect the buildup of products. These reactions are about a thousand-fold faster than those we followed by fast mixing in 1949.

106. "Reactions and Quenching of Vibrationally Excited Hydroxyl Radicals." G. Streit and H. S. Johnston, *J. Chem. Phys.*, **64**, 95−103 (1976).

122. "The Kinetics and Product Yield of the Reaction of HO with HNO_3." H. H. Nelson, W. J. Marinelli, and H. S. Johnston, *Chem. Phys. Lett.*, **78**, 495−499 (1981).

124. "Kinetics of the Reaction of Cl with ClNO and $ClNO_2$ and the Photochemistry of $ClNO_2$." H. H. Nelson and H. S. Johnston, *J. Phys. Chem.*, **85**, 3891−3896 (1981).

127. "Reaction Rates of Hydroxyl Radical with Nitric Acid and with Hydrogen Peroxide." W. J. Marinelli and H. S. Johnston, *J. Chem. Phys.*, **77**, 1225−1234 (1982).

[†] Part of the special issue "Harold Johnston Festschrift".

[‡] Grouped by subject matter and with comments.

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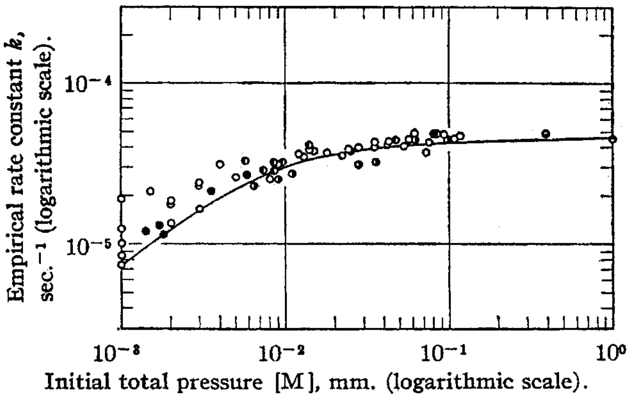


Fig. 6.—Comparison of experimental with computed rate constants; decomposition of pure N_2O_5, 27°, curve given by Equation 21: O, Hodges and Linhorst; ●, Linhorst and Hodges; ◐, Ramsperger and Tolman; ◑, Schumaker and Sprenger; ◓, Daniels and Johnston; ⊖, Mills and Johnston.

Figure 2. Solution to the problem of the 1930s, in which theory and observations appeared to be highly discordant. Reproduced from ref 3.

2.3. Unimolecular Reactions. In a “unimolecular” reaction, one molecule isomerizes or is broken into two or more pieces by collision with a nonreacting molecule. A unimolecular reaction involves three processes: (a) activation by collision, (b) de-activation of the excited molecule by collision, and (c) reaction of the excited molecule to give products. At the low-pressure limit, the rate of reaction is the rate of activation by collision. At the high-pressure limit, the rate of reaction is the rate of product formation by an equilibrium distribution of excited reactant molecules.

2.3.1. Unimolecular Reaction Rates of N_2O_5. Using the 1949 fast reaction method at high pressures and two other systems suitable for intermediate and low pressures, 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. This study was the first to span high- to low-pressure limits at one temperature for a unimolecular reaction. At the low-pressure limit, the rate is that of collisional activation, and it is interpreted to give the rate of energy transfer by collisions between an excited reactant and an inert molecule. (See panel A-2, on the cover).

During the late 1920s and 1930s, Rice and Ramsberger developed a classical mechanical theory of unimolecular reaction rates, and Kassel developed the theory using quantum mechanical vibrational modes. These theories predicted that a unimolecular chemical reaction should be first order at high pressures and second order at low pressures. The decomposition of N_2O_5 was cleanly first order at atmospheric pressure, and the theory gave the pressure range over which the rate should change from first order to second order. Giants of gas-phase chemical kinetics of that period (Schumacher, Tolman, Daniels, and others) carried out careful experiments in large glass bulbs to find the predicted low-pressure region. They found second-order kinetics at extremely low pressures, pressures far lower than the theory indicated (Figure 2). There was great frustration that the widely studied decomposition of N_2O_5 should show a pressure dependence so strongly different from theory. When Richard Tolman was asked why he had shifted his field of research from physical chemistry to astrophysics, he replied, “Because chemistry is hard,” reflecting on the N_2O_5 situation. We showed that what they had measured was not the rate of N_2O_5 decomposition, but rather the net effect of four elementary reactions, one of which was the subject appropriate for the theories. The elementary unimolecular decomposition is

$$N_2O_5 \rightarrow NO_2 + NO_3$$

Upon addition of nitric oxide, the nitrate free radical was removed

$$NO_3 + NO \rightarrow 2NO_2$$

and the observed rate was that of the elementary unimolecular reaction. The rate of N_2O_5 with NO is the rate of the elementary decomposition of N_2O_5, for which the Rice–Ramsberger–Kassel theory was applicable. Our results for the reaction of NO and N_2O_5 agree well with the RRK theory for N_2O_5.

2. “Reinvestigation of the Reaction Involving Nitrogen Pentoxide and Nitric Oxide.” Harold S. Johnston and Robert L. Mills, *J. Chem. Phys.*, **18**, 997 (1950).

3. “Decomposition of Nitrogen Pentoxide in the Presence of Nitric Oxide.” Robert L. Mills and Harold S. Johnston, *J. Am. Chem. Soc.*, **73**, 938–944 (1951).

8. “Decomposition of Nitrogen Pentoxide in the Presence of Nitric Oxide. II. Details at Low Pressure.” Harold S. Johnston and Richard Perrine, *J. Am. Chem. Soc.*, **73**, 4782–4786 (1951).

2.3.2. Energy Transfer Rates from Low-Pressure Studies of Unimolecular Reactions. At low pressures, the rate of an elementary unimolecular reaction is the rate of activation by collision, which proceeds by a second-order rate law:

$$\text{rate} = a_{MA}[A][M]$$

where the reactant is A and the total gas concentration is [M]. The relative efficiency for a molecule to activate the reactant is a_{MA}/a_{AA}. Articles 14 and 18 give the relative efficiencies for five noble gases and for five diatomic or polyatomic gases. Other studies of energy transfer include:

14. “Decomposition of Nitrogen Pentoxide in the Presence of Nitric Oxide. III. Effect of Foreign Gases.” Harold S. Johnston, *J. Am. Chem. Soc.*, **75**, 1567–1570 (1953).

18. “Decomposition of Nitrogen Pentoxide in the Presence of Nitric Oxide. IV. Effect of Noble Gases.” David J. Wilson and Harold S. Johnston, *J. Am. Chem. Soc.*, **75**, 5763 (1953).

19. “Thermal Decomposition of Nitryl Chloride. I. Second-order Unimolecular Rate Study.” Herman F. Cordes and Harold S. Johnston, *J. Am. Chem. Soc.*, **76**, 4264–4269 (1954).

23. “Kinetics of the Thermal Decomposition of Nitric Acid Vapor. III. Low Pressure Results.” Harold Johnston, Louise Foering, and J. White, *J. Am. Chem. Soc.*, **77**, 4208–4212 (1955).

25. “Energy Transfer Processes in the Unimolecular Decomposition of Nitryl Chloride.” Milton Volpe and Harold Johnston, *J. Am. Chem. Soc.*, **78**, 3903–3910 (1956).

26. “Effect of Products on Energy Transfer Rates in Unimolecular Reactions.” Milton Volpe and Harold Johnston, *J. Am. Chem. Soc.*, **78**, 3910–3911 (1956).

2.3.3. Other Studies of Unimolecular Chemical Reactions.

9. “Interpretation of the Data on the Thermal Decomposition of Nitrous Oxide.” Harold S. Johnston, *J. Chem. Phys.*, **19**, 663–667 (1951).

12. “High Concentration Limit of Unimolecular Reaction Kinetics.” Harold S. Johnston, *J. Chem. Phys.*, **20**, 1103–1107 (1952).

118. “The Thermal Dissociation of N_2O_5 in N_2.” Peter Connell and Harold Johnston, *Geophys. Res. Lett.*, **6**, 553–556 (1979).

22. “Statistical Interpretations of Unimolecular Reaction Rates.” Harold S. Johnston and James D. White, *J. Chem. Phys.*, **22**, 1969−1973 (1954).

2.3.4. Thermal Ionization of Noble Gases. The thermal ionization of noble gases has several properties in common with the unimolecular decomposition of molecules. The measured reaction rate constants as a function of temperature give Arrhenius activation energies far less than the energy of ionization, and this feature is rather well understood.

43. “Rate and Mechanism of the Thermal Ionization of Xenon.” Harold S. Johnston and Wade Kornegay, *Trans. Faraday Soc.*, **57**, 1563−1577 (1961).

54. “Kinetics of Thermal Ionization. II. Xenon and Krypton.” Harold Johnston, Christopher Parr, and Wade Kornegay, *J. Chem. Phys.*, **38**, 2242−2247 (1963).

2.3.5. Example of Pure Science Applied to a Practical Problem: Unimolecular Decomposition of Nitric Acid Vapor. A rocket engine, being developed by M. W. Kellogg Co., used fuming nitric acid and hydrazine as fuels, which conveniently ignite upon being mixed together, but the rocket engine designers had trouble with damaging mini-explosions in the engine. By use of our new fast-reaction method, we found the cause of the explosions and gave a prescription that solved the problem, which was to replace nitric acid with nitrogen dioxide in the engine. This worked.

4. “The Kinetics of the Thermal Decomposition of Nitric Acid Vapor.” Harold S. Johnston, Louise Foering, Yu-Sheng Tao, and G. H. Messerly, *J. Am. Chem. Soc.*, **73**, 2319−2321 (1951).

16. “Kinetics of the Thermal Decomposition of Nitric Acid Vapor. II. Mechanism.” Harold S. Johnston, Louise Foering and R. J. Thompson, *J. Phys. Chem.*, **57**, 390−394 (1953).

23. “Kinetics of the Thermal Decomposition of Nitric Acid Vapor. III. Low Pressure Results.” Harold Johnston, Louise Foering, and J. White, *J. Am. Chem. Soc.*, **77**, 4208−4212 (1955).

46. “Kinetics of the Thermal Decomposition of Nitric Acid Vapor. IV. A Shock Tube Study Between 800-1200 K.” Halstead Harrison, Harold S. Johnston, and E. R. Hardwick, *J. Am. Chem. Soc.*, **84**, 2478−2482 (1962).

2.4. Complex and Elementary Chemical Reactions. 2.4.1. Complex Reactions Resolved into Elementary Steps. A chemical reaction may be “elementary,” one that occurs upon single collision between the reactants, or it may be “complex,” a process in which two or more elementary reactions occur to generate the products. The “chemical mechanism” is the set of elementary chemical reactions that work together to give an observable complex reaction. For a time it was my specialty to resolve complex reactions into their component elementary steps.

7. “Four Mechanisms Involving Nitrogen Pentoxide.” Harold S. Johnston, *J. Am. Chem. Soc.*, **73**, 4542−4546 (1951).

15. “The Mechanism of the Reaction Between Ozone and Nitrosyl Chloride.” Harold S. Johnston and Frederick Leighton, Jr., *J. Am. Chem. Soc.*, **75**, 3612 (1953).

137. “Unimolecular Decomposition of NO_3 to Form NO and O_2 and a Review of N_2O_5/NO_3 Kinetics,” H. S. Johnston, C. A. Cantrell, and J. G. Calvert, *J. Geophys. Res.*, **91**, 5159−5172 (1986).

2.4.2. Highly Complex Reactions. We followed the rate of photo-oxidation of organic chemical compounds by simultaneously obtaining the mass spectra of reactants and products, using time-of-flight mass spectrometry. For the case of acetone, we followed the reactant and 10 reaction products, but we inferred there could be up to 140 elementary reactions occurring in this system. For this system, it is impossible to determine elementary reactions from measurement of all reactants and all products.

50. “Photochemical Oxidations. I. Ethyl Iodide.” Julian Heicklen and Harold S. Johnston, *J. Am. Chem. Soc.*, **84**, 4394−4402 (1962).

48. “Photochemical Oxidations. II. Methyl Iodide.” Julian Heicklen and Harold S. Johnston, *J. Am. Chem. Soc.*, **84**, 4030−4039 (1962).

59. “Photochemical Oxidations. III. Acetone.” Harold S. Johnston and J. Heicklen, *J. Am. Chem. Soc.*, **86**, 4249−4254 (1964).

60. “Photochemical Oxidations. IV. Acetaldehyde.” Harold S. Johnston and J. Heicklen, *J. Am. Chem. Soc.*, **86**, 4254−4258 (1964).

51. “The Photo-oxidation of the Simple Alkyl Iodides.” J. Heicklen, J. Newton, and H. S. Johnston, *Bull. Soc. Chim. Belg.*, **71**, 744 (1962).

76. “The Photolysis of Dimethyl Peroxide.” L. M. Toth and H. S. Johnston, *J. Am. Chem. Soc.*, **91**, 1276−1282 (1969).

2.4.3. Chemical Uncertainty Principle. If there are more than two free radical intermediates, the mechanism cannot be deduced by a kinetic study based on analysis of all products and all reactants. This general statement called for direct observation of the free radical intermediates. To obtain an unambiguous mechanism, one must abandon conventional indirect methods and measure directly the concentrations of free radical intermediates.

65. “Highly Complex Photochemical Mechanisms.” H. S. Johnston and F. Cramarossa, pp 1−26, in *Advances in Photochemistry*, Vol. 4, W. A. Noyes, Jr., G. S. Hammond, J. N. Pitts, Jr., Eds., Interscience Publishers, New York, 1966.

2.4.4. What Is an Elementary Reaction? Quoting from the article cited here: “Different levels of the field of chemical kinetics are related to each other by the following outline:

- Practical chemical systems
  - Elementary chemical reactions
    - Elementary chemical-physical reactions
      - Elementary physical reactions
        - Time-dependent quantum mechanics.

“Elementary chemical reactions are the components of practical chemical kinetics. The field of elementary chemical reactions has now (1968) become so mature that it is worthwhile to produce handbooks of data on the rate constants of elementary reactions in terms of appropriate macroscopic variables. In this way tables of elementary rate constants and the theory of elementary chemical reactions can make an important contribution to other areas of chemistry, including chemical problems of the most practical sort. Theories of elementary chemical reactions are forced to make extensive (plausible) assumptions about potential-energy functions, suitable coordinates, reaction cross sections, and molecular distribution functions.

“Direct experiments with molecular beams and new optical techniques (lasers) are capable of giving actual observed data where the theory of elementary chemical reactions has traditionally been forced to make assumptions. The theory of elementary chemical-physical and elementary physical reactions is fundamental, many-particle quantum mechanics. There is considerable room for the development of effective new theoretical techniques to calculate elementary reaction rates. The field of chemical kinetics has a unity and a connectedness across its various levels of abstraction that should be understood and appreciated by all of its practitioners.”

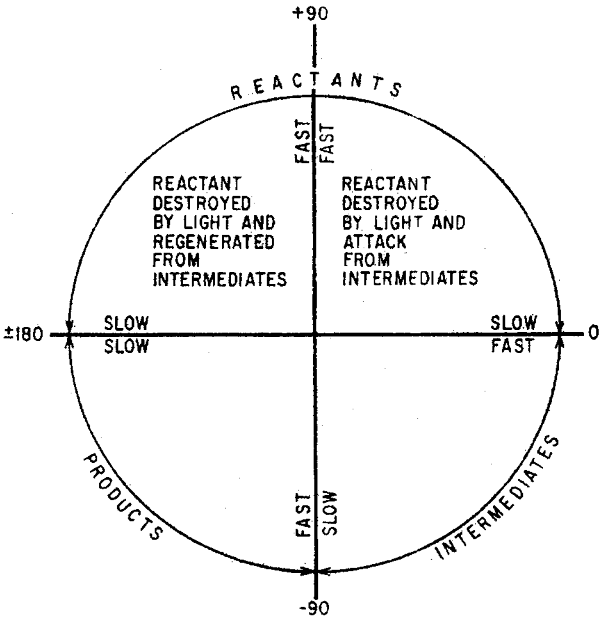


Figure 3. Phase relations between photolysis light, reactants, intermediates, and products in complex photochemical reactions. Courtesy of Harold Johnston.

74. "Gas-phase Elementary Chemical Reactions." Harold S. Johnston, *Ber. Bunsen-Ges. Phys. Chem.*, **72**, 959−966 (1968).

My career spans the first three steps in the ladder given above. The reaction of my Ph.D. thesis ($2NO_2 + O_3 \rightarrow N_2O_5 + O_2$) is a "Practical chemical system", which we resolved into two elementary chemical reactions. I was a part time consultant with the National Bureau of Standards to prepare tables of empirical rate constants and empirical activation energies for a big NBS monograph. I objected to tabulating rates for overall complex reactions and said NBS tables should be prepared only for elementary chemical reactions. Early in our work on unimolecular reactions, I became interested in combining best features of the classical mechanical RR theory with the coarse-grained quantum mechanical Kassel theory. This interest is an example of "Elementary chemical-physical reactions." With the concepts of transition state theory, Marcus and Rice (1952) added quantum mechanical features to the RRK theory to produce the highly successful RRKM theory, which is still used in 2000. In connection with our work on elementary bimolecular reactions (section 2.1) we added additional quantum mechanical features to Eyring's activated complex theory to calculate "pre-exponential factors" (section 3.1) and to calculate kinetic isotope effects (section 3.3).

In my work on urban photochemical "smog" (section 5.2), I sought the "Elementary chemical reactions" to account in part for the overwhelmingly complex "Practical chemical system." In my work on global atmospheric chemistry (part II) I contributed to the big job of finding the "Elementary chemical reactions" in the highly complex "Practical chemical system" in the stratosphere.

2.5. Molecular Modulation Method and Results. We developed a new experimental method to measure trace amounts of free radicals in complex photochemical systems (Figure 3). A dc light was used as probe for free radical intermediates, and an ac light was used to photo-excite or to photolyze a reactant. The detector was sensitive only to ac signal, which was produced by buildup and decay of free radical intermediates. Spectral data were obtained by scanning through a spectral absorption, and rate data were obtained from phase shifts. Subsequent development of molecular beams and lasers provided methods vastly superior to the molecular modulation method.

68. "Molecular-modulation Spectrometry. I. New Method for Observing Infrared Spectra of Free Radicals." Harold S. Johnston, G. B. McGraw, T. Paukert, L. Richards, and J. van den Bogaerde, *Proc. Natl. Acad. Sci. U.S.A.*, **57**, 1146−1153 (1967).

72. "Digital Phase Sensitive Detector." E. D. Morris, Jr., and Harold S. Johnston, *Rev. Sci. Instrum.*, **39**, 620−621 (1968).

75. "Molecular-modulation Spectrometry: CH_3ONO Photolysis and Detection of Nitroxyl." G. E. McGraw and H. S. Johnston, *Int. J. Chem. Kinet.*, **1**, 89−104 (1969).

78. "Molecular Modulation Kinetic Spectrometry. ClOO and ClO Radicals in the Photolysis of Chlorine in Oxygen." Harold S. Johnston, Earl Morris, Jr., and J. van den Bogaerde, *J. Am. Chem. Soc.*, **91**, 7712−7727 (1969).

81. "Spectra and Kinetics of the Hydroperoxyl Free Radical in the Gas Phase." Thomas Paukert and Harold Johnston, *J. Chem. Phys.*, **56**, 2824−2838 (1972).

82. "Molecular Modulation Mass Spectrometry Kinetic Study of the ClO Free Radical." Ching-Hsong Wu and Harold Johnston, *Bull. Soc. Chim. Belg.*, **81**, 135−153 (1972).

130."Rate of the Resonant Energy-Transfer Reaction between $O_2(^1\Delta_g)$ and HOO." James R. Podolske and Harold S. Johnston, *J. Phys. Chem.*, **87**, 628−634 (1983).

131."Measurement of Vibration-rotation Line Strengths of HO Using a Tunable Diode Laser." J. R. Podolske and H. S. Johnston, *J. Chem. Phys.*, **79**, 3633−3638 (1983).

138. "High-Frequency-Modulation Spectroscopy with a Lead-Salt Diode Laser," M. Gehrtz, W. Lenth, A. T. Young, and H. S. Johnston, *Opt. Lett.*, **11**, 132−134 (1986).

3. Gas Phase Reaction Rate Theory

This book includes some interpretations and calculations not published elsewhere. I made heavy use of the old and the new method of expressing molecular partition functions.

67. *Gas Phase Reaction Rate Theory*. Harold S. Johnston, The Ronald Press Company, New York, pp 1−362 (1966).

3.1. Pre-exponential Factors. The temperature dependence of reaction rate coefficients is given by the expression $k = Ae^{-B/kT}$. The term A is named the "pre-exponential factor", and the term B is the "activation energy". Fast bimolecular gas-phase reactions were treated by old and new methods of transition state theory, with mixed results.

28. "Theoretical Pre-exponential Factors for Twelve Bimolecular Reactions." Dudley Herschbach, Harold Johnston, Kenneth Pitzer, and Richard Powell, *J. Chem. Phys.*, **25**, 736−741 (1956).

Selected Excerpts from Article 29. "For a series of bimolecular reactions involving hydrogen atom abstraction, pre-exponential factors in the Arrhenius equation $k = A\ \exp(-E/RT)$ have been calculated by means of activated complex theory. The structure and mechanical properties of the activated complex are unambiguously assigned from a set of empirical rules from the fields of molecular structure and molecular spectroscopy. Bond distances around the transferred hydrogen atom are evaluated by Pauling's rule for fractional bond, stretching force constants are assigned by means of Badger's rule, reduced moments of inertia for internal rotation are evaluated by means of Pitzer's simple approximate method, bending force constants are assigned by analogy with hydrogen-bonded molecules, and the reaction coordinate is explicitly introduced as the (highly perturbed) antisymmetric vibrational mode of the atom transferred. With these assignments of structure and force constants,

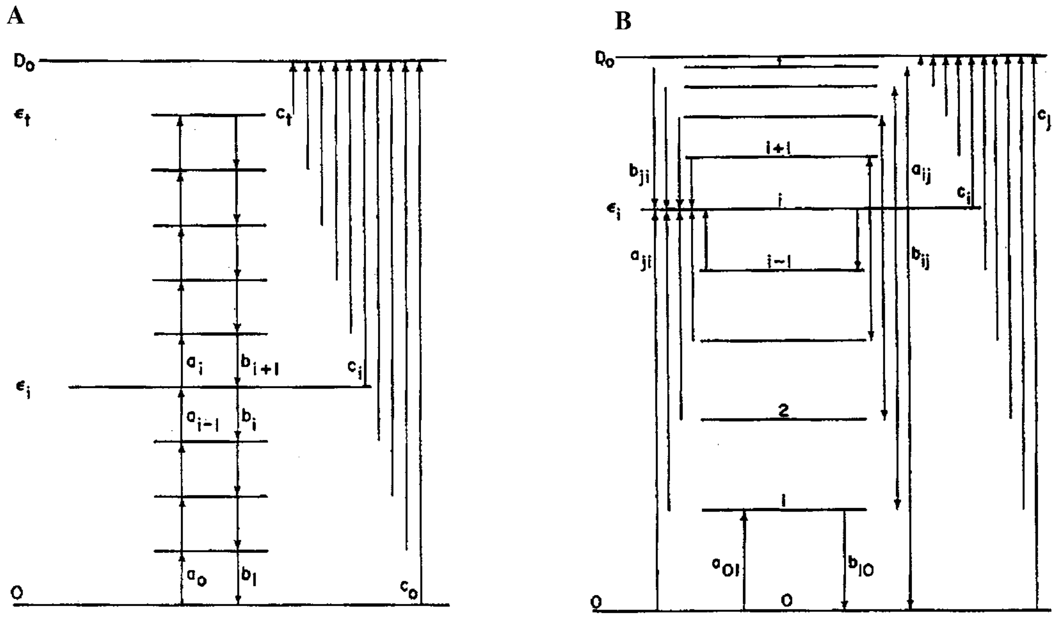


Figure 4. (A) Truncated harmonic oscillator: Only nearest neighbor transitions are considered for energy transfer. All states dissociate to continuum. (B) Morse function. All vibrational transfers allowed. All states dissociate to continuum. Reproduced from ref 86.

a vibrational analysis was carried out by Wilson's FG matrix method; for the larger activated complexes this detailed vibrational analysis was made only for degrees of freedom close to the transferred hydrogen atom. For eight cases out of nine the agreement between calculated and observed pre-exponential factors is quite satisfactory."

29. "Theoretical Pre-exponential Factors for Hydrogen Atom Abstraction Reactions." David Wilson and Harold Johnston, *J. Am. Chem. Soc.*, **79**, 29−32 (1957).

34. "Rate Constants and Molecular Structure." Harold S. Johnston and Kenneth Pitzer, *AIChE J.*, **5**, 277−284 (1959).

47. "Theoretical Interpretation of Reactions Occurring in Photochlorination." Harold S. Johnston and Paul Goldfinger, *J. Chem. Phys.*, **37**, 700−709 (1962).

3.2. Activation Energies. Theory of activation energies requires large scale quantum mechanical calculations. We made an effort to find a simple method for a limited class of reactions. This method had limited and mixed results:

55. "Activation Energies from Bond Energies. I. Hydrogen Transfer Reactions." Harold S. Johnston and Christopher Parr, *J. Am. Chem. Soc.*, **85**, 2544−2551 (1963).

56. "Continuity of Bond Force Constants Between Normal Molecules and Lennard-Jones Pairs." Harold S. Johnston, *J. Am. Chem. Soc.*, **86**, 1643−1645 (1964).

61. "Correlation of Activation Energies and Bond Energies of CF_3 Reactions." H. Carmichael and Harold S. Johnston, *J. Chem. Phys.*, **41**, 1975−1982 (1964).

Extensive experimental data for the rate of dissociation H_2, N_2, O_2, F_2, Cl_2 Br_2, and I_2 in Ar have been obtained in high-temperature shock tubes. An interesting feature of the data is that in each case the activation energy is substantially less than the bond dissociation energy. A model in many chemists' minds is that the "activation energy" represents a "barrier" between reactants and products, and thus there is a serious conceptual problem in having the observed activation energy be far less than the endothermicity of the reaction. However, this viewpoint puts the pictorial model (barrier height) ahead of the defining relation: $E = -R[\mathrm{d}\ln k/d(1/T)]$. The "activation energy" is just a name for how the rate constant k changes with temperature. We used two models for the system (Figure 4). The observed activation energy for the dissociation of diatomic molecules is substantially less than the bond dissociation energy, and the activation energy decreases with increasing temperature.

This effect is readily explained by models that allow dissociation to occur from any and all vibrational states and with allowance for nonequilibrium distribution over vibrational states. Two such models were set up that permitted the calculation of dissociation rate constants from separately determined vibrational relaxation times, vibrational frequency, and hard-sphere collision cross section—with no adjustable parameters. The nonequilibrium versions of these models give satisfactory predictions of rate constants and a good account of the observed low activation energies. These calculations suggest that diatomic molecules dissociate from all vibrational states, but with strongly different state-to-continuum rates.

86. "Activation Energies for the Dissociation of Diatomic Molecules Are Less Than the Bond Dissociation Energies." Harold Johnston and John Birks, *Acc. Chem. Res.*, **5**, 327−335 (1972).

3.3. Statistical Mechanics: A New and Completely Different Method for Expressing Molecular Partition Functions Was Derived. The usual treatment of rates and equilibria according to the transition state theory is found in terms of the $3N$ normal coordinates: three translations, two or three rotational coordinates, and $3N - 6$ (or $3N - 5$) vibrations and internal rotations. In the limit of classical mechanics, equilibrium constants, and reaction rate constants have zero dependence on mass of atoms in reactants or products or transition states. Kinetic isotope effects and the mass dependence of equilibrium constants are 100% due to quantum mechanics. Instead of using normal coordinates of reactants and products, the (then) new method depends on local coordinates and the departure of normal coordinate motions from the classical mechanical state. This method has an advantage of giving a factor of unity to low-frequency vibrations and has a strong dependence on high vibrational frequencies; the usual partition functions have a strong dependence on low-frequency vibrations, which are hard to observe, and a factor of unity for high frequencies.

37. "Molecular Partition Functions in Terms of Local

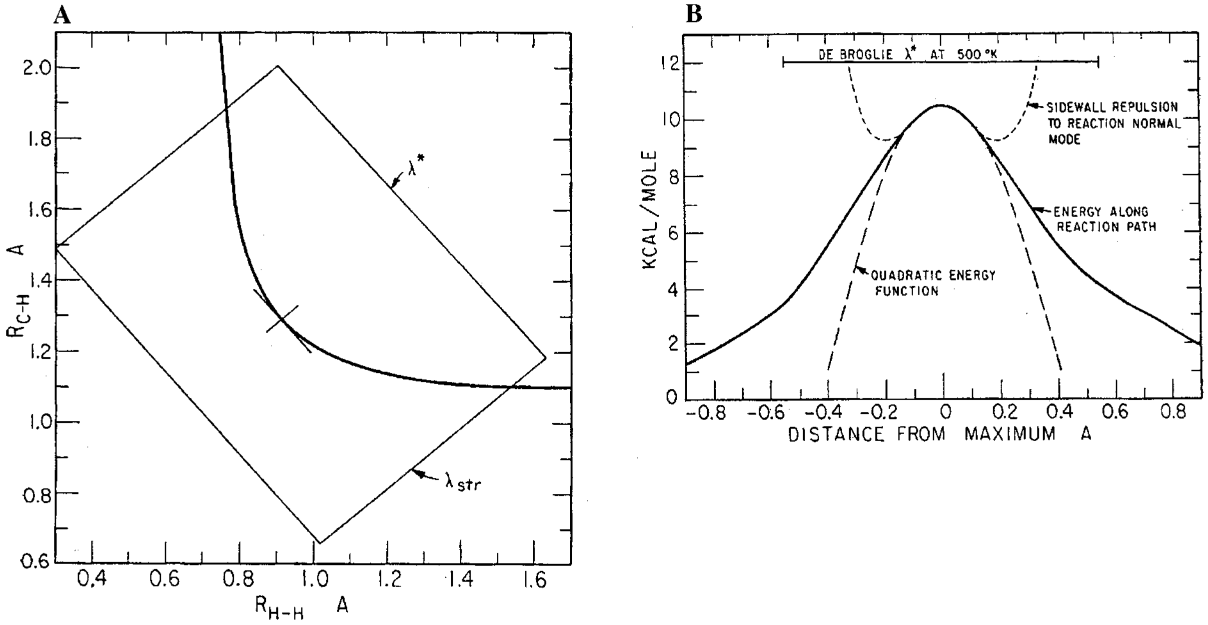


Figure 5. (A) Different way to look at quantum effects in hydrogen atom transfer reactions, which implies large degrees of two-dimensional quantum mechanical "tunneling". Reaction path for the reaction $H_3C + H_2 \rightarrow CH_4 + H$. The point of maximum energy is indicated by the point where the lines cross, the length of these lines gives the region where the normal modes are separable, and the de Broglie wavelengths λ for motion along and normal to the reaction coordinate are indicated. (B) One-dimensional potential energy profile of reaction path for $H_3C + H_2$. The region described by the quadratic potential energy is indicated by the inner dotted line curve. The upturned dotted-line curve is an intuitive estimate of the side-wall repulsion encountered by the extension of the tangent to the reaction path as shown in Figure 5A. Reproduced from ref 41 with permission from John Wiley & Sons, Inc. Copyright 1960.

Properties." Dudley Herschbach, Harold Johnston, and Donald Rapp, *J. Chem. Phys.*, **31**, 1652−1661 (1959).

3.4. Quantum Mechanical Calculations. We used computer programs developed by Professors H. F. Schaefer III and W. A. Lester, Jr. to calculate potential energy surfaces for Ne−H−H and the nitrate free radical.

99. "Ne−H−H Potential Energy Surface Including Electron Correlation." John Birks, Harold Johnston, and Henry Schaefer III, *J. Chem. Phys.*, **63**, 1741−1747 (1975).

140. "The Vertical Electronic Spectrum of NO_3: $^2A_2'$, $^2E''$-($^2A_2$, $^2B_1$), and $^2E'$ States." B. Kim, H. S. Johnston, D. A. Clabo, Jr., and H. F. Schaefer III, *J. Chem. Phys.*, **88**, 3204−3210 (1988).

146. "Ab Initio Study of the Vibrational Spectra of NO_3." B. Kim, B. L. Hammond, W. A. Lester, Jr., and H. S. Johnston, *Chem. Phys. Lett.*, **168**, 131−134 (1990).

3.5. Kinetic Isotope Effects Measured in the Laboratory and Interpreted Using Quantum-Mechanical Tunneling Theory. Atomic hydrogen has two nonradioactive forms, hydrogen, H, mass of 1.0, and deuterium, D, mass of 2.0. The rate of reaction of atomic chlorine with hydrogen is slightly different for the reactions:

$$\text{(i) } HD + Cl \rightarrow H{-}D{-}Cl \rightarrow H + DCl$$

$$\text{(ii) } HD + Cl \rightarrow D{-}H{-}Cl \rightarrow D + HCl$$

depending whether DCl or HCl is the reaction product. This problem involves a relatively well understood and easily calculated classical mechanical effect, and there is a quantum mechanical feature labeled the "tunnel effect."

3.5.1. Bimolecular Gas-Phase Reactions Involving Hydrogen-Atom Transfer Treated by Transition State Theory, with Emphasis on Calculations of All Normal Coordinates. DeBroglie wavelengths extended along the normal coordinates at the saddlepoint of the transition state are much longer than the classical mechanical separable lengths, indicated by the crossed lines. A box with sides equal to the two DeBroglie wavelengths is superimposed on a standard potential energy surface. In two dimensions, the "particle" is equally likely to be in any part of the rectangle in Figure 5A. Figure 5B shows the same features in one dimension of motion.

41. "Large Tunneling Corrections in Chemical Reaction Rates." Harold S. Johnston. From *Advances in Chemical Physics*, Vol. III, I. Prigogine, Ed., Interscience Publishers, Inc., New York, pp 131−170 (1960).

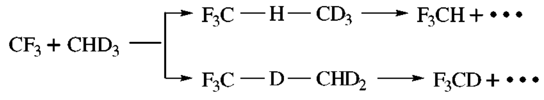
3.5.2. Tunneling Effects. Other Articles Concerning Kinetic Isotopic Effect.

42. "Large Tunneling Corrections in Chemical Reaction Rates. II." Harold S. Johnston and Donald Rapp, *J. Am. Chem. Soc.*, **83**, 1−9 (1961).

44. "Hydrogen-deuterium Kinetic Isotope Effect at Very High Temperature." Harold S. Johnston and Eugene Tschuikow-Roux, *J. Chem. Phys.*, **36**, 463−468 (1962).

45. "Tunneling Corrections for Unsymmetrical Eckart Potential Energy Barriers." Harold S. Johnston and Julian Heicklen, *J. Phys. Chem.*, **66**, 532−533 (1962).

3.5.3. Kinetic Isotope Effects over a Wide Range of Temperature. "An experimental study of the kinetic isotope effect for the reaction



$$CF_3 + CHD_3 \rightarrow \begin{cases} F_3C{-}H{-}CD_3 \longrightarrow F_3CH + \cdots \\ F_3C{-}D{-}CHD_2 \longrightarrow F_3CD + \cdots \end{cases}$$

has been carried out between 300 and 700 K, and also the Arrhenius parameters $k = A\exp(-E/RT)$ were obtained for the individual reactions. A special effort was made to avoid systematic errors; and the precision obtained was good. We made a detailed test of activated complex theory utilizing the method of London−Polanyi−Eyring−Sato with corrections for quantum mechanical tunneling (Figure 6). Because reactants were identical for both reactions, all the kinetic isotope effect

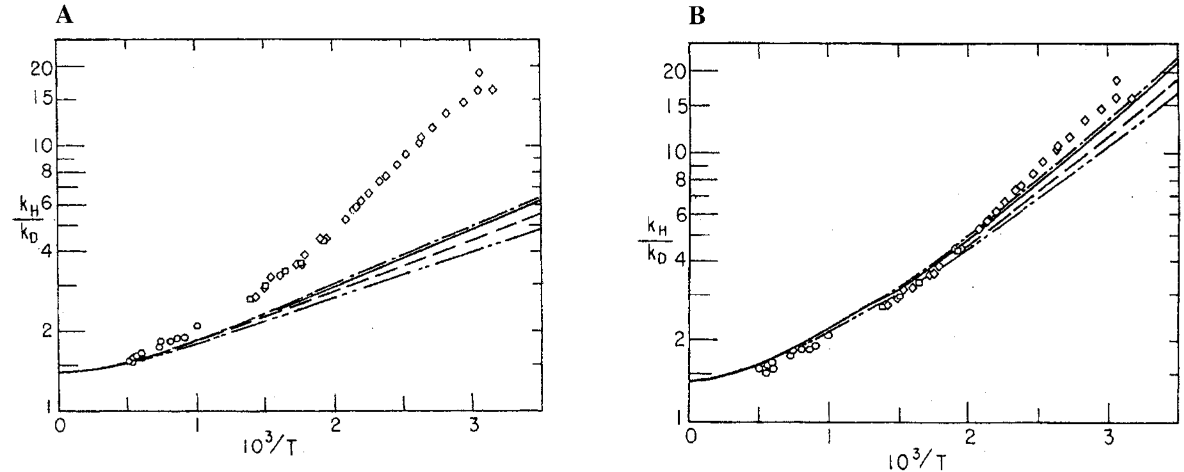


FIG. 4. Observed kinetic isotope effect (○ Roux and Johnston; □ McNesby; ◇ this study) over a wide range of temperature. Theoretical kinetic isotope effect excluding tunneling for various models of the activated complex: three-mass-point including reactants — — —; four-mass-point —•—•—•; five-mass-point —••—••—••; and full nine-atom model ———.

FIG. 6. Observed and theoretical isotope effect including Johnston and Rapp's correction for tunneling (symbols as in Fig. 4).

Figure 6. (A, B) Kinetic isotope effect over a wide range of temperature, calculated with and without tunneling effects. (Compare panel A-3, on the cover.) Reproduced from ref 49 with permission from the American Institute of Physics. Copyright 1962.

depends on differences in the two activated complexes. The vibrational frequencies of the two nine-atom models of the complex were evaluated by a computer programmed to E. B. Wilson's FG-matrix methods, and the effect of replacing the full nine-atom model by simpler five-, four-, or three-atom models was tested. The five or nine-atom models with tunneling corrections were in fairly good agreement with experiment from 300 to 1800 K.

49. "Hydrogen-deuterium Kinetic Isotope Effect, an Experimental and Theoretical Study over a Wide Range of Temperature." Terry E. Sharp and Harold S. Johnston, *J. Chem. Phys.*, **37**, 1541−1553 (1962).

3.5.4. Other Studies of Kinetic Isotope Effects.

31. "Carbon Isotope Effect During Oxidation of Carbon Monoxide with Nitrogen Dioxide." Harold S. Johnston, William Bonner and D. Wilson, *J. Chem. Phys.*, **26**, 1002−1006 (1957).

52. "Kinetic Isotope Effect in Photochlorination of H_2, CH_4, $CHCl_3$, and C_2H_6." G. Chiltz, R. Eckling, P. Goldfinger, G. Huybrechts, Harold S. Johnston, L. Meyers and G. Verbeke, *J. Chem. Phys.*, **38**, 1053−1061 (1963).

58. "Hydrogen-deuterium Kinetic-isotope Effect: The Problem of Potential-energy Surface." J. D. Davy, C. R. Guerra, H. S. Johnston, C. E. Weaver, and C. E. Young, *J. Chem. Phys.*, **41**, 1517 (1964).

4. Photochemistry

4.1. Spectroscopy.

35. "Absorption and Emission Spectra of Nitrosyl Fluoride." Harold S. Johnston and Henry J. Bertin, Jr., *J. Mol. Spectrosc.*, **3**, 683−696 (1959); "Heat of Formation of Nitrosyl Fluoride." Harold S. Johnston and Henry J. Bertin, Jr., *J. Am. Chem. Soc.*, **81**, 6402−6404 (1959).

71. "Ultraviolet Spectrum of the ClOO Radical." E. Morris, Jr. and Harold Johnston, *J. Am. Chem. Soc.*, **90**, 1918−1920 (1968).

87. "Gas-phase Ultraviolet Absorption Spectrum of Nitric Acid Vapor." Harold Johnston and Richard Graham, *J. Phys. Chem.*, **77**, 62−63 (1973).

103. "New Cross Sections for the Absorption of Near Ultraviolet Radiation by Nitrous Oxide (N_2O)." H. S. Johnston G. S. Selwyn, *Geophys. Res. Lett.*, **2**, 549−551 (1975).

113. "Nitrous Oxide Ultraviolet Absorption Spectrum at Stratospheric Temperatures." Gary Selwyn, James Podolske, and Harold Johnston, *Geophys. Res. Lett.*, **4**, 427−430 (1977).

123. "Ultraviolet Absorption Spectrum of Nitrous Oxide as Function of Temperature and Isotopic Substitution." G. S. Selwyn and H. S. Johnston, *J. Chem. Phys.*, **74**, 3791−3803 (1981).

128. "Temperature-dependent Ultraviolet Absorption Spectrum for Dinitrogen Pentoxide." Francis Yao, Ivan Wilson, and Harold Johnston, *J. Phys. Chem.*, **86**, 3611−3615 (1982).

125. "Absorption Cross Sections and Line Shape for the NO_3 (0−0) Band." W. J. Marinelli, D. M. Swanson, and H. S. Johnston, *J. Chem. Phys.*, **76**, 2864−2870 (1982).

129. "Quantum Yield for NO_2 Production from Photolysis of $ClONO_2$." W. J. Marinelli and H. S. Johnston, *Chem. Phys. Lett.*, **93**, 127−132 (1982).

134. "Oxygen Absorption Cross Sections in the Herzberg Continuum and Between 206 and 327 K." Harold S. Johnston, Mark Paige and Francis Yao, *J. Geophys. Res.*, **89**, 11661−11665 (1984).

150. "Photoabsorption Cross Sections of $(FSO_3)_2$ and FSO_3." J. D. Burley and H. S. Johnston, *J. Photochem. Photobiol. A: Chem.* **66**, 141−151 (1992).

154. "Spectroscopy and Photoabsorption Cross Sections of FNO." J. D. Burley, C. E. Miller, and H. S. Johnston, *J. Mol. Spectrosc.* **158**, 377−391 (1993).

4.2. Chemiluminescence. Upon contact of reactants, some reactions give off visible light.

40. "Nitric Oxide-fluorine Dilute Diffusion Flame." Donald Rapp and Harold S. Johnston, *J. Chem. Phys.*, **33**, 695−699 (1960).

98. "Chemiluminescence of IF in the Gas Phase Reaction of I_2 and F_2." John W. Birks, Steven Gabelnick, and Harold S. Johnston, *J. Mol. Spectrosc.*, **57**, 23−46 (1975).

4.3. Fluorescence. After absorption of light, some molecules emit light at longer wavelengths. Rates of reaction are studied by rapidly following the emitted light.

77. "Kinetics of Nitrogen Dioxide Fluorescence." Steven E. Schwartz and Harold Johnston, *J. Chem. Phys.*, **51**, 1286−1302 (1969).

147. “Radiative Lifetimes of Nitrogen Dioxide for Excitation Wavelengths from 400 to 750 nm.” K. O. Patten, Jr., J. D. Burley, and H. S. Johnston, *J. Phys. Chem.*, **94**, 7960−7969 (190).

4.4. Photolysis is the breaking apart of a molecule upon its absorption of visible or ultraviolet light. We used lasers that emitted pulses of radiation at microsecond rates, and we used a “probe laser” to detect the buildup of products. These reactions are about a thousand-fold faster than those we followed by “fast” mixing after 1949.

88. “Photolysis of Nitrogen Dioxide to Produce Transient O, NO_3, and N_2O_5.” Alan B. Harker and Harold Johnston, *J. Phys. Chem.*, **77**, 1153−1156 (1973).

91. “Photolysis of Nitric Acid Vapor.” Harold S. Johnston, Shih-Ger Chang, and Gary Whitten, *J. Phys. Chem.*, **78**, 1−7 (1974).

93. “Photochemistry of NO_x and HNO_x Compounds.” Harold S. Johnston and Richard Graham, *Can. J. Chem.*, **52**, 1415−1423 (1974).

114. “The Photochemistry of NO_3 and the Kinetics of the N_2O_5-O_3 System.” Richard A. Graham and Harold S. Johnston, *J. Phys. Chem.*, **82**, 254−268 (1978).

121. “Photodissociation Quantum Yields for the NO_3 Free Radical.” Frank Magnotta and Harold Johnston, *Geophys. Res. Lett.*, **7**, 769−772 (1980).

124. “Kinetics of the Reaction of Cl with ClNO and $ClNO_2$ and the Photochemistry of $ClNO_2$.” H. H. Nelson and H. S. Johnston, *J. Phys. Chem.*, **85**, 3891−3896 (1981).

132. “NO_3 Quantum Yields from N_2O_5 Photolysis.” Diane Swanson, Brian Kan, and Harold S. Johnston, *J. Phys. Chem.*, **88**, 3115−3118 (1984).

155. “Dissociation Energy and Photochemistry of NO_3.” H. F. Davis, B. Kim, H. S. Johnston, and Y. T. Lee, *J. Phys. Chem.* **97**, 2172 (1993).

162. “NO_3 photolysis product channels: Quantum yields from observed thresholds.” H. S. Johnston, H. Floyd Davis, and Yuan T. Lee, *J. Phys. Chem.*, **100**, 4713−4723 (1996), see panel A-4, on the cover.

4.5. Photolysis-Induced Fluorescence. When high-energy light hits a molecule, it may break the molecule into two pieces, one of which emits light. These articles report new experimental data and seek to interpret such data in terms of the energy distribution of light-emitting nitrogen dioxide.

139. “Nitrogen Dioxide Fluorescence from N_2O_5 Photolysis.” D. Oh, W. Sisk, A. Young, and H. Johnston, *J. Chem. Phys.*, **85**, 7146−58 (1986).

149. “NO_3 Radical Studied by Laser-Induced Fluorescence.” B. Kim, P. L. Hunter, and H. S. Johnston, *J. Chem. Phys.* **96**, 4057−4067 (1992).

156. “Internal Energy Distributions from Nitrogen Dioxide Fluorescence. 1. Cumulative Sum Method.” H. S. Johnston, C. E. Miller, B. Y. Oh, K. O. Patten, Jr., and W. N. Sisk, *J. Phys. Chem.* **97**, 9890−9903 (1993).

157. “Internal Energy Distributions from Nitrogen Dioxide Fluorescence. 2. Collisional Energy Transfer from Excited Nitrogen Dioxide.” K. O. Patten, Jr., and H. S. Johnston, *J. Phys. Chem.* **97**, 9904−9915 (1993).

158. “Internal Energy Distributions from Nitrogen Dioxide Fluorescence. 3. Photolysis of Jet-Cooled N_2O_4.” W. N. Sisk, C. E. Miller, and H. S. Johnston, *J. Phys. Chem.* **97**, 9916−9923 (1993).

159. “Internal Energy Distributions from Nitrogen Dioxide Fluorescence. 4. Variable Wavelength Photodissociation of $ClNO_2$ and $HONO_2$.” C. E. Miller and H. S. Johnston, *J. Phys. Chem.* **97**, 9924−9933 (1993).

5. Chemical Kinetics as a Global Atmospheric Science

In 1992, I reviewed the history and science of several aspects of my atmospheric work from 1942 to 1992. I obtained the information for the review from my two filing cabinets, which include detailed notes I took at meetings, abstracts and proceedings of meetings, preprints and reprints of journal articles, technical monographs, correspondence, notes of telephone calls, newspapers, magazines, and a 600 page summary that I wrote in 1976.

This review article shows the three stages of my experience with meteorology and atmospheric sciences. (i) From 1942 through 1945, I did laboratory research at Caltech and field research with the Dugway Proving Ground Mobile Field Unit of the U.S. Chemical Warfare Service, which involved micrometeorology and some meteorology (pp 6−7). (ii) From 1950 to 1970, I did some work on the chemical mechanisms, regional air transport, and laboratory work concerning photochemical smog, with an emphasis on the formation of ozone (pp 10−13). (iii) From 1971 to the present, I have been primarily concerned with the global ozone balance (pp 2−5) and ozone changes by aircraft (pp 13−24, 29−32) and by chlorine (pp 5, 25−29) in the stratosphere.

153. “Atmospheric Ozone,” H. S. Johnston, *Annu. Rev. Phys. Chem.* **43**, 1−32 (1992).

5.1. Micrometeorology, World War II Chemical Warfare Project in Florida (1943−1945). Pages 6−8 in Reference 153. Professor Roscoe Dickinson at Caltech moved his National Defense Research Council (NDRC) research group to Bushnell, FL. With technical assistance from our group and several other NDRC groups, the Dugway Proving Ground Mobile Field Unit of the U.S. Chemical Warfare Service detonated on the ground or dropped from aircraft poison gas bombs in the semi-tropical jungle of central Florida, during November and December of 1943. The NDRC groups, including most of our group, moved on to Panama for sites more nearly like jungles on the southwest Pacific islands. I remained in Florida as “head of the meteorology department” of the Dugway Proving Ground Mobile Field Unit. Through 1944 and the summer of 1945 we continued to explode real bombs, on the ground and from aircraft, and simultaneously my group made appropriate micrometeorological measurements. Using recording instruments and integrating samplers placed around a target site, other NDRC groups and army technicians measured the amount of war gas that each station had been exposed to. The army prepared extensive tables of how the area covered by lethal amounts of gas depends on terrain and meteorological variables.

Our project could not afford a meteorological tower up through the canopy of the forest. I persuaded Captain Nolen, head of the project, to let us strip a pine tree that grew about five meters above the average canopy and to equip it with micrometeorological instruments (Figure 7A).

We developed and used an electrically recording gustiness meter, which produced data that gave the absolute value of average vertical air velocity (Figure 8). We used this instrument over a California flat vegetation-free dry-lake bed, California desert brush, rough Florida meadow, and Florida forest. The reports of this work were classified as “Confidential,” they were declassified a few yeas ago, and I obtained a copy through the freedom of information act. In view of the difficulty of obtaining these reports, I give here a portion of one of them.

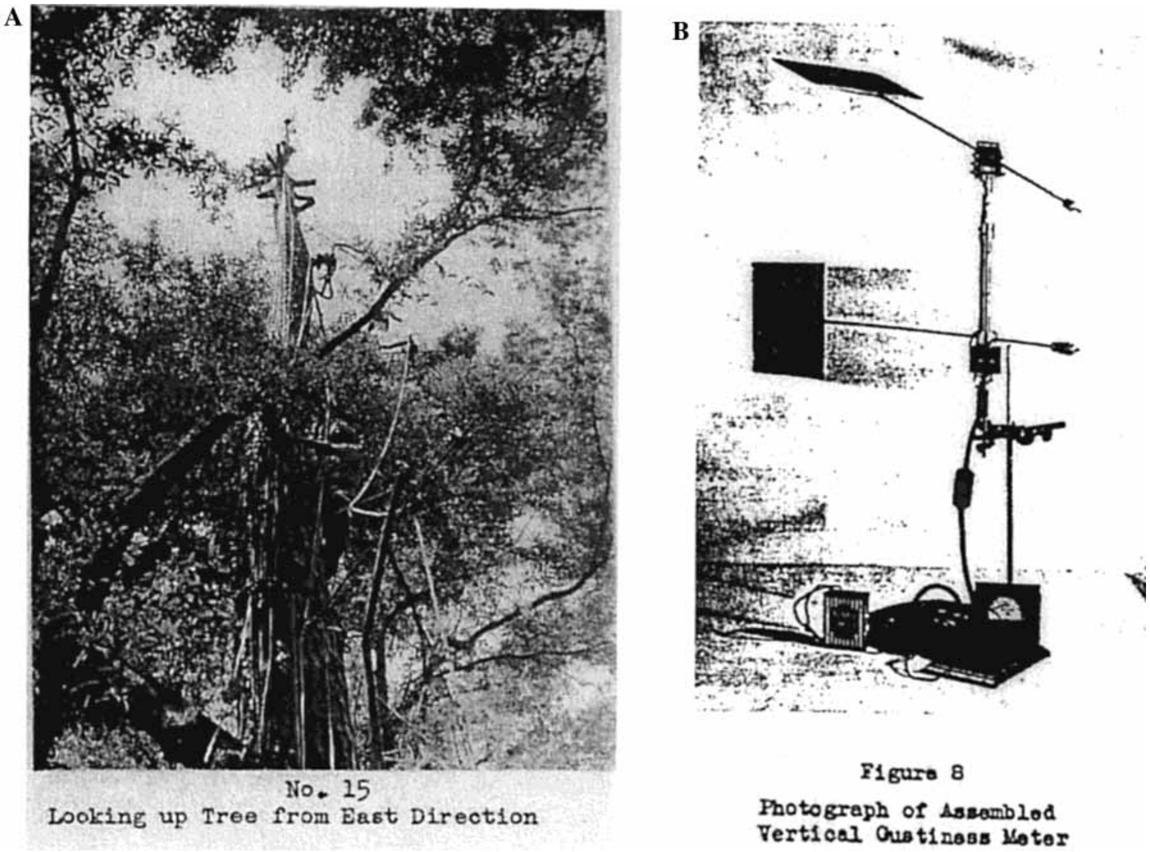


Figure 7. (A) Our instrumented meteorological "tower." We measured temperature, wind direction, and wind-speed profiles up through a semi-tropical forest. Bushnell, FL, 1944−45. (B) Our recording meter of vertical air gustiness. U.S. Army photographs.

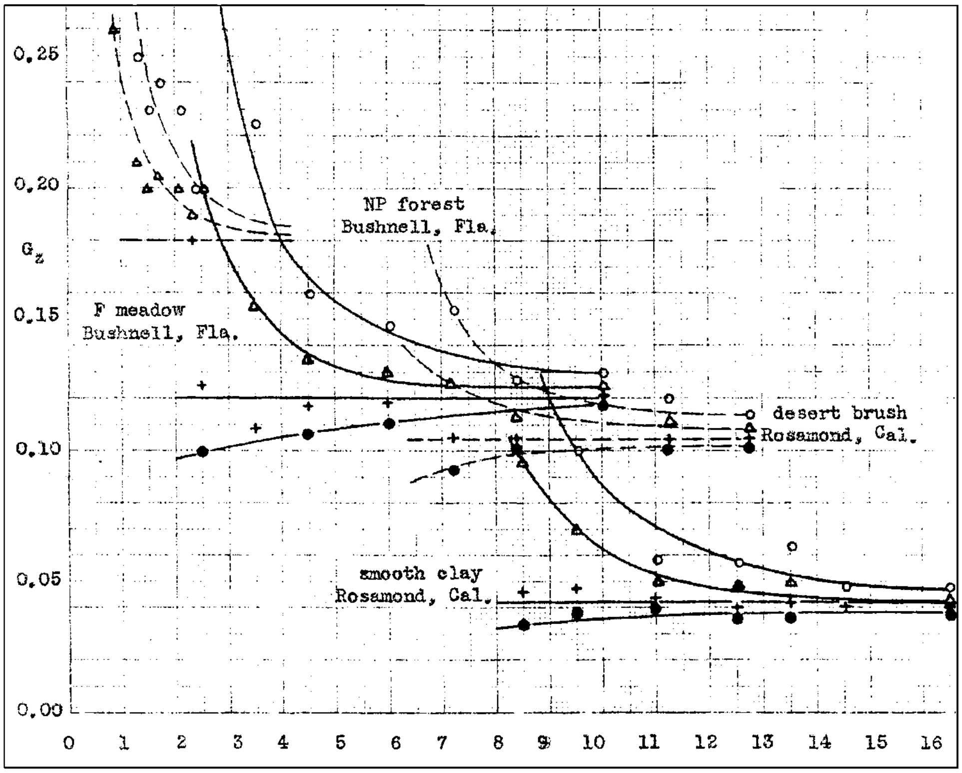


Figure 8. Vertical gustiness (which gives vertical component of turbulent velocity) plotted against wind speed (miles per hour) at 2.0 m above the ground. For each terrain, the temperature K at 2.0 m minus the temperature at 0.3 m was: Filled circle, +0.5; symbol +, 0.0; triangles, −1.0; open circles, −2.0.

Report #1. "Micrometeorology of the woods and open areas within the Withlacoochee land use project," D.P.G.S.R. No. 35, Project E 7a-2. 30 pages plus 20 pages of figures. Harold Johnston assisted by Arthur Pardee, Second Lieutenant Alan Englander, Second Lieutenant William Ironside, 1944.

Report #2. "A study of turbulent diffusion of gas clouds over several terrains," Report OSRD No. 6185, 84 pages, by Harold Johnston, Robert Merrill, and Robert Mills. 1945. (part I) An Empirical Approach to the Effect of Turbulent Diffusion on Gas Clouds over Several Terrains, pp 1-23; (part II) A Critical Examination of the British Statistical Diffusion Theories, pp 24−46.

5.2. Urban Photochemical "Smog." Pages 10−13 in Reference 153. In the early 1950's, A. J. Haagen-Smit, professor of biochemistry at Caltech presented a simple, elegant theory of photochemical smog. In the 1920's, Max Bodenstein characterized the reaction of nitric oxide with oxygen and obtained definitive values of the rate parameters. Bodenstein's reaction initiates a photochemical cycle that converts molecular oxygen to ozone as catalyzed by NO and NO_2, abbreviated NO_x.

$$\begin{array}{ll} & 2NO + O_2 = 2NO_2 \\ & NO_2 + \text{sun} = NO + O\text{, twice} \\ & O + O_2 + M = O_3 + M\text{, twice} \\ \hline \text{net:} & 3O_2 + \text{sun} = 2O_3\text{, catalyzed by } NO_x \end{array}$$

Ozone itself is a toxic lung irritant, it damages materials, especially rubber, and it spoils a number of vegetable crops. Ozone reacts with hydrocarbons and other volatile organic compounds, which come from automobile exhaust, oil refineries, and other industries, to make particles that reduce visibility, cause eye irritation, and other unpleasant effects

$$O_3 + \text{volatile organic compounds} \rightarrow \text{smog}$$

I wrote a letter to Haagen-Smit, pointing out that under atmospheric conditions in Los Angeles, the fraction of nitric oxide was one part per million or less. At these low concentrations, it requires 55 hours or more for half of the nitric oxide to be converted to nitrogen dioxide by Bodenstein's reaction, which is much too slow to account for the rapid rise of ozone concentration in the morning hours. Also, Harvey Crosby in my laboratory had just (1950) measured the fast reaction of nitric oxide with ozone. It would be more than 1000 times faster than Bodenstein's reaction, under smog conditions. Haagen-Smit acknowledged my letter, dropped the Bodenstein reaction as a source of ozone, and it took about ten years for others to discover the cause of ozone production in smog.

During the period of 1950−52, I suggested a free-radical mechanism for Haagen-Smit's model of urban "smog". Thermal combustion produces organic peroxyl radicals and thus probably photochemical combustion would do likewise. I proposed that ozone is formed by the reaction of peroxyl radicals with oxygen: $ROO + O_2 \rightarrow RO + O_3$. Many years later others found that this reaction occurs, not as an elementary reaction but as a three-step sequence:

$$\begin{array}{ll} & ROO + NO \rightarrow RO + NO_2 \\ & NO_2 + \text{sun} \rightarrow NO + O \\ & O + O_2 + M \rightarrow O_3 + M \\ \hline \text{net:} & ROO + O_2 \rightarrow RO + O_3 \end{array}$$

where R could be H or one of many organic radicals in smog. The smog reactions are catalytic cycles in nitrogen oxides and consumptive of hydrocarbons. From time to time, I did some work on smog reactions.

13. "Chemical Reactions in Los Angeles Smog." Richard Cadle and Harold S. Johnston, Proceedings of the Second National Air Pollution Symposium, 1952.

27. "Photochemical Oxidation of Hydrocarbons." Harold Johnston, *Ind. Eng. Chem.*, **48**, 1488−1491 (1956).

39. "Sulfur Dioxide Sensitized Photochemical Oxidation of Hydrocarbons." Harold S. Johnston and Kapil dev Jain, *Science*, **131**, 1523−1554 (1960).

85. "The Oxides of Nitrogen and Photochemical Smog in Atmospheric Chemistry and Air Pollution." Harold Johnston, Air Resources Center, Oregon State University, Corvallis, OR, 1972.

105. "The Oxides of Nitrogen with Respect to Urban Smog, Supersonic Transports, and Global Methane." Harold S. Johnston and Edward Quitevis, *Proceedings Fifth International Congress of Radiation Research*, Seattle, WA, July 14−20, 1974, O. F. Nygaard, H. I. Adler, W. K. Sinclair, and M. J. Loop, Eds., Academic Press Inc., New York, 1975. pp 1299−1313.

5.3. Global Atmospheric Gas-Phase Chemistry. 5.3.1. Method of Instantaneous Rates and the Global Ozone Balance. We distinguish among ozone differential rate equations in a model, model results, and interpretations of model results. A way to clarify these differences is to use an analogy. A horse race photographed by a moving picture camera is an analogy for an atmospheric model calculation. At any time, from start to finish, a single frame of the film may be examined in detail. Focusing on one frame at a time is analogous to the "method of instantaneous rates."

90. "Instantaneous Photochemical Rates in the Global Stratosphere." Harold Johnston and Gary Whitten, *Pure Appl. Geophys.*, **106-108**, 1468−1489 (1973).

100. "Chemical Reactions in the Atmosphere as Studied by the Method of Instantaneous Rates." Harold S. Johnston and Gary Whitten, *Int. J. Chem. Kinet.*, 1−36 (1975).

104. "Global Ozone Balance in the Natural Stratosphere." Harold Johnston, *Rev. Geophys. Space Phys.*, **13**, 637−649 (1975).

119. "Instantaneous Global Nitrous Oxide Photochemical Rates." Harold Johnston, O. Serang, and J. Podolske, *J. Geophys. Res.*, **84**, 5077−5082 (1979).

120. "Instantaneous Global Ozone Balance Including Observed Nitrogen Dioxide." Susan Solomon, Harold Johnston, M. Kowalczyk, and Ivan Wilson, *Pageoph*, **118**, 58−84 (1980).

163. "Global Thermodynamic Atmospheric Modeling: Search for New Heterogeneous Reactions," H. W. Fairbrother, D. J. D. Sullivan, and H. S. Johnston, *J. Phys. Chem. A* **101**, 7350−7358 (1997).

5.3.2. Catalytic Cycles, Definitions of Odd Oxygen, and Steady States. Article 116 organizes the great complexity of stratospheric chemistry, according to four families of species and eight homogeneous catalytic cycles. Each catalytic cycle implies a steady-state relation, and when all such relations are used, the ozone differential equation is changed from a set of small differences between large quantities into a set of small positive or negative terms. Including a species in the definition of "odd oxygen" has the same mathematical effect as making the steady state assumption for that specie. This article makes extensive use of the properties of odd and even counting numbers: odd or even number of electrons in molecules, odd or even number of oxygen atoms in a molecule.

116. "Interpretations of Stratospheric Photochemistry." Harold Johnston and J. Podolske, *Rev. Geophys. Space Phys.*, **16**, 491−519 (1978).

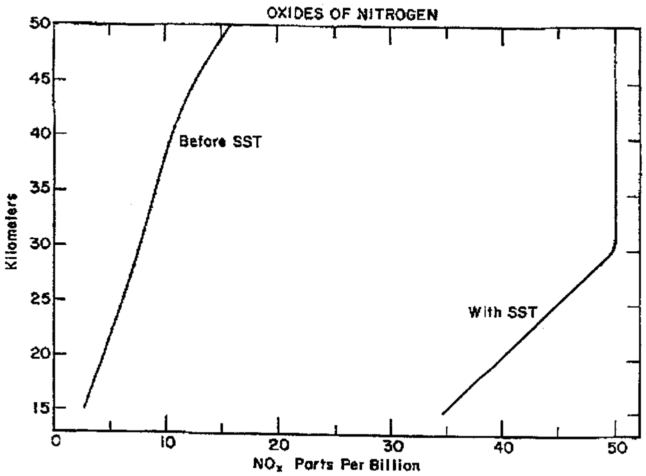


Figure 9. Park and London's assigned vertical distributions of nitrogen oxides in the atmosphere before and after there are 500 SST (U.S. 1971 design) cruising at 20 km altitude. Reproduced from ref 94 with permission from John Wiley & Sons, Inc. Copyright 1974.

6. Calculated Global Ozone Change by Human Activities

6.1. Ozone Change by Nitrogen Oxides from Supersonic Transports. 6.1.1. My August 1971 Article. A detailed review of this article is given on pp 13−25 in article 153 (*Annu. Rev. Phys. Chem.*, 1992). The caption to panel B-1 (see cover) gives the essential features of this article, which was to prove that NO_x could not be neglected in connection with stratospheric aircraft, although such was the consensus among atmospheric scientists in early 1971.

79. "Reduction of Stratospheric Ozone by Nitrogen Oxide Catalysts from Supersonic Transport [SST] Exhaust." Harold Johnston, *Science*, **173**, 517−522 (1971).

In the Spring of 1971, I prepared a 114 page laboratory report that was the basis for article 79. It goes into much more detail than article 79.

79-B. "Catalytic Reduction of Stratospheric Ozone by Nitrogen Oxides." Harold Johnston, Report by Lawrence Berkeley Laboratory, TID4500 (57th ed.), June 1971, 114 pages.

With some additions and omissions, I submitted this 1971 laboratory report for publication in 1972, and it was published in 1974 (article 94). Some material in this article that was not in ref 79 or 79-B is summarized here. At an informal meeting in March 1971, Park and London presented a plausible vertical distribution of natural NO_x and a distribution of NO_x upon operation of a large fleet of SST (Figure 9). They calculated 1.8% ozone reduction produced by this large injection of NO_x (Figure 10A). They found large ozone decreases above 25 km and large ozone increases below 20 km. In early April 1971, I discovered that Park and London had used a rate constant for Bodenstein's reaction, $2NO + O_2 = 2NO_2$, that was larger than that observed by a factor of 13 000. Upon redoing Park and London's calculation using the correct rate constant, I found no ozone increase below 20 km and an ozone column reduction of 40% (Figure 10B).

94. "Catalytic Reduction of Stratospheric Ozone by Nitrogen Oxides." Harold S. Johnston, pp 328−330, from *Advances in Environmental Science and Technology*, Vol. 4, J. N. Pitts, Jr. and R. L. Metcalf, Eds., John Wiley & Sons, Inc., New York, 1974. (Submitted in 1972).

6.2. Use of Paul Crutzen's Great 1971 Article (Pages 4−5 in Article 153). In October 1971, Paul Crutzen published his article that identified the natural source of stratospheric nitrogen oxides: Nitrous oxide (N_2O) is a natural byproduct in soils and in water of the biological nitrogen cycle; nitrous oxide is chemically inert in the troposphere (a 1967 article estimated it to have a 70 year residence time), atmospheric motions carry nitrous oxide upward into the stratosphere where it is broken down by solar ultraviolet radiation and by reaction with singlet atomic oxygen to form nitric oxide (NO) (Figure 11). Crutzen calculated the annual rate of NO production in the stratosphere and the annual NO_x output of 500 SSTs (US type) would approximately double the rate of production of NO_x in the stratosphere.

Crutzen's 1971 article gives an elegant example of global ecology: (i) The natural production of stratospheric nitrogen oxides is a byproduct of the biological nitrogen cycle, (ii) mid-stratospheric nitrogen oxides play the dominant role in determining the natural global ozone destruction (in 2000 as well as in 1971), (iii) stratospheric ozone controls the powerful ultraviolet sunlight (UV-B) that reaches the Earth's surface, and (iv) UV-B is damaging to the biological systems that produce nitrous oxide. Biological systems on the surface of the Earth control how much solar UV-B reaches the Earth's surface.

83. "Newly Recognized Vital Nitrogen Cycle (nitrogen oxides/stratospheric photochemistry/ozone balance)." Harold Johnston, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 2369−2372 (1972).

6.3. Relations between NO_x and ClO_x Systems (Pages 27−28 in Article 153). Rowland and Molina's model (1974) for chlorofluorocarbons (CFC) and the reactivity of chlorine oxides with respect to ozone in the stratosphere are "hand in glove" identical in most respects to Crutzen's natural nitrogen cycle (1971). In December 1973, Rowland and Molina were quite familiar with the parallels between the CFC/Cl_x system and the nitrous oxide/NO_x system.

The major difference between the two reaction systems concerns the role of hydroxyl radicals, OH, which convert active NO_x to inert nitric acid and which convert inert HCl into active chlorine radicals. This difference is highly significant. By way of talks at seminars during the period 1972−1976, I presented Figure 12A and later Figure 12B at many places.

102. "Pollution of the Stratosphere." Harold Johnston, *Annu. Rev. Phys. Chem.*, **26**, 315−338 (1975).

6.4. Miscellaneous Articles on Calculated Ozone Reduction by SST.

84. "The Concorde, Oxides of Nitrogen, and Stratospheric Ozone." Harold Johnston, *Search*, **3**, 276−282 (1972).

92. "Supersonic Aircraft and the Ozone Layer." H. Johnston, *Environ. Change*, 339−350 (1974).

95. "Photochemistry in the Stratosphere−With Application to Supersonic Transports." Harold S. Johnston, *Acta Astron.*, **1**, 135−156 (1974).

97. "Pollution of the Stratosphere." Harold S. Johnston, *Environ. Conservation*, **1**, 163−176 (1974).

6.5. At What Altitude Does NO_x Ozone Production in the Lower Atmosphere Crossover To Cause NO_x Ozone Reduction in the Stratosphere? In 1974, atmospheric modelers agreed that the oxides of nitrogen from the exhaust gases of large fleets of supersonic aircraft would significantly reduce stratospheric ozone and admit extra, biologically damaging, ultraviolet radiation to the earth's surface. Twenty years before, Haagen-Smit had established that the oxides of nitrogen and hydrocarbons in urban areas produce ozone through the photochemical smog reaction: "Ozone Formation in Photochemical Oxidation of Organic Substances." A. J. Haagen-Smit, M. M. Fox, *Ind. Eng. Chem.*, 1956, 1484−1487.

Article 105 reviews the properties of urban photochemical smog, the role of nitrogen oxides in the stratospheric ozone

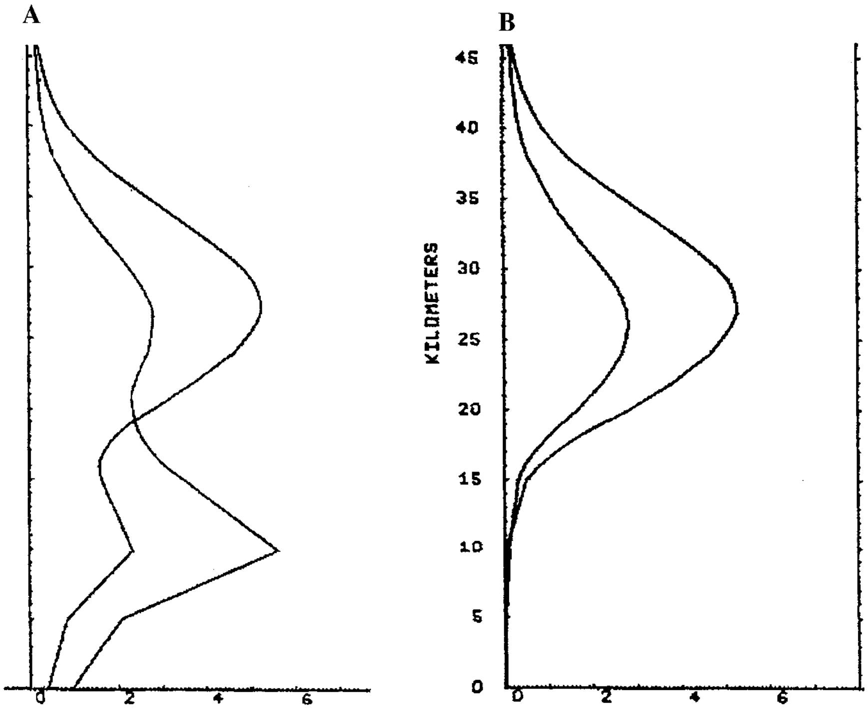


Figure 10. (A) Calculated vertical profiles of ozone based on Park and London's two NO_x profiles including their incorrect value for the rate of the reaction $2NO + O_2 \rightarrow 2NO_2$. The calculated ozone reduction was 1.8%. (B) Calculated vertical profiles of ozone based on Park and London's two NO_x profiles including the correct value for the rate of the reaction $2NO + O_2 \rightarrow 2NO_2$. The calculated ozone reduction was 40%. Reproduced from ref 94 with permission from John Wiley & Sons, Inc. Copyright 1974.

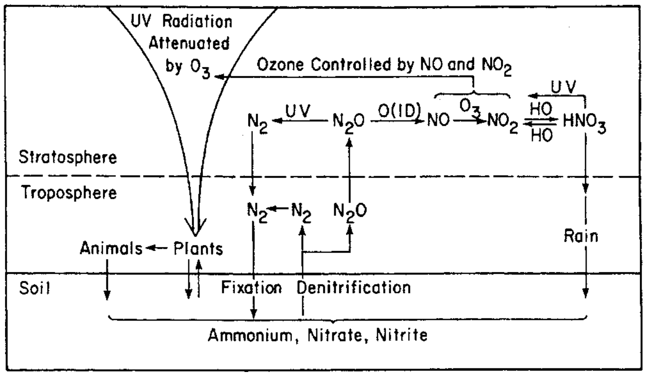


Figure 11. Nitrogen cycle and the newly recognized secondary cycle involving stratospheric NO_x and ozone. Figure 3 of ref 83, courtesy of Harold Johnston.

balance, and the role of methane and NO_x as a source of ozone in the global troposphere. We showed that a set of chemical reactions with measured rate constants gives reaction rates at all altitudes and predicts a crossover between formation and destruction of ozone by nitrogen oxides at about 13 km. This figure is qualitatively correct in 2000, but the quantitative profiles are quite different.

The methane/NO_x/smog reaction has a complex dependence on background O_3, CH_4, H_2O, and NO_x; and the ozone destruction reaction is proportional to the concentration of oxygen atoms and NO_2. There is a crossover at about 13 km between ozone destruction and ozone formation so far as NO_x is concerned. The methane/NO_x/smog reactions produce ozone in the troposphere. Figure 13A implied that subsonic aircraft, which cruise below about 12 km, would produce ozone, not destroy it, a new concept at that time, which was strongly rejected by CIAP top management in 1974.

105. "The Oxides of Nitrogen with Respect to Urban Smog, Supersonic Transports, and Global Methane." Harold S. Johnston and Edward Quitevis, *Proceedings Fifth International Congress of Radiation Research*, Seattle, WA, July 14–20, 1974, O. F. Nygaard, H. I. Adler, W. K. Sinclair, and M. J. Loop, Eds., Academic Press Inc., New York, 1975, pp 1299–1313.

Figure 13B gives (i) the gross ozone production from methane reactions, $P_{SEQ}(O_3)$, (ii) gross ozone loss, $L_{SEQ}(O_3)$, and (iii) net ozone change, $D_{SEQ}(O_3)$ over a wide range of altitudes for July, 42.5N. Where the net rate is negative, it is not shown on the logarithmic plot. For comparison, the rate of ozone production by photolysis of molecular oxygen is included. Below 14 km, the methane "smog" reactions make more ozone than that produced by O_2 photolysis.

Article 164 found the instantaneous rates of gross ozone production P_{SEQ}, gross ozone loss L_{SEQ}, and net change of ozone D_{SEQ} from 0 to 35 km from 47S to 67N latitudes, as caused specifically by methane (Table 3 and Figure 2 of article 164). So far as we know, no other publication has covered this ground (Figure 14B, above).

164. "Methane photo-oxidation in the atmosphere: Contrast between two methods of analysis." Harold Johnston and Douglas Kinnison, *J. Geophys. Res.*, **103**, 21967–21984 (1998).

6.6. Use of Carbon 14 and Strontium 90 from Nuclear Bomb Tests of 1961–2 To Calibrate Theories of Air Motions in the Stratosphere. At intervals from the mid 1950s through December, 1962, large scale nuclear bomb tests were conducted on the earth surface and in the atmosphere, sending large amounts of radioactive bomb debris into the atmosphere as high as the mid-stratosphere. The U.S. Atomic Energy Commission (AEC) made stratospheric and tropospheric measurements of the decline of carbon 14 and aerosol particles containing strontium 90 (and many other radioactive species) from 1955 to 1967 at intervals of every three months, and in the year 1970. AEC published excess (above natural background) carbon 14 and strontium 90 observations in its HASL reports as tables and two-dimensional contour maps. These measurements had high national priority, there was fear of impending nuclear war,

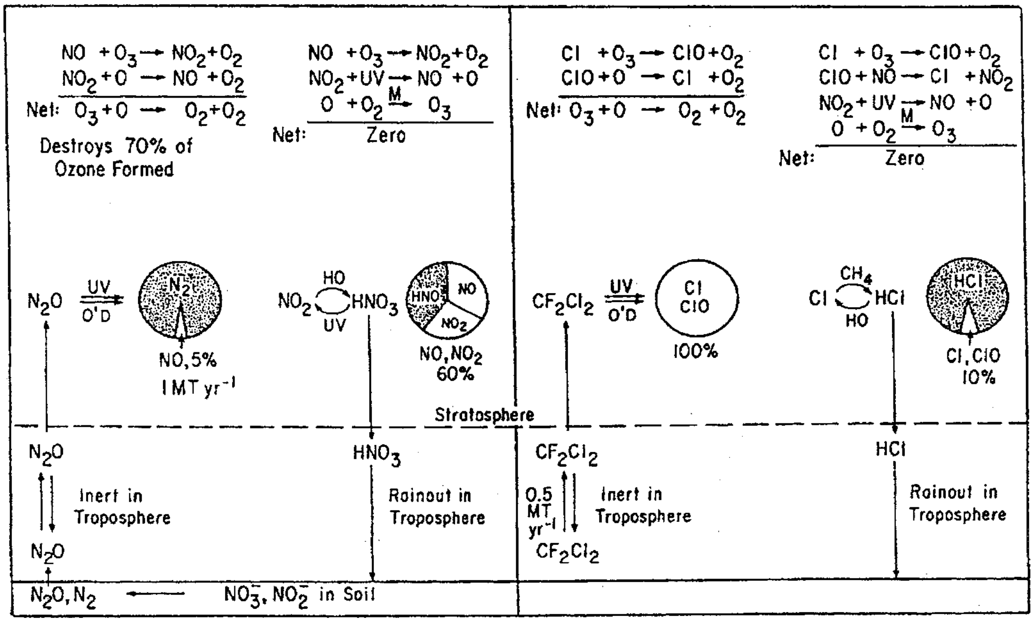


Figure 12. Parallels between the natural nitrogen oxides and the artificial chlorofluorocarbons with respect to stratospheric ozone. Both N_2O and compounds such as CF_2Cl_2 are inert in the troposphere and are broken down to active radicals in the stratosphere; the active radicals engage in catalytic cycles that destroy ozone and in competing "do nothing" cycles; the active species are reversibly bound up as inactive gaseous acid species; the acids are rained out of the troposphere when they are transported into it. Reproduced from Figure 1 of ref 102 with permission from the *Annual Review of Physical Chemistry*, Vol. 26, 1975, by Annual Reviews (www.AnnualReviews.org).

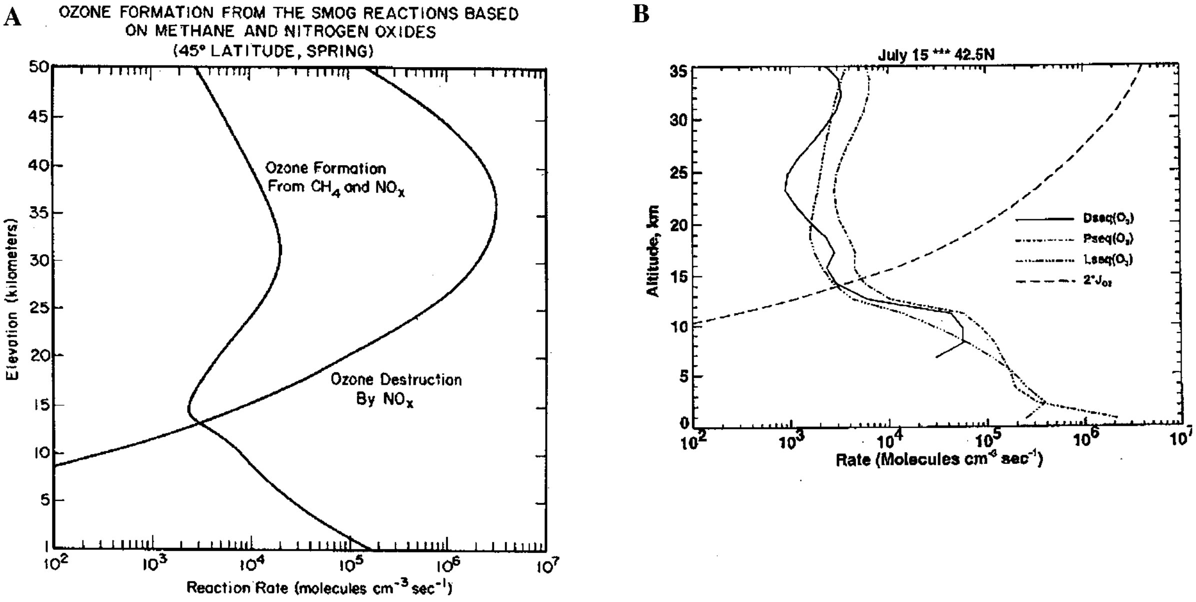


Figure 13. (A) Vertical profiles of the rate of formation of ozone from the methane/NO_x/smog reaction and of rate of ozone destruction from the NO catalytic cycle. Reproduced from ref 105 with permission from Academic Press. Copyright 1975. (B) Calculated vertical profiles by the sequence SEQ method. Reproduced from ref 164 with permission from the American Geophysical Union. Copyright 1998.

and no money was spared to find where and how long radioactive bomb-products remained in the atmosphere and where and when they fell out.

The concentrations of carbon 14 and strontium 90 from nuclear bomb tests, 1961–62, provide a unique set of data characterizing vertical air motions of inert tracers in the stratosphere from 1963 to 1970 and settling velocities of sulfate aerosols. If this "experimental study" of atmospheric motions were allowed to be repeated, it would surely cost much more than a billion dollars. We transcribed entries from these tables and from the contour plots to construct vertical profiles of carbon 14 and strontium 90 from spring 1963 to 1967 and for fall 1970.

89. "Effect of Nuclear Explosion on Stratospheric Nitric Oxide and Ozone." Harold Johnston, Gary Whitten, and John Birks, *J. Geophys. Res.*, **78**, 6107–6135 (1973).

145. "Evaluation of Excess Carbon l4 and Strontium 90 Data for Suitability to Test Two-Dimensional Stratospheric Models," H. Johnston, *J. Geophys. Res.*, **94**, 18, 485–18493 (1989).

6.6.1. Test of One-Dimensional Models with Respect to Vertical Mixing and Stratospheric Residence Time. In 1974, most stratospheric models were one dimensional, with atmospheric motions determined by a "vertical eddy diffusion function, K_z." The atmospheric models of 1974 had widely varying K_z functions and gave drastically different predictions for ozone reduction. When Richard Lindzen heard of the great variation of results among the one-dimensional models, he said,

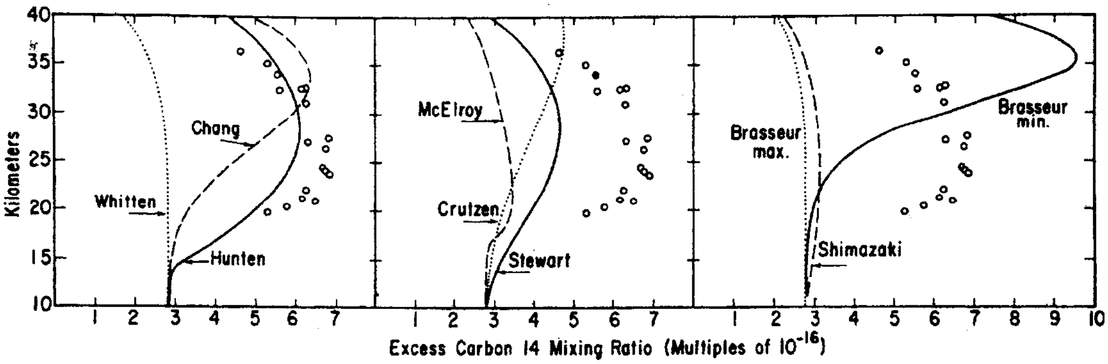


Figure 14. (A−C) Comparison of directly observed carbon 14 mixing ratios in November 1970 (points) with those calculated by nine models of K_z (lines). Reproduced from ref 107 with permission from the American Geophysical Union. Copyright 1976.

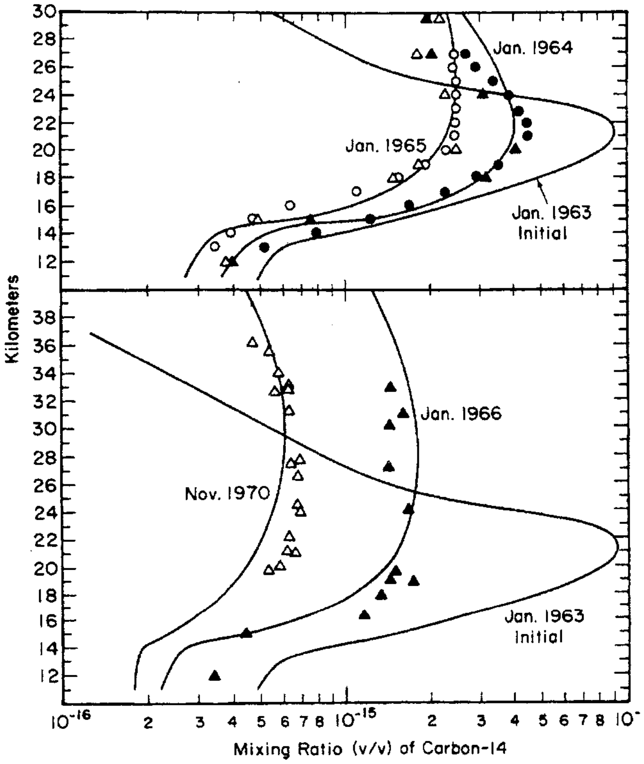


Figure 15. Calculated and observed excess carbon 14 mixing ratios in the stratosphere 1, 2, 3, and 8 years after January 1963 (corrected for transport to southern hemisphere). The curves were calculated by Hunten's model. Open and solid circles, northern hemisphere average; open and solid triangles, direct observation at 30° N. Reproduced from ref 107 with permission from the American Geophysical Union. Copyright 1976.

"Why don't you pay some attention to the physics of the problem?" Lindzen gave some references (verbal communication from Don Hunten, 1974). Hunten took Lindzen's general theory, drew a simplified shape of the vertical profile that the vertical eddy diffusion function K_z should have, fitted it to observed vertical distributions of methane and nitrous oxide, and from then on, Hunten made no further changes and used no adjustable parameters.

We tested nine one-dimensional models, each with a different K_z function, with respect to how well they agreed with the carbon 14 observations of 1963−1970. All models, except Hunten's seriously failed.

From January 1964 to November 1970, calculated vertical profiles based on Hunten's model are compared (Figure 14) to observed carbon 14 with initial conditions based on the observed vertical distribution of January 1963 (or other times as sensitivity study). Figure 15 shows remarkably successful agreement between observations and model, especially in view of the fact that no parameters were adjusted to fit the carbon 14 data.

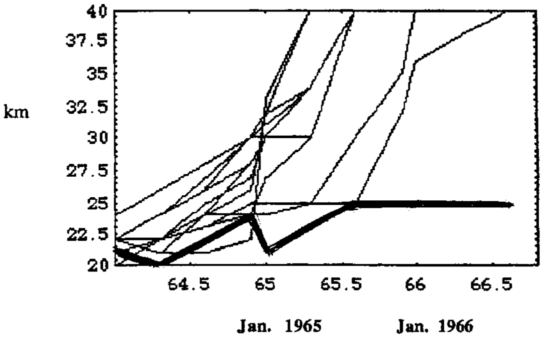


Figure 16. Altitude of maximum mixing ratio (mole fraction). Observed carbon 14 is the heavy line. The eleven other lines are the values calculated by the different models.

107. "Use of Excess Carbon 14 Data to Calibrate Models of Stratospheric Ozone Depletion by Supersonic Transports." Harold Johnston, David Kattenhorn, and Gary Whitten, *J. Geophys. Res.*, **81**, 368−380 (1976).

6.6.2. Test of Two-Dimensional Models with Respect to Vertical Mixing and Stratospheric Residence Time. In 1992−93, eleven models, two- or three-dimensional, were used to predict the two-dimensional distributions of carbon 14. The models initial vertical profile was the same as that observed in January 1964, and we tested three models for initial values outside the range of observations. Between 1964 and 1966, all models show a rapidly rising altitude of maximum mixing ratio from 21 to more than 40 km, whereas the measured values increased slowly from 21 to 25 km, Figure 16. This figure indicates a major failure of all these models with respect to rate of vertical transport in the stratosphere.

Figure 17A gives the vertical profiles at 30° and 70° N of (excess) carbon 14 mixing ratios from 20 to 38 km for five atmospheric models and for direct observations in the fall of 1970, seven years after the conclusion of the nuclear bomb tests of 1961−62. Only five of the eleven models are shown to avoid overcrowding of the figures, but the omitted models show similar shapes of the vertical profile. The observations show a broad maximum of carbon 14 mixing ratio at 25 km, slowly decreasing above. The models indicate a maximum mixing ratio above 40 km, show a strongly different shape, and some give much less carbon 14 at 25 km than that observed.

It is generally agreed that major features of stratospheric air motions include upward flux of tropospheric air into the tropical stratosphere, net transport of air from the tropical region to polar regions through advection and turbulent diffusion, and down-

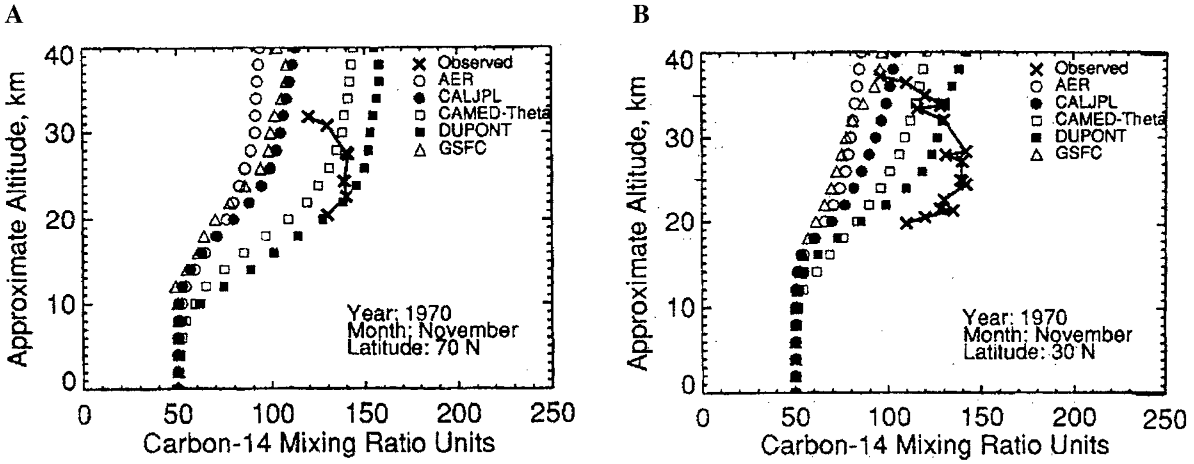


Figure 17. (A, B) Calculated and observed vertical profiles of carbon 14 in the fall of 1970. All models out of 11 disagreed with the shape of the measured vertical profiles. Reproduced from ref 161 with permission from the American Geophysical Union. Copyright 1994.

ward flux in polar regions with lateral and downward exit to the troposphere. As the air is transported from tropics to polar regions across mid-latitude zones, it has a component of upwardly directed vertical transport, largely due to turbulent diffusion. Obviously, the net rate of vertical transport is much less than the net rate of latitudinal transport, but the shapes of profiles in Figure 17 indicate all the models greatly overestimate the rate of net vertical transport relative to net latitudinal transport.

161. “Model study of atmospheric transport using carbon 14 and strontium 90 as inert tracers.” D. E. Kinnison, H. S. Johnston, and D. J. Wuebbles, *J. Geophys. Res.*, **99**, 20647−20664 (1994).

6.6.3. Another Study of Carbon 14 and Strontium 90.

112. “Expected Short-term Local Effect of Nuclear Bombs on Stratospheric Ozone.” Harold Johnston, *J. Geophys. Res.*, **82**, 3119−3124 (1977).

6.7. Calculated Global Ozone Change by CFC and SST As Predicted with Homogeneous Gas Phase Chemical Reactions. 6.7.1. Chlorofluorocarbons (CFC). The models of 1985 predicted that chlorine from chlorofluorocarbons (CFC) would reduce the ozone column by 2−4% over a period of about 100 years. This prediction was the consensus of stratospheric modelers in 1985.

6.7.2. Ozone Reduction As Calculated by Modelers in 1985 for 500 U.S. SST Cruising at 20 km Altitude. The models of 1985 predicted that NO_x from 500 SST cruising at 20 km would reduce the ozone column by about 10%. For example, the group at Lawrence Livermore National Laboratory (LLNL) calculated a 12.2% reduction of global ozone, assuming emission of 2000 NO_x molecules cm^{-3} s^{-1} of NO_x at 20 km altitude. (Article 141, p 727).

141. H. S. Johnston and F. Kaufman, Co-Chairmen for “Results of Model Calculations” Chapter 13 of *Atmospheric Ozone 1985, Vol. III* (World Meteorological Organization Global Ozone Research and Monitoring Project, Report No. 16), pp 722−770.

6.8. History of Calculated Ozone Changes As Caused by CFC and SST, 1974−1988. Panel B-2 on the Cover Cartoon. Scientists at LLNL maintained a baseline of the calculated effects of two global perturbations through the years of the maturing of stratospheric science. Figures similar to panel B-2, covering various periods of time, have appeared in several places and in several forms. One curve (circles) shows the calculated future, steady-state, ozone-column change for the continuous usage of chlorofluorocarbons at the 1974 rate, where the time to reach steady state is 50−100 years. The other curve (triangles) shows the calculated future, steady-state, ozone column change for an assumed continuous worldwide injection of 3.0×10^{34} NO_x molecules per year, spread over a 1 km band centered at 20 km altitude, where the time to reach steady state for this aircraft model is about 10 years. For these constant assumed perturbations, the calculated future ozone changes vary with the date of calculation, each of which used its current knowledge of the stratosphere. The variations of the results between the years 1976 and 1981 were largely caused by new laboratory measurements of rate coefficients of 11 reactions in the HO_x family and the discovery of new species to include in the models (Johnston, 1984, article 133). High calculated hydroxyl radical concentrations in the lower stratosphere resulted in high HNO_3/NO_2 ratios ($HO + NO_2 = HNO_3$) and low rates of ozone destruction by NO_x. High calculated hydroxyl radical concentrations in the lower stratosphere resulted in low calculated HCl/Cl ratios ($HO + HCl = H_2O + Cl$) and fast ozone destruction by chlorine reactions. For about 2 years, 1978−1979, the models calculated that NO_x from stratospheric aircraft increased the ozone column, and at the same time they calculated that chlorine reactions reduced global ozone by 20%. Calculations using this model gave ozone reduction by NO_x in the middle stratosphere but gave an even larger ozone increase in the upper troposphere and lower stratosphere. After all HO_x reactions were remeasured by modern direct methods, the models calculated that NO_x injected at 20 km reduces the ozone column. Since 1981, the calculated ozone reduction by supersonic aircraft (about 10%) is greater than that calculated for CFCs (about 5%). These calculations were all made with homogeneous gas chemistry.

6.9. Two Large “Ozone Holes” Reported in 1985. In 1985, two “ozone holes” were reported, one in the Antarctic lower stratosphere and one at all latitudes in the uppermost stratosphere.

6.9.1. Measurements Implying Large Ozone Reductions. Farman et al. (1985) published an article entitled “Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interactions” in which they reported seasonally variable 5−30% reduction of the south polar ozone column during 1980−1984 relative to 1957−1973, as shown by Figure 18A. Later in 1985 Robert Watson of NASA (National Aeronautics and Space Administration) called an informal meeting of several atmospheric scientists, including me, to discuss the reported Antarctic “ozone hole”. He said, in effect, that all models had failed to

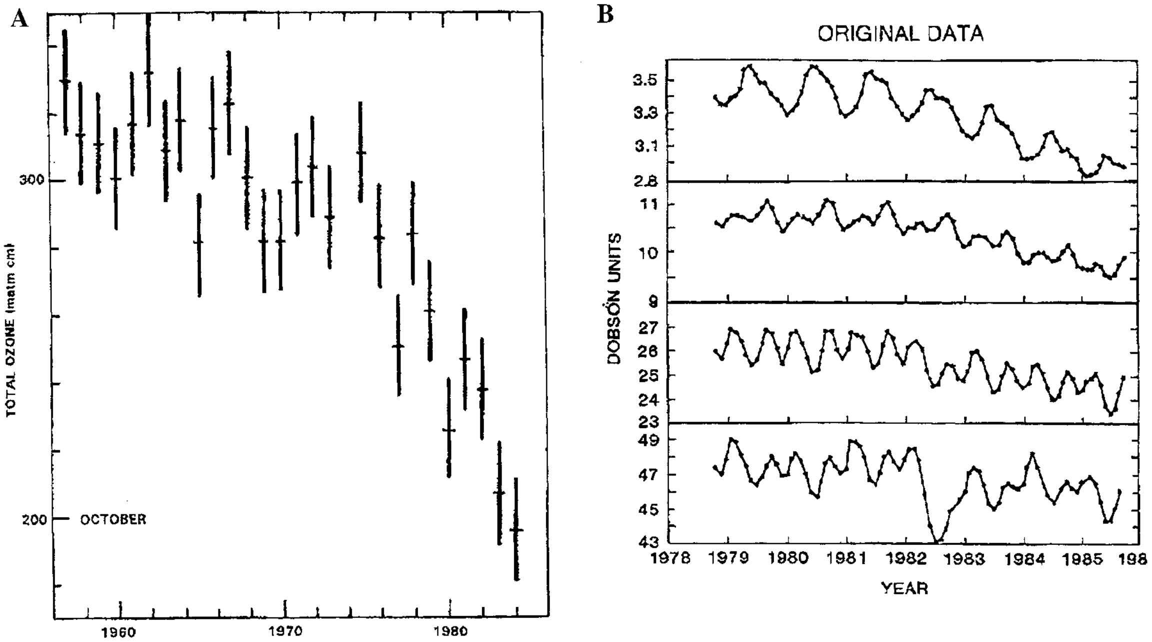


Figure 18. (A) Observed south polar ozone columns during October from 1957 to 1984 from ground based Dobson station. "Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction." Farman, J. C., B. G. Gardiner and J. D. Shanklin, *Nature*, **315**, 201 (1985). Reproduced with permission of Nature. Copyright 1985. (B) The trend in global average ozone mixing ratios between 70° S and 70° N as a function of year and altitude, 1979-1985; based on measurements by Solar Backscattered Ultraviolet (SBUV) satellite instrument. Altitudes in km from top panel down: 43−48, 38−43, 33−38, 28−33. Don Heath as presented in Chapter 5 of WMO, Global ozone research and monitoring project-Report No. 18, "Report of the International Ozone Trends Panel 1988," Geneva, 1990. NASA figure.

predict the phenomenon, and everyone appears not to understand it. He said that it might turn out to be an error in the instrument, or it might be real. If it is real, what is the explanation? What can we do in field observations, in laboratory measurements, or in modeling that will lead us to understand it. The discussion centered on what measurements need to be made.

The Solar Backscattered Ultraviolet (SBUV) satellite was launched late in 1978. SBUV data give the vertical distribution of ozone from the top of the stratosphere to the lower troposphere. Donald Heath examined the record from 1979 through 1984; the data showed a conspicuous ozone decrease of 17% at 50 km but no reduction below 28 km (Figure 18B). A few weeks after his group discussion of the Antarctic ozone hole, Robert Watson brought together the same group to discuss Heath's findings. Again he said, in effect, that all models had failed to predict so fast an ozone reduction from chlorofluorocarbons. He said that it might turn out to be an error in the instrument, or it might be real. If it is real, what is the explanation?

These considerations led to a research program (Ozone Trends Panel) of more than 100 scientists to study these two simultaneously discovered ozone reductions. John Gille was chair of Chapter 2 "Spacecraft instrument calibration and stability," C. Rogers was chair of Chapter 3, "Information content of ozone retrieval algorithm," F. S. Rowland was Chair of Chapter 4, "Trends in total column ozone measurements;" and I was Chair of Chapter 5, "Trends in ozone profile measurements."

6.9.2. Cause of the Reported Ozone Reduction in the Upper Stratosphere. We compared the SBUV vertical profiles against previous measurements made by three other satellite systems, by ground-based optical methods, and by rockets. Every day, the SBUV satellite measured total ozone columns and ozone vertical profiles over the sun-lit earth, but the other methods provided only a fraction of this coverage. Comparisons were made only for intersections between the SBUV trajectory and the path of the other device within a grid size of 0.3 days, 7° longitude, and 1° latitude. None of the other methods confirmed the SBUV ozone decrease at 50 km, and in most cases the ozone reported by the SBUV was substantially and significantly lower than that found by the comparing system. We found the reported ozone hole in the uppermost stratosphere to be caused by degradation of an optical component in the instrument.

The panel report concluded, "This assessment does not support the previous reports based on SBUV... data of large global decreases since 1979... in the ozone concentration near 50 km altitude... These reports used data archived as of 1987, and the trends obtained were erroneously large because of unjustified and incorrect assumptions about the degradation of the diffuser plate common to both the SBUV and TOMS satellite instruments."

141. "Trends in Ozone Profile Measurements," Chapter 5 of *Report of the International Ozone Trends Panel−1988, Vol. I* (World Meteorological Organization Global Ozone Research and Monitoring Project, Report No. 18), pp 383−442.

6.9.3. Cause of the Reported Ozone Reduction in the Antarctic Stratosphere. Under the scientific direction of Susan Solomon, NASA sent two large expeditions to Antarctica, one in 1986 and one in 1987. From ground based stations, instrumented aircraft, and satellites, a large amount of data were obtained in 1986, but these data were not enough to establish the mechanism of the large ozone loss the in the Austral Spring. Based on the findings of the 1986 studies, the 1987 expeditions collected a massive amount of pertinent data, but it required a couple of years to interpret and publish it.

The 1987 expedition, new laboratory results, continued satellite measurements, and model calculations proved that heterogeneous Cl/ClO chemistry, in an unusual environment produced by atmospheric winds and low temperatures, caused the large reductions of Antarctic ozone. The Antarctic clouds consist of ice particles and particles also including nitric and sulfuric acids. Out of the five identified NO_x/ClO_x heterogeneous reactions occurring in the Antarctic stratosphere, two are illustrative and important:

Hydrolysis:

$$N_2O_5\ (\text{gas}) + H_2O\ (\text{part of aerosol}) \rightarrow 2\ HNO_3\ (\text{adsorbed or gas})$$

Catalysis:

$$ClONO_2\ (\text{gas}) + HCl\ (\text{adsorbed}) \rightarrow HNO_3\ (\text{adsorbed or gas}) + Cl_2\ (\text{gas})$$

The first of these two reactions converts photochemically active nitrogen pentoxide into inactive nitric acid. The second of these reactions converts inactive chlorine nitrate and inactive hydrogen chloride into inactive nitric acid and strongly photochemically active molecular chlorine. Even with the sun barely above the horizon during the arrival of Austral Spring, near ultraviolet solar radiation and blue visible light dissociate chlorine to form atomic chlorine and chlorine monoxide,

$$Cl_2 \rightarrow 2\ Cl, \text{ followed by } Cl + O_3 \rightarrow ClO + O_2$$

which catalytically react to destroy ozone by two important mechanisms.

The existence of the Antarctic hole was confirmed and explained.

6.9.3. Implications of Solutions to the Problems Posed by Two Ozone Holes Reported in 1985. Atmospheric observations, made over a period of years, indicated that ozone depletion had occurred in two different regions of the stratosphere, possibly caused by chlorofluorocarbons. Scientists who suggested human-induced ozone reduction were subjected, by some people, to unmannered criticism as being prejudiced against the chlorofluorocarbon industry and, as sometimes said, being against the American way of life. Most scientists who worked on the problem of one ozone hole also worked on the other ozone hole. This group of scientists found that one of the reported ozone holes was spurious and the other was real. If the scientists, who concluded that ozone depletion in Antarctica was real and caused by CFC, were prejudiced against the CFC industry, then were the same scientists who concluded that the ozone depletion at 50 km altitude was unreal prejudiced in favor of the CFC industry? How can a person be both prejudiced against and prejudiced for the CFC industry? Unfettered operation of the scientific method sometimes leads to results that affect the interests of the political or corporate world, but without further evidence, such results and the scientists who developed them should not be regarded as "for" or "against" anything.

6.10. Renewed Interest in Supersonic Transport, 1986–1989. Update to 1989 of the Calculated Effect of NO_x from Supersonic Transports on Ozone. After 1975, there was little apparent interest in SSTs and no significant new research, but in his state of the union address in 1986, President Reagan advocated building a "Tokyo express" that would fly from New York to Tokyo in 2 h, which would require aircraft of Mach number 10. This proposal led to new interest in supersonic and hypersonic civil transports. In article 144, we used the LLNL two-dimensional atmospheric model to update the 1975–1976 calculated effects of 500 supersonic aircraft on ozone. These calculations were made using gas-phase chemistry. A portion of the results is given by Table 1, where injection latitudes are 37° to 49° N.

The calculated ozone reduction increases rapidly with injection altitude: 0.7% at 16.5 km, 8.6% at 22.5 km, and 9.6% at 25.5 km, but it is about the same from 25.5 to 34.5 km. With an eight-fold increase in NO_x injection at 22.5 km, the calculated ozone column reduction increases by a factor of 6.8.

TABLE 1: Calculated Changes in Global Ozone Vertical Columns as a Result of NO_x Injections by Stratospheric Aircraft[a]

injection altitude/km	NO_x input, Tg of NO_2/a	calcd global ozone change, %
16.5	1.8	−0.7
25.5	1.8	−9.6
34.5	1.8	−9.2
22.5	0.6	−2.8
22.5	1.8	−8.6
22.5	4.8	−19

[a] Based on LLNL two-dimensional model. Gas phase chemistry.

144. "Nitrogen Oxides from High-Altitude Aircraft: An Update of Potential Effects on Ozone," H. S. Johnston, D. E. Kinnison, and D. J. Wuebbles, *J. Geophys. Res.*, **94**, 16351–16363 (1989).

6.11. Heterogeneous Chemistry in the Global Atmosphere. 6.11.1. My Laboratory Did Only a Small Amount of Experimental Study of Heterogeneous Reactions.

151. "Ionic Mechanisms for Heterogeneous Stratospheric Reactions and Ultraviolet Photoabsorption Cross Sections for NO_2^+, HNO_3, and NO_3^- in Sulfuric Acid." J. D. Burley and H. S. Johnston, *Geophys. Res. Lett.* **19**, 1359–1362 (1992).

152. "Nitrosyl Sulfuric Acid and Stratospheric Aerosols," J. D. Burley and H. S. Johnston, *Geophys. Res. Lett.* **19**, 1363–1366 (1992).

6.11.2. My Experience with the Reaction, N_2O_5(gas) + H_2O (on Aerosol Particles) → $2HNO_3$. In the 1961, C. E. Junge discovered a thin world-wide, sulfuric acid haze in the lower stratosphere. These aerosol particles were about 25% water by weight.

In the 1950s, I did a great deal of laboratory work with N_2O_5, and I found that it did not react with water in the gas phase, but that it reacted strongly with adsorbed water on glass or metal surfaces. During 1971–1972, I heard about the Junge layer of sulfuric acid aerosols in the stratosphere, and I felt sure N_2O_5 would react with it to produce nitric acid, but I did not know the surface area of the aerosol nor the collision efficiency, and so I could not calculate the reaction rate. During and after 1972, I strongly advocated that CIAP (Climatic Impact Assessment Program, SST research program, 1972–1975) fund a laboratory study of N_2O_5 reactions on sulfuric acid surfaces. I have saved relevant correspondence in which I recommended to CIAP that they should study the heterogeneous reaction of N_2O_5 plus H_2O to form $2HNO_3$. Between 1971 and 1974, I published three articles that pointed out the need for research on this problem. After my continued heavy persuasion, they reluctantly and late in the program had SRI make one test. CIAP managers told me that SRI found that the reaction coefficient per collision was less than 10^{-5}. Such a low value meant that the reaction would have no significant effect on stratospheric chemistry.

79. "Reduction of Stratospheric Ozone by Nitrogen Oxide Catalysts from Supersonic Transport Exhaust." Harold Johnston, *Science*, **173**, 517–522 (1971), page 518.

94. "Catalytic Reduction of Stratospheric Ozone by Nitrogen Oxides." Harold S. Johnston, pp 263-380, from *Advances in Environmental Science and Technology*, Vol. 4, J. N. Pitts, Jr. and R. L. Metcalf, Eds., John Wiley & Sons, Inc., New York, 1974, p 312. (Submitted Sept 1972).

91. "Photolysis of Nitric Acid Vapor." Harold S. Johnston, Shih-Ger Chang, and Gary Whitten. *J. Phys. Chem.*, **78**, 1–7 (1974), p 1.

When laboratory chemists restudied this problem almost 15 years later, they found the reaction of N_2O_5 with sulfuric acid aerosols would occur at a rate 10 000 times faster than that reported by the hurried study in 1974. At this fast rate the reaction plays an extremely important role in the global ozone balance below 25 kilometers and on ozone perturbations by human activities. See panel B-3, on the cover.

6.11.4. Heterogeneous Chemistry with Respect to Global Atmospheric Chemistry. Modelers in 1991 calculated global ozone and its changes without and with heterogeneous reactions on the sulfuric acid/water aerosols. Using homogeneous chemistry, they found little if any ozone changes during the previous ten years. Using heterogeneous chemistry, they found significant ozone reductions over mid-latitude and polar regions, for example, Stolarski et al.: "Total ozone trends deduced from Nimbus 7 TOMS data." R. S. Stolarski, P. Bloomfield, D. R. McPeters, and J. Herman, *Geophys. Res. Lett.*, **18**, 1015−1018 (1991). See panel B-3, on the cover.

6.12. Interest in Supersonic Transport, 1989-1999. 6.12.1. History of Calculated Effects of Stratospheric Aircraft on Ozone, Including Only Homogeneous Reactions. Until 1991 modelers using only gas phase chemistry calculated significant reductions of global ozone by stratospheric aircraft. Panel B-2 (on the cover) gives the history of calculated ozone change by a standard fleet of 500 SST (or high-speed civil transport, HSCT, as SST were renamed in 1989) for the period 1973−1988, and it gives the calculated ozone change caused by long term continuous emission of CFC at the rate of production in 1974. From 1982 to 1988, the calculated ozone reduction by CFC was about 4−5% to build up over a period of about 100 years; the calculated ozone reduction by 500 SST was about 10−12%, which would build up over a period of about 10 years.

6.12.2. Calculated Effects of Stratospheric Aircraft on Ozone, Including Heterogeneous Reactions. See panel B-3 on the cover and its caption.

Heterogeneous chemical reactions on natural sulfuric acid aerosols deactivate nitrogen oxides in the lower stratosphere. The reaction of nitrogen pentoxide with global sulfuric acid aerosols (and other heterogeneous reactions) leads to a large reduction in the calculated ozone destruction by nitrogen oxides and thus from SSTs. Weisenstein et al. (1991) added a single heterogeneous chemical reaction to their model, using recently made measurements that showed the reaction probability per collision is about 0.1:

$$N_2O_5\ (\text{gas}) + H_2O\ (\text{on particles}) \rightarrow 2HNO_3\ (\text{gas})$$

The calculated ozone reduction with the heterogeneous reaction included was about an order of magnitude less than that with homogeneous chemistry alone, and zero ozone reduction was within the error limits of the models. "Impact of Heterogeneous Chemistry on Model-Calculated Ozone Change Due to High Speed Civil Transport Aircraft." Weisenstein, D. K., M. K. W. Ko, J. M. Rodriguez, and N. D. Sze, *Geophys. Res. Lett.*, **18**, 1991−1994 (November 1991).

The calculated ozone reduction from Mach 2.4 HSCT with EI(NO_x) of five has been very small since 1991. I demonstrated this radical double shift from previous model calculations in Article 160. The talk was presented in 1991, the article was submitted for publication in 1992, it was published in 1994, and it included panels B-2 and B-3 in the cover cartoon.

160. "Stratospheric aircraft: Impact on the stratosphere?" H. S. Johnston, CHEMRAWN VII, A World Conference, *The Chemistry of the Atmosphere: Its Impact on Global Change*, Edited by J. G. Calvert. Blackwell Scientific Publications, London, 1994.

7. Miscellaneous Publications

7.1. Reviews. 7.1.1. Annual Reviews of Physical Chemistry.

32. "Kinetics of Reactions in Gases." Harold Johnston, *Annu. Rev. Phys. Chem.*, **8**, 249−272 (1957).

102. "Pollution of the Stratosphere." Harold Johnston, *Annu. Rev. Phys. Chem.*, **26**, 315−338 (1975).

133. "Human Effects on the Global Atmosphere," Harold S. Johnston, *Annu. Rev. Phys. Chem.*, **35**, 481−505 (1984).

153. "Atmospheric Ozone," H. S. Johnston, *Annu. Rev. Phys. Chem.* **43**, 1−32 (1992).

7.1.2. Book Reviews

38. "Review of Free Radicals. An Introduction, by A. F. Trotman-Dickenson." Harold S. Johnston, *Science*, **130**, 1570 (1959).

64. "Review of 'Chemical Kinetics of Gas Reactions,' by V. N. Kondratiev." Harold Johnston, *J. Am. Chem. Soc.*, **87**, 3791 (1965).

7.2. Books or Booklets.

67. *Gas Phase Reaction Rate Theory*. The Ronald Press Company, New York, 1966, 362 pages.

73. *Gas Phase Reaction Kinetics of Neutral Oxygen Species*. U.S. Department of Commerce, National Bureau of Standards, NSRDS-NBS 20, 1968, 49 pages.

148. *The Atmospheric Effects of Stratospheric Aircraft: A Topical Review*, H. S. Johnston, M. J. Prather, and R. T. Watson, NASA Reference Publication 1250, January 199l, 28 pages.

7.3. Chapters in Books.

78-B. "Atmospheric Chemistry and Physics," H. S. Johnston, J. N. Pitts, James Lewis, Leo Zafonte, Tom Mottershead, Task Force no. 7, Volume IV, Chapter 5, Project Clean Air, University of California Press, September 1, 1970, pp 105.

80. "The Effect of Supersonic Transport Planes on the Stratospheric Ozone Shield." Harold Johnston, *Environ. Affairs*, **1**, 735−781 (1972).

126. "Odd Nitrogen Processes." H. S. Johnston, Chapter 4 in *Stratospheric Ozone and Man, Vol. I*, F. A. Bower and R. B. Ward, Eds., CRC Press, Inc., Boca Raton, FL, 1982, pp 87−140.

141. "Trends in Ozone Profile Measurements," Chapter 5 of *Report of the International Ozone Trends Panel−1988, Vol. I* (World Meteorological Organization Global Ozone Research and Monitoring Project, Report No. 18), pp 383-442.

7.4. Articles That Include My Name as a courtesy for My Giving Minor Advice, but in Which I Did Not Help in Conceiving the Work or in Writing the Article.

66. "Computed High-temperature Rate Constants for Hydrogen-atom Transfers Involving Light Atoms." W. S. Mayer, L. Schieler, and Harold S. Johnston, *J. Chem. Phys.*, **45**, 385−391 (1966).

135. "Kinetic Study of the NO_3-CH_2O Reaction and Its Possible Role in Nighttime Tropospheric Chemistry." Christopher A. Cantrell, William R. Stockwell, Larry G. Anderson, Kerry L. Busarow, Dieter Perner, Art Schmeltekopf, Jack G. Calvert, and Harold S. Johnston, *J. Phys. Chem.*, **89**, 139−146 (1985).

136. "A Laboratory and Field Study of the Equilibrium $N_2O_5 = NO_3 + NO_2$," D. Perner, A. Schmeltekopf, R. H. Winkler, H. S. Johnston, J. G. Calvert, C. A. Cantrell, and W. R. Stockwell. *J. Geophys. Res.*, **90**, 3807−3812 (1985).

143. "Rate Constants for $CH_2(^3B_1)$ Removal by O_2, NO, and C_2H_2 from Infrared Diode Laser Flash Kinetic Spectroscopy," D. C. Darwin, A. T. Young, H. S. Johnston, and C. B. Moore, *J. Phys. Chem.*, **93**, 1074−1078 (1989).