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University of California
Berkeley, California

Harold S. Johnston, Ph.D.
ATMOSPHERIC CHEMISTRY RESEARCH AT BERKELEY

An Interview Conducted by
Sally Smith Hughes, Ph.D.
in 1999

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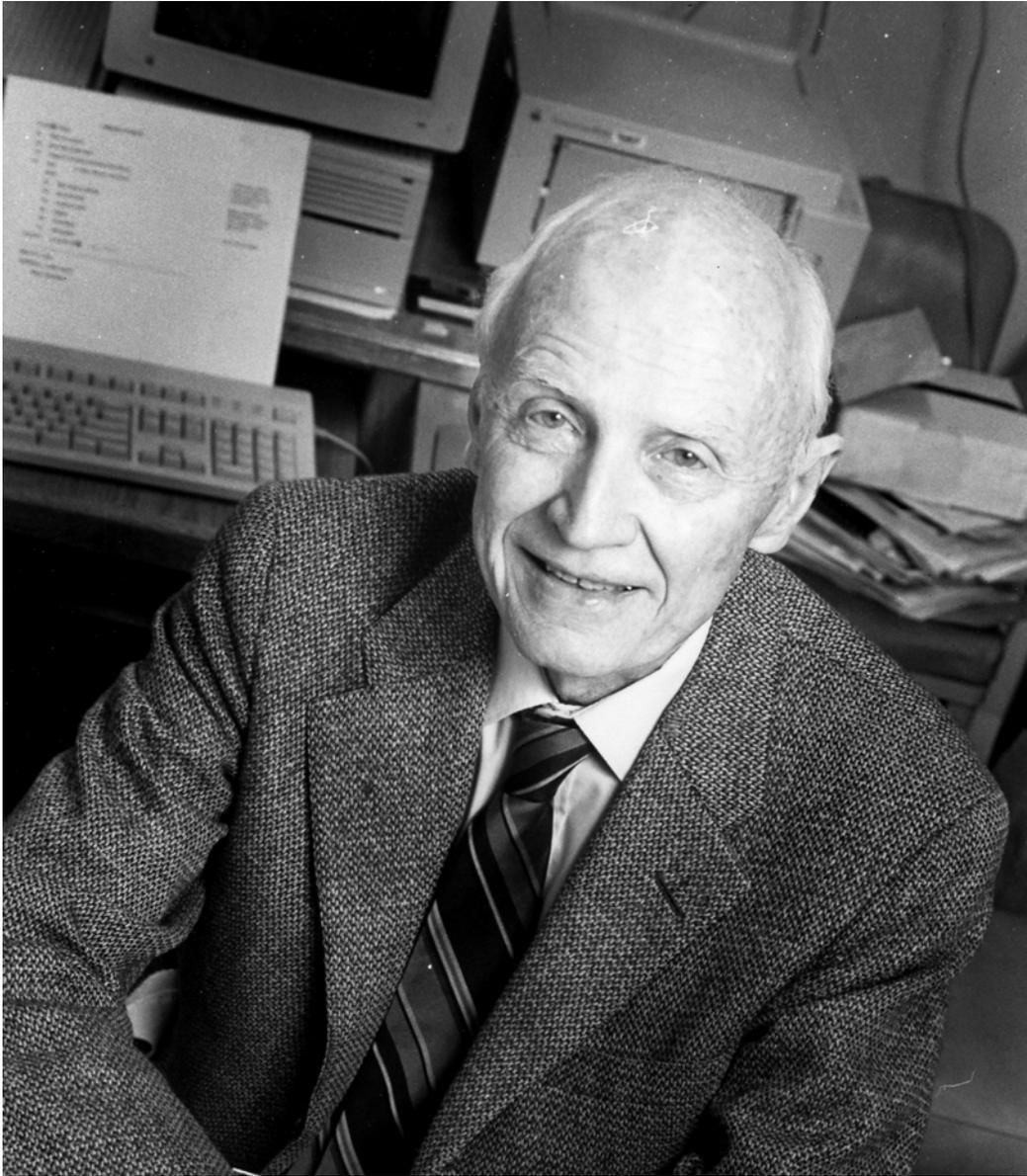
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Harold S. Johnston

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INTERVIEW HISTORY--Harold S. Johnston

The interviews with Harold S. Johnston, Professor Emeritus of Chemistry at the University of California, Berkeley, document his many contributions as a pioneer of chemical kinetics and atmospheric chemistry. His basic research in these fields led to several practical applications, including early research into the molecular mechanisms creating smog. He was a leading voice in sounding the alarm in the 1970s that human activities can and do harm the earth's ozone layer. His concern was based on decades-long research on chemical reactions in mixtures of gases and how they are affected by light. His views were viciously attacked but have been subsequently substantiated by, among other things, the discovery of ozone holes over the poles. Never afraid of controversy despite his gentle personality, he was also a prominent opponent of the proposal in the late 1960s and 1970s to build a fleet of supersonic transport planes. He describes in the interviews the evidence he presented that nitrogen oxide emitted by the planes would further deplete the ozone layer, evidence that helped to terminate the plan for the supersonic transport. Partly as a result of this work, Congress established a major program on stratospheric research. In 1997, Dr. Johnston received the prestigious National Medal of Science, the nation's top scientific award. A family man as well as a scientist, Dr. Johnston talks in the interviews of his wife, Mary Ella, and his four children.

The Oral History Process

The eight interviews took place in Dr. Johnston's office on the Berkeley campus. Modest, soft-spoken but not self-effacing—he takes credit, for example, for prompting discovery of the Antarctic ozone hole—he spoke slowly and carefully, pausing sometimes to reflect and refer to written material. At the end of each session, we went over topics for the next interview, and, in characteristically diligent fashion, Dr. Johnston prepared in advance for the upcoming discussion.

Dr. Johnston reviewed and extensively edited the interview transcripts over a period of several years, interrupting the work to write and publish two books. He omitted segments, rearranged and re-wrote others, and added graphs, references, and other text enhancements. The resulting document, extensively reworked, is not strictly an oral history. The reader, one hopes, will welcome and respect Dr. Johnston's effort to convey his science fully and precisely. Certainly, the interviewer, out of her depth in respect to Dr. Johnston's field, appreciates his intense effort to clarify and augment. The general reader, daunted as is the interviewer by elaborate formulae, can skip these additions and still learn the contours and context of Dr. Johnston's contributions. For the reader-scientist able to grasp the technicalities of Dr. Johnston's research, this volume may provide a useful synthesis of his contributions and place them in political context in a way which formal scientific publications seldom do. A useful corollary to the oral history are the verbatim tapes and Dr. Johnston correspondence, both available for research in the Bancroft Library. I wish to thank Dr. Johnston for his long and hard work on producing a document worthy of his accomplished life.

The Regional Oral History Office was established in 1954 to augment through tape-recorded memoirs the Library's materials on the history of California and the West. Copies of all interviews are available for research use in The Bancroft Library and in the UCLA Department of Special Collections. The office is under the direction of Richard Cándida Smith, Director, and the administrative direction of Charles B. Faulhaber, James D. Hart Director of The Bancroft Library, University of California, Berkeley.

Sally Smith Hughes, Ph.D.
Historian of Science

September 2005

INTERVIEW 1: JULY 13, 1999

Hughes: Dr. Johnston, I've been reading the draft of chapter one of your very interesting book, which is a combination of personal biography and a saga of your war work. I think together we want to pick up on some of that history to give a background to your science career. Would you start with your family history, beginning with your grandparents?

Johnston: Yes. Most, perhaps almost all, of my ancestors, those of my mother and father, came to this country from either England or Scotland or Ireland. They settled primarily in South Carolina and North Carolina. The section we lived in, which is thirty miles northwest of Atlanta, is Cherokee County. The town is Woodstock, Georgia, and its population was 420 in 1930 and 419 in 1940. It was a local center for services for the cotton farmers.

My great grandfather was named Doctor Medicine Johnston, and my grandfather was named Doctor Medicine Johnston, Jr. When Grandfather was nine years old, he witnessed and heard the Battle of Kennesaw Mountain, Georgia, as the Northern troops slowly forced their way toward Atlanta. Their home was inspected by Union soldiers. They looked inside the house and found there was just an old man and his old wife and two small children. So out of kindness, they didn't burn it, as they were doing to most of the places, but they took all the horses and cattle and chickens. My grandfather lost three brothers in the war and then another one died on the way home after the war was over. So that family was pretty well wiped out.

My great-grandfather died in 1869, when my grandfather was fourteen years old. All of a sudden, he had to take care of his old mother and his sister. He worked as a farm laborer and in the gold mines of north Georgia, and he became a farm sharecropper. He worked hard, saved money, and then borrowed a hundred dollars to buy a farm of his own. He worked on this farm and saved money. Cotton was quite a profitable crop. The land had recently been virgin forest, and the trees had been cleared and burned a generation before, but the land was still good. He kept buying more farmland. In 1888, he sold his farm and moved to the town of Woodstock, Georgia. He set up a general merchandise store. As time went on, he prospered. He became a buyer and seller of cotton, founder of a small bank, bought and sold land. As an investment he bought farm land in south Georgia. He became the patriarch of the town.

He went to court and changed his name from Doctor Medicine Johnston, Jr., to J H Johnston, just plain J H, no periods after the letters, no meaning for the letters. It is a mystery where the Doctor Medicine name came from. It could be that a large illiterate family needed yet another name. Or maybe it was parents wanting some novelty. Anyhow, he didn't like it, and he changed it. With the disruption of the Civil War and its follow-up, he went to school only six weeks in his life. With his later financial success, he saw himself as an example of wherein one has no need for higher education. He could accept grammar school and possibly high school, but college was a waste of time and spoiler of the young.

One example of my grandfather's attitudes was that he liked to play chess. He boasted that few men and no women knew how to play chess [laughs]. I learned how to play chess by reading the *Encyclopedia Britannica* and played some games with him. He won all the games, but I gave him a surprise. He had to pay attention!

[Reading from a page in *A Bridge Not Attacked*] “When the men of the family came back from hunting or fishing, they dumped their dead ducks or fish or whatever into the kitchen sink, and ‘pore little Grandma’ had to pull out the feathers or scrape off the scales and clean them, as well as cook them. In later years, she had help from a house servant. Several times a year on holidays or on a Sunday, Grandfather and Grandmother fed their grown children and their grandchildren a huge and varied mid-day dinner, typically including two or three meats, such as turkey, ham, roast beef, occasionally venison or opossum, on one occasion bear, and many vegetables. The men ate first, and the grandchildren were warned most strongly to behave even though they were hungry. The men sat around talking politics long after eating their fill. Finally the women and children got their turn. Grandma warmed up some of the food, but much of it was cold, and she sat around eating nothing herself until the women and children had almost finished.”

Grandma Johnston had nine children, and seven of them survived to adulthood. My father, Smith Lemon Johnston, wanted to go to college be a Methodist preacher.

Hughes: Was that the usual route to joining the ministry?

Johnston: Ministers had to have a couple of years of college, something like that. I’m not sure whether my grandfather opposed it because he thought it was a waste of a life to be a preacher, or whether he just hated to see his son going to college. Anyhow, they had a fall-out for a time. My father locked himself in his room, sort of went on a strike. When he reached age twenty-one, he went to Young Harris College, but he had to pay his own way. A year working and taking courses was all that he could stand. Then he gave up and went back to work at the store. I think he got some accounting training.

Hughes: He dropped out of college because his money ran out?

Johnston: That, and probably continued pressure from home.

On my mother’s side side of my family , we’ll go back further and move along faster. Before 1830, the Cherokee Indians had their nation on the property we grew up on. They had a written language and their own newspaper; they were farmers, not hunters and gatherers. They wanted to get along with white people, to coexist as separate nations. Gold was discovered in Dahlona, Georgia, in about 1830, and there was a minor gold rush. Many people came in temporarily and occupied the territory. The legislature of the state of Georgia step by step moved in against the Cherokee Indians. The legislature declared that the whole area was to be surveyed into 200-acre lots and forty-acre lots.

After the Cherokee land was surveyed, the state legislature declared that anybody who wanted to apply for free land could join the lottery. Many people won land in the lottery. The forty-acre lots were where there was some prospect of gold. One source of gold was Rose Creek, which flows close to Woodstock. The 200-acre lots were for people who wanted to farm. The Cherokees were forcibly ejected from the land and went on the Long March to Oklahoma.

Hughes: The Trail of Tears.

Johnston: Yes. The Trail of Tears is a famous, sad story in our history. The Cherokees were forcibly uprooted and sent to Oklahoma, where they stayed until oil was found on their land, and then they were sent somewhere else. By lottery, the state of Georgia gave white settlers portions of land according to the state survey.

One of my ancestors, Great-Great Grandfather Joseph Stallsworth Dial (1793-1867), was born in South Carolina and moved into the Woodstock area after the lottery was over. Apparently, he had some money and he bought and sold farms. When people gave up and left, he'd buy their farm cheap, and when somebody else came and wanted a farm, he'd sell it to them at a higher price. He accumulated extensive acreage between Woodstock and Sweats Mountain. He lost some of his land in a lawsuit, and he built up enormous acreage for himself, more than two thousand acres in what is now suburbs of Atlanta.

Hughes: Is that land still in the family?

Johnston: No. A little bit of it came to my mother's estate, about sixty acres, which she sold in her old age.

Joseph Stallsworth Dial built a large home on his working farm, but it had no gleaming white columns on the front porch. When he died, his properties were divided among his four children. My great-grandfather, William Choice Dial, inherited a fairly large block of land. When he died, he divided it up four ways, among his children. One of his children was my maternal grandfather, "Grandpa Dial." My maternal great grandfather, William Choice Dial, 1826-1902, was a captain in the Cobb Cavalry, and was wounded three separate times in the civil war. For a time, he was a member of the Georgia state legislature.

My maternal grandfather, William Choice Dial, Jr. (1868-1940), well dressed, handsome, and arrogant in his photograph at age twenty, eloped at age twenty-one with Dollie Gresham, age eighteen. The newspaper in 1889 wrote a short story about the triumph of young love over parental disapproval. Thirty months later, Dollie died of pneumonia leaving Florine age fifteen months and Dollie age six weeks. Dollie was reared by her Grandmother Gresham, and Florine, my mother, was reared by her aunt, Elizabeth Dial Latham, who ran a boarding house in Woodstock for working young ladies and for traveling salesmen. The next picture we have of Grandpa Dial shows him at age twenty-five with bleary eyes and a desolate face.

Hughes: Was that unusual, to have a family broken up?

Johnston: Yes, but William Dial became a heavy periodic drinker. I don't know if that was some of the reason for the Greshams' disapproval or whether that came later after his wife died. After his father died in 1902, Grandpa Dial farmed on his inherited one hundred and sixty acres, married again, and had three children. In time he sold half his farm, then lost the rest to the bank except for one acre and his home. The house burned down, and he moved to a small house in Woodstock, which my father, Smith Lemon Johnston, Sr., bought and gave to him. Grandpa Dial brought with him his two large Belgian work horses, which he worked for hire. To fund his necessities, these fine horses turned into a pair of ordinary horses, later they turned into two mules, then one mule, and then it was

gone. At age seventy-two he died in the early morning hours on a cold January night beside the street in Woodstock.

My mother was extremely interested in education. She read books from an early age, and she played the piano rather well, and wished she could go to college. A well-to-do relative had promised her that when she got out of high school, he would pay her way through a four-year college, and she looked forward to that, of course. When she graduated from high school ready to go to college, this relative had died, and his money was all gone. So she couldn't go to a four-year college. Her aunt and uncle supported her for two years at a teacher's college. Then she taught school when she was still quite young, and many students were bigger than she was.

After Father and Mother were married, they built a home in Woodstock on about a one-acre lot, across the street from the railroad track. The train rumbled in and out two or three times a day. The front of the lot had the house, and behind the house was the garden, and further back there was a cow barn. They kept one cow and rented a pasture for it. They usually kept a pig or two and a flock of chickens—and lots of flies. [laughter] There were still lots of horses and wagons. The farmers would typically bring their cotton or their sorghum cane into town on a horse-pulled wagon.

When my father came back from one year at college, he joined the store, the family business. He had been very anxious to have education of his own, and so both parents were strongly determined to see that their children got a college education. I have three brothers, one older and two younger, and all four of us were given a college education.

Hughes: Which was unusual for Woodstock?

Johnston: Yes. Furthermore, my older brother and I went through college during the worst of the Depression. The economy had been based on cotton raising. Back in the early days, when the land was fertile, people made large amounts of money raising and selling cotton. But by the time of the Depression, the cotton-growing lands had been stripped of their fertility, most topsoil had been washed away, leaving gullies in what were once fertile fields. The boll weevil, an insect that eats cotton buds, arrived from Texas and moved in. So it was quite a sacrifice on my father's part to see that all of us got to and through college.

Hughes: How did he manage?

Johnston: Well, the general merchandise store was still going. He also had a small insurance agency on the side. He was a partner in the little bank.

Hughes: He sounds as though he was quite a figure in a small town.

Johnston: Not in the way you might think. Each of these jobs was small and yielded only a little money. He was a very fine man, he lived a fairly hard life, in that he was totally overshadowed by his father, who was a stern, domineering fellow.

When I was thirteen, I had rheumatic fever, which did moderate to severe heart damage. At first the doctors wouldn't tell me what the prognosis was, but I could read and found out that the average survival time was about fifteen years.

Hughes: Fifteen years from diagnosis?

Johnston: Yes. As time has gone on, I've had a moving ten-year life expectancy. Almost every decade I have understood that I probably wouldn't last till the next one.

Hughes: Did it shape your ambition?

Johnston: Yes. I couldn't do sports, and I couldn't do all kinds of things, but I did a lot of reading.

Hughes: With a shorter expected life span than the average, you might have felt pressured to try to accomplish faster.

Johnston: Yes, you've figured that out! I really wanted to do something special, so I decided I'd write the Great American Novel. You've heard that before! In high school, I worked on the newspaper. The high school was a two-story building. I was not supposed to climb stairs, not even one flight. My home room was upstairs, so I was given a desk in the library on the first floor. When the students marched down to chapel every day, I'd get in line with my class. When they went back up, I filed off and returned to the library. I finished my high school requirements with courses offered on the first floor!

One of the courses I took in high school was journalism, which I liked very much. I took the course in my junior year, and then I was editor of the high school paper in the senior year. The *Atlanta Journal* newspaper sponsored scholarships at Emory University for the best high school newspapers in three categories according to the size of the school. My school was in the smallest category, and I got the scholarship, \$200 in 1937. That determined where I was going to college, although I probably would have gone there anyway, since my brother Smith had entered there two years before. I recently came across the total of my expenses during the first year at college—\$676.50, so the \$200 paid almost a third.

Hughes: You mentioned some of the facts about your parents, but did you feel close to them? What was their attitude about discipline? How did the family interact?

Johnston: I'll work on that. Back in those days, corporal punishment was the expected thing, and if an infraction was serious, we'd get whipped by Father when he came home, and that created a certain distance. I came to admire him after I was grown, but during childhood it was a struggle. All kinds of things were sins in those days: playing the game of bridge, dancing, any work on Sunday, and it went on from there. Mother had to switch us when the crimes weren't too bad. That made for some tension.

My older brother, Smith Lemon Johnston, Jr., was a star baseball player. He loved it. At home after school for practice, he'd toss rocks up in the air and hit them with a stick. In the neighborhood he was the leader in interesting activities, including mischief. With the older brother I had some competition, some conflict. My brother, Richard Johnston, three years younger, was a friend. We walked in the woods, climbed trees, and scoured newly ploughed fields for Indian arrowheads and other artifacts, and went fishing. My youngest brother, William John Johnston came along about twelve years later, and he was the baby. He and I became very good friends.

Hughes: And remain so today?

Johnston: Yes. I go back and visit there about once a year—the three brothers, their wives, children, and grandchildren.

Hughes: They're all in Woodstock?

Johnston: In Woodstock or near there. Some of their children live far away, but there is still a large contingent in north Georgia.

Hughes: Was church-going a big part of the family routine?

Johnston: Absolutely! You couldn't look at the funny paper on Sunday until after church! There were revival meetings in the Bible Belt, which would go a week or two in the summer and twice a day. Very emotional stuff. I became a closet religious fanatic from about age ten to sixteen or so.

Hughes: In what way?

Johnston: Well, I read the Bible all the way through twice—begats and all. And I was active in the Sunday school and indignant about the sins of others. I never told anyone that I planned to be a Methodist preacher.

As I say, I've done much reading, and some of it was about religions. At age sixteen and seventeen, when I was in college, I made a point of going to a different church every Sunday—other Protestant denominations, Catholic, Eastern Orthodox, and some "Holy Roller" meetings. I read about Jewish, Islamic, and Hindu religions. I asked myself, how could all these sects believe that everybody else was going to go to hell, but not them? All of sudden, one day I just saw through it all. No big turmoil or spat about it. I just figured they were all wrong.

Hughes: Did religion drop out of your life at that point?

Johnston: Yes. When our children came along, we went to church some to give them some experience and contact. When they complained about it, we stopped.

Let me give some additional information about my parents. In the 1930s, there was bad luck in the cotton industry. The boll weevils came up from Texas. The farming practiced there had not been concerned with soil conservation, and the topsoil was almost gone. Gullies appeared in the fields, and productivity went down. And then there was the Depression, when the price of cotton dropped to very low values.

Hughes: Do you remember that?

Johnston: Yes. My father worked with farmers to shift from cotton farming into the chicken business. Now, chickens are raised in huge factories. Then, an individual farmer could have a house and a couple thousand chickens and make a living.

Hughes: Your father was looking for something that didn't require growing because the soil was depleted?

Johnston: Yes. The soil was in bad shape. Later, the Soil Conservation Service came in, and where fields were badly gullied, they planted kudzu vine. That stopped the land from eroding, but the kudzu vines overran the fields.

When I went to Emory University, I majored in English literature the first three years.

Hughes: Was that because of your journalism experience?

Johnston: Journalism, and ambition to write a great novel. I tried in the summer to do some writing, but I came to see that anything I did was derivative—I had no good ideas.

Hughes: What was Emory's reputation in the late thirties?

Johnston: It was a small school. There is quite a bit of good marble in north Georgia. Just twenty miles north of us there was a rich vein. Some of the best marble anywhere has come from there. Sam Tate, the man who developed the marble business, was rich, and to Emory University he donated marble to build the outside of the buildings. They were gorgeous buildings, spaced far apart on a large campus with a lot of trees. I heard an administrator sigh: "I wish we had some of that marble money on the inside." The Depression lasted there at least until the war started. Emory was a good local school; it was not in the running so far as top research was concerned.

Hughes: The student body was local?

Johnston: Mostly, but a significant number came from other Southern states, and a fairly large contingent came from New York and New Jersey.

Hughes: Why was that?

Johnston: It was a pretty place, relatively nice winter climate, not very expensive, and gave good undergraduate instruction.

Hughes: Was that your first real dealing with Northerners?

Johnston: Yes.

Hughes: Did you have any feelings about that?

Johnston: No, no resentment whatsoever!

Hughes: Your family wasn't still fighting the Civil War?

Johnston: No. Grandpa Dial still was. I played the clarinet for a time, and I often practiced on the front porch. Once when I saw that Grandpa Dial was approaching, I played "Marching Through Georgia." Grandpa Dial didn't get mad; he just start telling the story about his father "carrying to his grave a Yankee bullet in his back." So he was still fighting the Civil War, but not my parents.

Hughes: How was the instruction at Emory?

Johnston: It was very good in most courses.

Hughes: Had you been well prepared by your local high school?

Johnston: Yes.

During my junior year in college, I realized that I wasn't going to write a great novel. Simultaneously, World War II was pending. A lot of people predicted it was going to start.

Hughes: Was it pretty clear that the United States would be involved?

Johnston: Yes. The war in Europe started in 1939, between sophomore and junior years. We were in the Lend-Lease Program, shipping all the goods and military equipment we could to Britain. I took a course from a brilliant history teacher, Moses Harvey, at that time. He later moved on to somewhere else. He was young, pessimistic, and passionate. In World War I, there was in this country some propaganda that pictured the Germans as Huns and savages and villains. Recollections of that propaganda survived. The students at that time thought, "We're not going to pay attention to all this scare stuff about the Nazis. It's just the same thing over again."

Once in the history class Harvey was challenged on the subject, and he gave an almost passionate lecture, how Germany had just knocked out Poland and was beginning to knock out France. He predicted, "Germany will turn and defeat Russia next." At the time, Germany and Russia they were still allies. "Hitler will have all the power and fury of the whole European continent behind him, and then he will take on Britain. If we join the war soon enough, we can survive as a country. If not, with that much power massed against us, we're in for a bad ride, possibly an invasion. You can be cynical now, but in a year or two all of you will have uniforms on."

Hughes: What year was he saying that?

Johnston: Nineteen-forty. Yes, the spring of 1940.

I knew I wouldn't be drafted. That was not the point. But I'd be left out! I thought I could be of more use if I switched to a science rather than if I tried to stick to English and write a book. The only science I had taken through my junior year was a course in freshman chemistry. So the only science I could major in and get out in one year would be chemistry.

Hughes: Had you felt anything particular about the chemistry course?

Johnston: The freshman chemistry course was rather easy.

Hughes: It wasn't all of a sudden a light bulb going on?

Johnston: No. The professor, J. Sam Guy, made analogies like this, "If every molecule of sugar in one pound of sugar was as big as the one-pound box, you could pack them in a freight train which would go to the moon and back five billion times." In the dormitory, my

buddies and I would imitate him with different examples. Some of it was slightly off-color, so I won't go into that.

But one or two other things gave me some latent liking of chemistry. At the junior high school level I read and liked *Boy's Life* magazine. There were two or three articles that made an impression. One was a story about a rich old man who had bought a run-down house and was going to fix it up. It had a weedy yard. He had hired a young man to clean up the yard for him. He came there with three companions to check up on the boy's work. He declared that the yard boy wasn't doing the job right, so he gave him a terrible verbal lashing. He went over to test the water pipe to "be sure it was off." He and his three witnesses wandered off. A few minutes later, the yard boy saw purple flames through the window, and the house burned down. The owner collected the insurance, and the boy was charged with arson. The motives were clear: the boy took revenge for the criticism he had received. Three disinterested witnesses supported the old man's account.

The boy was almost certain to go to jail, but in the trial he described the purple flames. He had never seen flames like those before. The pharmacist of that town had a suspicion as to what might have happened. He found that the water hose went into the house, and he found the metal fittings at the end of the hose. At what had been the end of the hose, he collected ashes, analyzed them, and found them to be high in potassium. Potassium is a metal which catches fire in contact with water. To me, it was the fascinating that water should start a fire. Somebody discovered that the old man had bought two pounds of potassium and kept it in kerosene. He put potassium in the house, brought the end of the hose there, and started the fire by turning on the hose. I was very impressed by this story. I did a lot of reading in the encyclopedia at that time about such things.

Sodium is the younger brother of potassium, it also catches fire in water, but not so violently. An advertisement in *Boy's Life* offered three ounces of sodium for sale through the mail, and I bought it for \$1.65. It came in a little kerosene can. If one tosses three ounces of sodium in a stream or a lake, it would give a good Fourth of July display for a few minutes. But I figured out how to get more fun out of it. Take a little tiny piece, about the size of a pea, put it in a small can with a thin layer of water on the bottom, and the sodium starts jumping around and sparking. Then put a big tub on top of that—and run! When sodium reacts with water, it generates hydrogen, which mixes with the air. The sparks would be the sparkplug to set off the explosion, which sends the tub up about ten to twenty feet. We did this operation over and over again.

Hughes: Had you just figured that out, or had you been reading?

Johnston: I read about sodium in the encyclopedia, but I had never heard of anyone blowing up tubs this way. And another thing: I did get a chemistry set for Christmas one time.

Hughes: You liked that?

Johnston: Well, some, but it wasn't a big cause for my choosing chemistry.

Hughes: If the war had not come along, you might not have ended up in chemistry?

Johnston: That is correct. I had one year of freshman chemistry—no math, no physics—and I wanted to get out of there in one year. So I went to summer school and took extra courses all through the senior year. I did a full chemistry major in one year.

Hughes: Was it apparent to you that you had ability?

Johnston: The standard instruction at Emory was three courses per quarter; each one met five times a week. An honor student was permitted to take four courses, and nobody was permitted to take five. After the second quarter, I took four courses every quarter. I was making almost all A's. I had learned how to study and make good grades.

As I approached the end of the senior year at Emory, I thought that I would get a job in some industry nearby. Twelve miles from Woodstock, Lockheed had set up a big aircraft factory, probably in anticipation of war, where I might get a desk job. The head of the chemistry department, J. Sam Guy, said, "No, you should go to graduate school." I wouldn't have known to go to graduate school unless he suggested it.

Hughes: Because he recognized that you were very bright and able?

Johnston: He suspected that I might be able to do it. I asked him, "Where should I go?" He said, "Caltech. It's the best in the country. Apply there." He also recommended that I apply to several lesser schools.

Hughes: And had you ever heard of Caltech?

Johnston: No. Anyhow, I applied to Caltech and for some reason got in.

Hughes: Did you have all A's in chemistry?

Johnston: Yes. The B's I made were in English and German. I guess Caltech figured I might be a good student or I would flunk by Christmas, so they took a chance.

Hughes: Is this your surmise?

Johnston: Yes. My physical chemistry teacher, Bill Jones, at Emory spent a sabbatical year at Caltech the same time I was coming out, and I rode out with him and his wife. We spent two weeks on the way out. We saw lots of canyons, mountains, and motels. Yellowstone, Grand Canyon, Zion Canyon—and more. A wonderful trip. We drove in over the San Bernardino Pass into Los Angeles. I had heard talk about the beauty of Los Angeles, pictures with the green orange trees and the orange oranges and the blue sky and so forth. By golly, the Los Angeles basin was smoky and dirty looking. Smog hadn't been discovered yet. It wasn't true smog yet, but it was the precursor.

When I was accepted, Caltech said that I should expect to take four years to get a Ph.D. degree rather than the usual three because I had some catching up to do. I took the physical chemistry course, and Linus Pauling's "Nature of the Chemical Bond," and a course of inorganic chemistry.

The physical chemistry was far beyond what I'd had at Emory. Professor Stuart Bates came into class the first day, he named the textbook, and he assigned some problems to

be turned in next time, and then he walked out. At the next class meeting he asked, "Did anybody have any trouble with the problems?" He sat and talked to the bright guys, asking them how they had done the problems, went to the board and with his back to us, he demonstrated another good way to do the problems. I really had trouble.

I received a scholarship to Caltech, which covered full tuition plus fifteen dollars a month. My assignment for the scholarship was to grade the problems of students in the undergraduate course in physical chemistry. They used the same textbook as the graduate students, and they went faster than the first-year graduate students. When I got their papers, I soon came to understand that two students always got them right. So I learned how to do the problem by "correcting" their papers. In that way, I passed the graduate physical chemistry course. The inorganic chemistry course, taught by Professor Don Yost, was well taught and of high quality, but it had some concepts I'd never seen before.

The challenge was Professor Linus Pauling. He would come strolling into his class with a big smile on his face and with no notes. He was a brilliant lecturer. He had a pleasant, clear voice, enunciated clearly every syllable of every word, and he was athletic in his presentations. He'd write stuff on the blackboard; he'd write other things in the air.

For a long time, I didn't understand anything Pauling said. I took copious notes and studied the book, but he was always about two weeks ahead of me. I spent the full time during the Thanksgiving holiday trying to understand that course, and finally I saw what he was up to.

Hughes: Were other people having trouble, too?

Johnston: Not so far as I could tell. The other graduate students came from Princeton and Harvard and Berkeley. There may have been some person in my state of ignorance. I didn't tell anybody I was having trouble. If Pauling had given the final exam before Thanksgiving, I would have flunked and probably gone back to Georgia to work at the Lockheed plant. When the exam was given in early December I had learned enough to get a grade of B. I got by the fall quarter with two A's and one B.

Caltech expected every graduate student to start research during the first quarter. I talked to some of the professors about their research work and about what my initial assignment would be. Pauling awed me so much, I didn't think of doing work with him. I had no idea what some of the professors were talking about. Professor Roscoe Dickinson was the acting dean of the graduate division, and my correspondence had been with him. Dickinson was a very capable and a friendly person, I understood some of the research he was doing, and during the first quarter he became my research director.

Hughes: You chose him because of his personality rather than because of the sort of research he was doing?

Johnston: I understood some of what he was doing! That was a good part of it.

For several months Professor Dickinson had directed a secret war project. His work was behind locked doors in the Crellin Laboratory. The people on the project wouldn't talk

about it. I went to Professor Dickinson in mid-December and asked to join his project. He asked me why I wanted to do so, and I gave a naive patriotic speech. He managed not to laugh and said, "No, your job is to take more courses, continue your education, and I may or may not call on you in the future."

I worked hard during the second quarter, and I managed to get three A's. Then Dickinson called me in and asked if I'd still like to join his project." Oh, yes, yes!" So he said I'd have to pass the FBI security test. I filled out a questionnaire, which required me to list every residence I had had since birth. It was going to take two or three weeks to get clearance for the project. I took that time off to take a trip back to Woodstock. I caught the train in Pasadena and rode across the country and learned how big a state Texas is by riding across it in a slow train. I had a vacation in Georgia and came back.

When I got back, I'd been cleared for confidential but not yet for secret. Secret is, of course, the higher classification. I could join the project provided I didn't read anything labeled "secret." I promised, and although Dickinson's desk was often covered with secret documents, I didn't read any of them.

When I got inside the project, I discovered that they were working on poison gases, that is, chemical warfare. I expected something more exotic. I soon learned that our gas masks were inadequate, we had no effective protection against a gas attack, and all of a sudden we were in a very serious war. Our army had to have good gas masks immediately.

Dickinson's project was to take a small cylinder filled with a charcoal that could go into gas masks and to see how well the charcoal absorbed a poison gas. As a controlled scientific experiment we generated a stream of air with the desired poison gas in it and passed it through the charcoal to see how long it took to come out. The better the charcoal, the longer it would take.

Dickinson's group had an ingenious way to measure how fast the gas came through. An air stream with a gas in it was sent through a charcoal, through a furnace to break down the gas, and then through a flowing stream of water to make ions in solution. The ions had a different electrical resistance from the reference pure water. The resistance of the solution was sent to a strip chart recorder, which recorded the time it took for the gas to break through the charcoal. This procedure was pretty well developed before I arrived.

We got another shipment of things every couple of weeks or so. We did not know where it came from. But somewhere somebody was figuring out from chemistry and physiology books what might be effective poisons. Somebody somewhere else tested the poisons with animals, and if the poison seemed toxic enough on the animals, it would be sent to us to test on charcoals.

On the project Professor Dickinson was the director, John Otvos was a third-year graduate student, and Arthur Stosick was a postdoctoral fellow. They had elaborate systems set up; much of it was automatic. Art was very good at electronics, and so he built fancy electronic circuits and controls coupled to a recording meter.

Hughes: Why had Caltech been chosen for this gas work?

- Johnston: The National Defense Research Committee [NDRC] was made up of high-level academics. In consultation with high officers in the army and navy, top management of the National Defense Research Committee placed research and development projects in many research universities across the country. There were about seven hundred scientists working on NDRC chemistry projects, including work on explosives, rocket fuel, war gases, aerosols, smoke screens, napalm, and incendiary devices. They recognized that charcoals used in gas masks should be tested against old and possible new war gases. They placed contracts to do this work in several universities, one of which was Caltech. Professor Dickinson and Professor Yost were given projects in this field.
- Hughes: And what was the field?
- Johnston: The ability and equipment to handle corrosive gases and to study gas reactions, and especially ingenuity and creativity in research.
- Hughes: So it was a logical assignment.
- Johnston: Yes, and Dickinson was invited to apply.
- Hughes: What state was the chemistry of gases in when the war came along? You were taking what I presume was fairly basic chemical research and applying it to killing the enemy!
- Johnston: Just before and when the war started, our country was found to be very poorly prepared to defend itself against war gases. At first we were testing whether our gas masks would protect our soldiers. We focused on saving our soldiers, not on killing the enemy.
- Hughes: That was the main thing.
- Johnston: At first, yes.
- Hughes: I didn't put that question very well. I'm trying to get at how much more chemistry needed to be done in order to make the knowledge applicable to the war effort.
- Johnston: Well, we're always citing the advantage of pure science. In a war like that, there is no time to do the basic science. We had to take what was known already and put things together in a different way.
- Hughes: So you could pretty much take the knowledge and bend it to the purpose without having to backtrack, so to speak.
- Johnston: Yes. Now, let me reword that. Professor Dickinson and Dr. Stosick had enough knowledge to do these things without looking things up in books.
- Hughes: So the knowledge was there, which was why the committee had made the assignment.
- Johnston: We have to go back one step then. Very early in my experience in the lab, when I was still very green, I noticed the big water bottle they had up on the shelf. They had lines on the bottle that showed the level of water, and the water level had to be measured frequently for us to calculate how fast the water was flowing, because the pressure kept

changing as the water level was going down. Water flowed through a constriction, which determined the flow rate. I looked at it and said to myself? “Why did he do it that way?”

So I pointed out that, instead of reading the water level at various times, we should install a glass tube through the rubber stopper on top of the bottle to go down to the bottom of the bottle and open to the outside [demonstrating]. Then we would always have the same pressure of one atmosphere on the water coming out.

Dickinson asked me, “Where’d you get that idea?” I had to admit, we used to raise chickens in the yard and we had to fence them in or they’d run out in the road and get run over. There’s a standard device that looks like a four-cornered star and is sold in the stores, which was to be screwed on the lid of a half-gallon jar. When it was turned upside down, the water would half fill the little troughs and maintain the level regardless of how much water was left in the jar. It had the same mathematics and physics as this new method I was proposing.

Hughes: It was like a hummingbird feeder?

Johnston: Yes. So I explained to Dickinson about the chicken device. He turned to John Otvos: “John, why didn’t you think of that?” John said, “I guess because I never was a chicken farmer.” [laughter]

John Otvos showed me around the laboratory and some of the various samples. He pulled one out, and he shook the glass; it was sealed at the top. There was a clear liquid inside. It’s no secret anymore; it was di-sulfur deca-fluoride, S_2F_{10} , and in the laboratory we called it “stoff-stoff,” pronounced in German. In a calm voice, John said: “It’s colorless, odorless, and poisonous as hell—four times as toxic as phosgene. One breath of it and you die in a few hours, drowning in your own blood and water. And there is nothing that anybody can do about it.” We had to find out quickly whether our charcoals would absorb it. The army wanted to obtain enough to test it in a bomb. We were about the only place in the country that could make it fast.

The army brought their container for transporting the material, and left it at nine a.m. for us to fill. Dickinson and Stosick transferred the S_2F_{10} to the army’s glass container, but they didn’t come back until long after lunch. After returning from a late lunch at about two p.m., Dickinson discovered that the glass container was cracked, and all the gas had escaped into the room. The room had two exhaust hoods, and the gas had been in a container near, but not in, a fume hood. That was an exciting day. Professor Don Yost, an inorganic chemist, had a big fluorine generator. Professor Dickinson borrowed this monster from Yost to manufacture a large sample of the stuff. It’s a long, tedious process to make a few grams per day. We saved each day’s product in a large glass container. Dickinson finally said, “We have enough; the army will come by and get it.”

Hughes: How did you deal with the leak?

Johnston: We didn’t. It was all over with when we discovered it. It was all gone.

Hughes: And you just waited until the fans took it out of the room?

Johnston: We couldn't tell if or when it was present. It was colorless and odorless, and "four times more poisonous than phosgene." Dickinson said the fans probably carried it up the chimney, or it could be that it all escaped during the hour we were out for lunch. I and the others were aware of the third possibility.

Hughes: You were lucky!

Johnston: Yes. We knew from reading the hazard pages that we could receive a fatal dose with no symptoms for up to six hours.

Hughes: Yes, how would you know?

Johnston: We couldn't know until symptoms appeared, which might take up to six hours. So rather than our sitting around a hospital room reading two-year-old *Reader's Digests*, Professor Dickinson put everybody back to work. The project had two rooms, and Dickinson sent John and me to make some more S_2F_{10} . He and Art Stosick put on gas masks and cleaned up. John and I manufactured more stuff that afternoon.

Hughes: Do you remember how you were feeling?

Johnston: Oh, yes! I vividly remember and later wrote it down. Well, when it was first discovered, I was sure I had been exposed to a fatal dose of gas, and I felt a full body fear. Then in a minute or two I got used to the idea, and instead of being terribly afraid, I felt a sad, slightly sick feeling for the rest of the afternoon.

The fluorine generator was a big hunk of equipment which, as I mentioned, we got from Professor Yost. Professor Yost had worked out a method to make S_2F_{10} much more efficiently than the method the army had used. It took about three hours to make a batch. The first two hours are very intense work for two people. We made fluorine and reacted it with sulfur at a moderately high temperature. The main product was SF_6 , and S_2F_{10} is a minor byproduct. The way to make fluorine was to pass a direct current through a solution of sodium fluoride in hydrofluoric acid. Sodium fluoride is a solid at room temperature. It is mixed with hydrogen fluoride, which is a gas at room temperature. At a moderately high temperature, the combination of sodium fluoride and hydrogen fluoride is a liquid, and being a liquid we passed a direct current through it to generate fluorine, F_2 , and hydrogen, H_2 . Of course, we had to keep those two gases separate because together they are wildly explosive.

To test whether any fluorine was coming out of our machine, John took long metal tweezers with a little piece of cotton on the end, dipped it just slightly in alcohol, and held it up. If it caught on fire, fluorine was coming out. [laughs] Then we diverted the fluorine into a monel tube furnace with a copper boat full of sulfur inside.

Hughes: Now, was this something that most chemists would know how to do?

Johnston: No, it was a highly specialized procedure.

Hughes: This was a synthetic technique that Dickinson had developed?

Johnston: Well, no. Most chemists wouldn't know how to do it, but others had developed it in the past.

Hughes: Was it in preparation for use as a war gas?

Johnston: No, S_2F_{10} is a byproduct in making of SF_6 , which has several uses. SF_6 is about the most unreactive compound known to chemistry. It's in the atmosphere and not destroyed by ultraviolet radiation, even in the stratosphere; it doesn't dissolve in water; it takes an extremely high temperature to break it down. But S_2F_{10} may be regarded as two SF_5 "radicals" hooked together through a sulfur-sulfur bond. There are enzymes in the lung that break sulfur-sulfur bonds, which in this case would form SF_5 , which is extremely reactive.

Hughes: Why would evolution create an enzyme to break down a sulfur-sulfur bond?

Johnston: It is an important biological process to have sulfur-sulfur bonds made and broken.

Hughes: Oh, it's part of normal physiological reactions?

Johnston: Yes, normal enzymes include sulfur-sulfur bond breakers. And when S_2F_{10} comes along enzymes break it down to highly destructive SF_5 .

Hughes: Please go back to your story.

Johnston: Well. That afternoon, between jobs, I did a lot of thinking.

After three hours of work, we got the sample and took it back to the laboratory. We still hadn't waited six hours to see if symptoms would develop. When we got to the other room, Professor Dickinson and Dr. Stosick were smoking. They were both chain smokers or pretty close to it. In some of the safety manuals we had, it stated that the first symptom of damage is a bitter taste in the mouth when one is smoking a cigarette. So they were smoking like crazy! They were testing themselves like canary birds. We didn't say anything, and they didn't say anything about why we were sitting around smoking and waiting.

Hughes: What could have been done?

Johnston: Nothing.

Hughes: Nothing?

Johnston: Beyond a certain degree of exposure, nothing. John Otvos had said when he first showed me the S_2F_{10} , "One breath of this, and in a few hours you die, drowning in your own water and blood, and there is nothing anyone can do about it." It reacts with the lungs, probably depositing up to ten units of hydrofluoric acid (HF), also called hydrogen fluoride. Hydrogen fluoride on the skin forms deep ulcers, which take several weeks to heal. It would be extremely damaging to the lungs. But fortunately, charcoal in our gas masks stopped it.

We had finished the preparation, and there wasn't time enough to do anything else. The professor said, "Well, if I had some beer I'd give it to you." And he started, most uncharacteristically, reminiscing about himself. He grew up in Puritan New England, and I noticed a number of parallels between Puritan New England and Bible Belt Georgia.

Dickinson explained to us that an outstanding chemist, Professor A. A. Noyes, was brought from MIT to Throop Polytechnic Institute in Pasadena. Noyes, astronomer George Ellery Hale, and physicist R.A. Millikan led the transformation of Throop Polytechnic Institute into the California Institute of Technology. Roscoe Dickinson came to Caltech with Noyes.

Hughes: So Dickinson had been at MIT.

Johnston: Yes. He got a chemical engineering degree at MIT, and then he went to work with Noyes at MIT as a lab associate, postdoc, whatever you call it. He didn't like the industry aspect of chemical engineering. He'd rather study something new rather than just be the servant of industry.

Hughes: He was a basic research person.

Johnston: Yes. He used x-rays to discover the positions of atoms in crystals before 1920. He wasn't the first one to do it, but he was one of the best at the time. He was the first person to receive the Ph.D. degree from Caltech.

Hughes: Was that fairly typical of Caltech, where the emphasis was primarily on pure research?

Johnston: Yes, indeed.

Hughes: Was there any stigma about having industrial connections?

Johnston: The chemical engineering division both at MIT and at Caltech had good people. They applied pure science to the problems of industry. There was no stigma attached to it. Dickinson preferred pure science to applied science.

Hughes: How interactive was the chemistry department?

Johnston: All of the professors knew each other well.

Hughes: Were the research projects relatively separate?

Johnston: Yes, they all were separate.

Hughes: So Pauling, for example, was off doing his thing, and Dickinson would be doing something else.

Johnston: Yes. Pauling had been one of Dickinson's graduate students. Dickinson used x-rays to find exactly where atoms were located in crystals. He used mostly inorganic chemical crystals in his x-ray work. Pauling went to Germany and came back with a method of electron diffraction, which gave information about how far the atoms were apart in

gaseous molecules. Later, using x-ray diffraction, Pauling studied the crystal structure of amino acids, poly-amino acids, and then the crystal structure of simple proteins. Before I left Caltech in 1947, Pauling was getting deeply into biology.

Hughes: And, of course, he eventually—we're jumping ahead—came close to working out the structure of DNA.

Johnston: Right. He was hot on the heels there.

I want to return to that afternoon when Dickinson was reminiscing. He told about his life and his youth. He came out to Pasadena. He could play the cello at a near professional level, and he often had others at his house who would make up a quartet. They played Beethoven string quartets, as well as others. It was a social feature in his life. He made friends with some people in Hollywood. In this chain of associations and friendships—what do you know—some of them were Communists.

When Dickinson got his invitation to set up the project, he went to the local FBI office and said that he would not give their names, but some of his friends and associates were probably Communists. Dickinson said that their political beliefs did not affect him one way or another, but if the FBI were going to object, he wouldn't waste time trying to set up the project. They looked the case over and gave him the go-ahead.

Hughes: Were you actually involved in testing how protective the gas masks were?

Johnston: We never tested a whole gas mask itself on our project, but we tested the ability of charcoals to stop these new things that might be war gases. On the shelf of our laboratory, there were a number of different charcoals. Dickinson told us what charcoals to test with each new case. We systematically went through many gases and many charcoals to see if our gas masks would be safe. One set of gases came in with a special warning. It had the ability to close down the pupil of the eyes, and it was also poisonous. Our charcoals stopped these new gases. After the war was over, these gases were found to be closely related to nerve gases.

Hughes: And nerve gases were not yet known?

Johnston: No, we discovered nerve gases when our soldiers found it in Germany after the war was over. We mistakenly thought we had tested against everything.

Hughes: Was intelligence feeding somebody in connection with your group the information that there were new gases out there to worry about?

Johnston: Our project itself never directly received intelligence information. There were toxicologists, chemists, medical experts whose job it was to look over all the various chemicals they could think of, which might be toxic or could be modified to be toxic. These were screened against animals and came to us to screen with effect of charcoals. Yes, there must have been input to Dickinson from higher levels of NDRC, which got its input from the army and navy.

The army in one of their labs had made tests with charcoals. They passed the gas through charcoals and periodically took gas samples into small evacuated bulbs, and

each of these samples was chemically analyzed by standard wet chemical methods. Our method with electronics and a strip chart recorder got the information needed at least a hundred times faster than the army's procedure.

Hughes: Who had devised that system?

Johnston: Dickinson, Stosick, and Otvos.

After we studied the charcoals for several months in the summer of 1942, there weren't many more poison gas candidates coming in. Professor Don Yost of Caltech stood up at a meeting of the National Defense Research Committee and proclaimed the need for research on offensive gas warfare, not just defensive. If so much gas was deposited in the field somewhere, how far would it go and how long for it to be dissipated?

The aspect of work we got into was to explore, understand, and characterize the dispersion of gases in the field. That had two components: One, we needed scientific instruments to measure the concentrations of the gases as a function of position and time. The method the army used was the cruel and crude one of putting concentric rings of goats around a bomb. They would shoot off the bomb, and see where on their grid the goats died. Two, we needed instruments to make pertinent meteorological and micrometeorological measurements.

During 1942 at Caltech, we developed instruments to measure air temperatures from the ground to about four meters above the ground and to measure wind speeds at different heights above the ground. Our machine shop built the British bi-vane that qualitatively measured vertical and horizontal air turbulence. Dickinson said we should miniaturize our method of measuring gas concentrations by electrical resistance to produce a portable instrument to measure gases in the field.

Our laboratory instrument involved a ten-gallon bottle of water mounted on a high shelf. It was filled with the distilled water, which flowed down a rubber tube into a meter-high buret with a platinum wire spiral in it. The gas being tested flowed up the buret and the water flowed down it. The spiraling water would take out all the soluble poison gases, and then we measured the electrical conductivity in the water that came through. It was necessary to use a pump to push or pull the poison gases into the system. This system was too cumbersome and heavy to be used in the field.

We started thinking about how we might reduce the apparatus in size. I started playing with a water-flow system. When others began making suggestions, Dickinson said, "Leave him alone." After trying several things, I set up a long, gently slanting tube, down which water flowed at a controlled rate, at the top it had a T-tube open to the air, and the flowing water sucked in bubbles of air. As the water slowly flowed down the tube, it looked like a string of pearls. This self-pumping system was key to making our instrument portable.

At our directions, our glass-blowing shop made a spiral of glass which had the length of a meter or two, and we installed it with a two-liter bottle of water mounted above. The water flow itself then pumped in outside air, which eliminated the need for a pump. The electronics and conductive cell were miniaturized to some extent. The output could go to a meter mounted in the box, or to an external strip chart recorder. The system was

mounted in a little box about the size of a briefcase. I have a picture of it. It was in to summer of 1943 before the fully operating system was ready, because we did many other things at the same time—learning micrometeorology and developing meteorological instruments and setting up in various places.

We made simulated tests out in the desert. We set off small smoke flares and took pictures of the smoke clouds, noting the meteorological conditions. Yost's project released sulfur dioxide, made chemical analyses to show where it went and how fast it dissipated, and we tested one of our new "Dickinson meters."

Hughes: You said the electronics had been miniaturized. Was there any prototype for the rest of the device, or was this all coming out of your head?

Johnston: I had nothing to do with the electronics.

Hughes: I know you didn't. But you had a lot to do with the device.

Johnston: Yes, but all the others made major contributions too.

In the fall of 1943, we developed the field instruments to the point that they were manufactured in the local machine shop. It was scheduled to have outdoor realistic chemical warfare tests in the tropical forests of Florida. We had thirty of these instruments in the back of a truck, which we drove to Florida. We also drove a 1942 Buick station wagon.

We arrived in Bushnell, Florida, in the middle of November. There were also the scientists with the NDRC stationed at Dugway, Utah, a group from the University of California at Berkeley, a large group from Northwestern University, and others. Berkeley had developed instruments that measured wind speed, air temperature, and gas concentrations, based on principles totally different from the ones we had developed at Caltech.

I think the army appreciated the help of the civilian scientists, instead of resenting it. The army provided the bombs loaded with poison gases and shot off the bombs. The NDRC teams put out instruments to measure the history of each gas cloud and instruments that measured the pertinent meteorological quantities.

Hughes: These were gas bombs?

Johnston: In Florida, yes. They used a 500-pound bomb of hydrogen cyanide or phosgene or cyanogen chloride, which was the worst of the three.

When I first went out to the test station, the forest was on fire. Both soldiers and civilians had to pitch in and help fight this forest fire. They wouldn't let me do it, because they knew I wasn't healthy. What caused the fire? It was the explosion of a hydrogen cyanide bomb. When they detonated a bomb with hydrogen cyanide, it more often than not caught fire, burned up, so there was no poison gas released.

Hughes: Why had they chosen to do these tests in a wooded area?

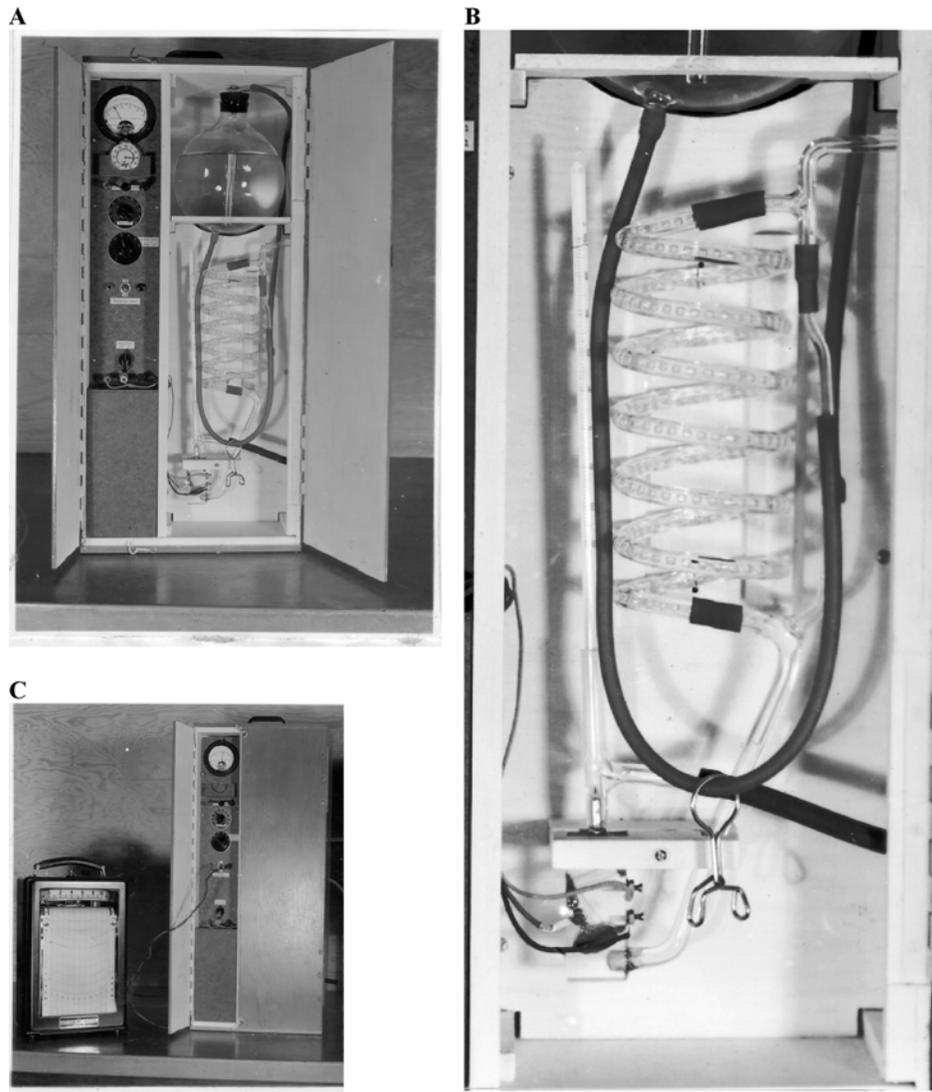


Figure 1. Egbert. Our portable instrument to measure gas concentrations in the field by the method of electrical resistance (conductance). Photographs supplied by John Otvos.

(A) The full instrument.

(B) The glass coil showing the bead of bubbles and the conductance cells at the bottom.

(C) The instrument hooked up to an Esterline Angus recording meter.

Johnston: War in the southwest Pacific.

Hughes: Oh, to simulate that.

Johnston: Yes. In 1942, we had done tests in the deserts of California to simulate North Africa.

So we helped the army do the experiments, collected a lot of meteorological data, and a large amount of data about how the gas clouds spread.

Hughes: Did you have meteorologists in your Caltech group?

Johnston: We had chemists who learned meteorology on the job. The army meteorologists were the weather forecasters. Micrometeorologists were quite different from meteorologists in many ways.

Hughes: Why?

Johnston: Well, the meteorologist was looking for storms coming from a thousand miles away and so forth. Micrometeorology measures what's going on at ground level and up ten or twenty or thirty feet. It's concerned with things like turbulence and local wind speed. Did I mention temperature inversion?

Hughes: No.

Johnston: When you go up in elevation, the temperature mostly goes down. That is caused by the fact that when winds force air up a hill, it rises, it expands, it cools, and that's a simple problem in physical chemistry. The normal thing is to have the temperature go down as altitude goes up. The opposite of that is called a temperature inversion where the temperature is cold below and warm above. With a temperature inversion, air is stable against vertical motion or mixing. It will flow freely from side to side, but it won't go up. It's almost like a different fluid. On the hillsides when the sun goes down, the surface loses heat by radiation, air near the surface is chilled and gets colder than the air above, and the cold air flows down the hill.

We measured that happening in a cow pasture in Pasadena. We had a tall pole with wind vanes about every foot or so up to the top of the pole. In the afternoon, the wind came in from the ocean, the prevailing ocean breeze. About a half hour before sunset, the bottom vane turned and pointed toward the mountains to the north, and a few minutes later, the second one turned, and eventually all the wind vanes pointed uphill. We could see the rise in depth of the cold-air river.

With a temperature inversion, the danger of poison gas is hundreds of times worse than it is during a sunny mid-day, so it was important for us to understand when and where inversions occur. In the Los Angeles basin, a relatively large-scale phenomenon creates inversions much of the time. The land is hot when the sun is on it, and air coming from the west is chilled by the cold Pacific Ocean. There is wedge of cold air pushing under the hot air. Well, that's a temperature inversion, hot air above cold air. That has a lot to do with the smog.

Hughes: And also with fog, right?

Yes. You can sometimes see the top of the inversion layer in Los Angeles or in San Francisco; the smoky haze will go up to a certain height and not more. Johnston:

Hughes: Had any of your group, before the war work came along, been interested in this kind of thing?

Johnston: Not our group. We were physical chemists. Meteorologists were scarce and needed to forecast weather for the air corps. We had to learn it ourselves.

Hughes: Did your group decide to acquire knowledge of meteorology or did the military require you to?

Johnston: At Caltech, we received our instructions from NDRC, not from the military. Things were decided at high levels at NDRC in consultation with the army. Division 10 of NDRC decided to do this sort of work in the summer of 1942, and Dickinson told us about it.

Hughes: Typically, wartime research moved in the direction in which you needed to acquire knowledge to do the job?

Johnston: Yes. At Berkeley, there was the same sort of thing.

At one stage, Dickinson's project was given the job of assessing the shoreline from the Mexican border to San Luis Obispo for particularly vulnerable places for gas attack. And Wendell Latimer's project at Berkeley was to make such assessments from San Luis Obispo to the Oregon border. All along the Pacific Coast there are regions of cold air advection from ocean and thermal inversions. But it became fairly obvious that the worst place was the Los Angeles basin.

Hughes: The military assumed that the Japanese or the Germans, whoever was attacking, would know that meteorology?

Johnston: I don't know the answer to that question. It's probable that they would but not necessarily. Conventional army people aren't very scientific. In the earliest part of the war, there was great fear because we were so poorly prepared to defend against gases, and the Germans had a history of magnificent chemists. And they developed nerve gases without our people knowing about it.

Hughes: There was also the World War I history of chemical warfare.

Johnston: Yes. Also, a gas attack against Ethiopia, as was done by Italy dictator Mussolini, was devastating, because the Ethiopians had no protection against poison gases. But with one prepared army against another, where each army had gas masks and protective clothing, there's no strong military advantage to using gas. If one side started to use it, the other would retaliate, and both sides would at least double their supply problem. But if the other side is weak or defenseless, it could be terrible.

Hughes: But the assumption was the Germans were not weak and defenseless.

Johnston: Yes. We were weak, at the first of the war.

Hughes: You were beginning to talk about the switch in orientation towards an aggressive use of poison gases. You just told me that if the two opposing forces have nearly equal capacity for chemical warfare, it's not a good way to fight.

Johnston: Yes, but it wasn't until two or three years after the war started that we were equal or almost equal. Don Yost wanted to be ready to take an offensive stand, so as to warn them not to start it against us.

During 1942, early 1943, NDRC and the chemical warfare people were searching around the country for suitable spots to carry out chemical warfare tests. One prospect they had was Santa Cruz Island, off of Santa Barbara, in the Channel Islands. And so I spent a most delightful two weeks there making meteorological measurements. Only two families lived there in two huge ranches. The navy had taken over part of one of them for a lookout station, but the owner of the other larger portion was adamantly opposed to having large-scale chemical warfare tests made on his island. Other people were probing other places. The Berkeley group was using non-oxic butane to test sites on Mt. Shasta. And there were actual gas tests carried out in Targee National Forest in Idaho, but that wasn't the jungles they were looking for.

A group composed of representatives from NDRC and the Chemical Warfare Service examined the federally owned Withlacoochee Land Use Area in central Florida, which was close to the town of Bushnell. It was a large area. There were swamps, ponds, and lakes alternating with land above water. Bald cypresses grew at the edge of ponds. Typically, the soil was sandy with scrub pine trees and palmettos. But in a number of places there were hammocks of lush hardwood forests. The group decided that the hammock area was fairly close to the jungles of the South Pacific.

There were interactions at a high level between the NDRC and the army. It was decided to carry out a series of chemical warfare tests there. The first part of it was to use nonpersistent gases, which include phosgene, hydrogen cyanide, and cyanogen chloride. Tests of these gases went on in Florida for about six weeks at the end of 1943. Most tests were with static bombs, that is, gas-filled bombs were exploded on the ground. Dickinson meters and other chemical analytical instruments were placed on a grid around the bomb, and the army placed goats on its grid. We had some air drops during November-December 1943, and we had many air drops in 1944 and 1945.

But then it was decided fairly early in our work that the semi-jungles of Florida were not the same as the jungles of the South Pacific. An NDRC and army team discovered San Jose Island, sixty miles from the Canal Zone, out in the Pacific Ocean, that had been occupied by the San Blas Indians, but they had abandoned it, and the island was uninhabited. And so it was decided to continue the work in Florida, but on a smaller scale, and really go for the ultimate goal by setting up a station on San Jose Island.

All the Berkeley group and all the Caltech group moved to Panama—except for me. I was 4-F in the draft and limited physically, but I had volunteered to go to Panama for this work. Knowing about my health problem, Professor W.A. Noyes, Jr., head of NDRC Division 10, turned down my application. The commanding officer at the station in Bushnell, Florida, was Captain Jake Nolen. He had a Ph.D. degree in chemical engineering at MIT and was very knowledgeable and tough. Dickinson, Noyes, and Nolen worked out a plan for me. I would remain in Florida as head of the

micrometeorological activities, I would report directly to Captain Nolen, and every three months I would have to take a physical exam from the army doctors at Bushnell.

W.A. Noyes, Jr., and Philip Leighton had written an important book on photochemistry. Leighton was a physical chemistry professor at Stanford, and Noyes was at one of the big Midwestern universities—I forget which. Both of them went into Division 10, which concerned the nonpersistent gases. Leighton was made a lieutenant colonel at Dugway to be their technical expert, and Noyes was head of Division 10 at the NDRC. Later Leighton was chair of the Stanford chemistry department, where I had my first job.

So I was left behind to be the chief meteorologist (a fancy title) for the gas warfare group left at Bushnell, and they were going to test persistent gases, mostly mustard. During November and December 1943, we had one standard meteorological station in a large meadow east of the forest, and an identical station in the forest on a brush-cleared site under tall trees. We made temperature measurements from 0.3 to 5 meters (one to 16 feet), where the trees were about sixty feet high. I went to the commanding officer, Captain Nolan, and told him that we needed a steel tower that would go above the tops of the trees so we could make our measurements up to and through the tree tops. He said, “Too bad.” The Bushnell project had been assigned only one metal tower, and the weather forecasting meteorologists in Dade City already had it.

I walked around near our forest station and noticed that in some places a lone pine tree grew up above the rest of the forest. I went back to Captain Nolen and proposed to him that we find a pine tree that extended above the surrounding forest and take off the branches, leaving the stubs, and turning that into a meteorological tower. He talked to the forester of the federal Withlacoochee Land Use Project. The forester had flown over the area many times and knew one place where a pine tree got particularly high above the canopy. It was about a mile away from the section of the forest that was being used for the bomb tests. A crew of soldiers went with the forester to cut off the limbs of the pine tree, leaving stubs for mounting instruments and to help in climbing the tree. Where the stubs were too far apart to climb, they put in spikes, such as those on telephone poles, so I could climb up 75 feet above the ground. We mounted instruments to measure and record temperature, wind direction, and wind speed from the ground to above the canopy of the forest.

Hughes: And you were doing that?

Johnston: Yes, I could do that. But I always had help. Our group included two second lieutenants from the air force and a sergeant who was a chemical warfare professional. He was very good. I have forgotten his name. And we'd have temporary help. Groups of soldiers were sent to the Bushnell operation and stay for a few months, and then they were sent out, probably to Europe. I'd get two or three of those men regularly. I actually did a lot of the work myself, the scientific part, but I didn't have to do any heavy physical work.

So far as I know, we were the first ever to be measure simultaneously the micrometeorology in the forest and in the adjacent meadows. We found some similarities and significant differences. We made these measurements before, during, and somewhat after the army exploded mustard bomb or bombs. The NDRC Division 9 group put out chemical samplers to collect airborne mustard gas. The main purpose of

the army tests was to find out how the gases were transported and dispersed by wind, both in the forest and in the meadow.

As I say, they were persistent gases, mostly mustard gas. Mustard gas or aerosol can cause fatal lung damage. Even a little bit of liquid on the skin leads to damaging blisters, and large amounts on the skin are lethal. Large amounts of vapor can kill by skin absorption. And so it's a crippling gas or a lethal gas, depending on size of the exposure.

The two army doctors at Bushnell rented a large old Victorian two-story wooden house outside of town, which had been a residence, and used it as doctors' offices and hospital. Once, when I was taking a routine quarterly medical examination, I was told that I would have to wait for a long time because an emergency call had come in. So I sat on the front porch, waiting.

A little bit later, a large truck drove up. A group of about eight soldiers stood on the back of the truck, holding onto the side panels of the truck. They were naked except some of them had a sheet draped over their shoulders. They had been injured by a test of mustard gas. They had put on protective clothing and gas masks. A set of five-hundred pound bombs filled with mustard had been shot off in the forest, and they marched in to simulate an actual war situation and stayed there overnight. They marched out, decontaminated themselves, removed their protective clothing, and most got dressed, but the injured ones were put on the truck and brought to the hospital. They had large blisters, typically six inches or more in diameter. One had an almost continuous blister from shoulder to knee. The weight of the fluid in the blisters caused them to sag. The injured soldiers hobbled into the hospital, assisted by other soldiers and by hospital nurses.

Hughes: Was it treated like a burn?

Johnston: Yes, I think probably so. They couldn't sit or lie down. There were about eight injured people who were brought in.

Another story: when they started dropping real live bombs from airplanes, they brought in a small number of planes and their crews. The pilots were very self-confident people. They bragged about their new high-precision bomb sights, and how they could do pinpoint bombing.

One big experiment was all set up to go—the instruments and the goats. The target was heavily marked with whitewash. The soldiers and NDRC Division 9 people who had set up the samplers left the forest and gathered in the meadow about three-quarters of a mile east of the test site. Just to be safe—because the commanding officer always had safety in mind—they crouched behind a double line of trucks. The planes z-z-zoomed overhead and a 500-pound mustard bomb exploded in a tall pine tree about a hundred yards to the east of us. A lot of the GIs had been taking sunbaths, and they scrambled to put on their shirts and gas masks. As we stood up, one NDRC guy said, "I don't call it precision bombing. They missed us by a hundred yards." [laughter]

Arthur Pardee, who was later a professor at Berkeley and a very outstanding cancer specialist at the Harvard Farber Institute, was also a graduate student at Caltech. He and

I worked together for a period of time. Then he got an invitation to work on the atomic bomb project at Berkeley. Of course, it wasn't called that. And so he stopped the chemical warfare research, and the commanding officer was enraged. Here he's giving up this real war research to go back to the ivory tower research in Berkeley!

Hughes: Was your group or anybody else at Caltech concerned with the biology of the reaction to the toxic gases?

Johnston: That would be Sam Ruben at Berkeley.

Hughes: Would this be a good time to get that story on the record?

Johnston: There was a setup in Utah, out in the Salt Lake desert, called the Dugway Proving Ground, which included many thousands of acres. It was a chemical warfare project. They tested the operation of chemical warfare weapons. They dropped gas from airplanes to see how many goats were killed. They hadn't gone about it in a scientific way. They appreciated what scientists in universities were doing and wanted scientists to come to Dugway to see what they were doing and give advice.

I was at Dugway for two weeks over Christmas 1942. I remember that very well. Sam Ruben and Kenneth S. Pitzer were the leaders of active chemical warfare work at Berkeley. Sam Ruben, an instructor of chemistry, visited Dugway in the Spring of 1943. Phosgene, a major gas in WWI, reacts in the lungs to release hydrochloric acid. From animal tests, phosgene was found to be much more toxic than the corresponding amount of hydrochloric acid. This problem was discussed with Ruben.

Sam Ruben and Martin Kamen were co-discoverers of carbon-14, which has a half life of 5,730 years and has been heavily used in carbon dating. Carbon-11 has a half life of about twenty minutes, and an experiment using carbon-11 must be finished within about an hour or two. Ruben at the University of California in Berkeley made carbon-11 in the cyclotron, converted it to carbon dioxide, exposed plants to it along with artificial illumination, removed a leaf or other plant part, found where the carbon-11 had gone, and identified the chemical products. These studies disproved a long-held theory of photosynthesis. At age twenty-six, Ruben and Kamen were world-famous in physics for discovering carbon-14, and at age twenty-nine Ruben was also world-famous in biology for his work on photosynthesis.

Early in 1943, Sam Ruben dropped his work on photosynthesis and devoted full-time work on the Berkeley chemical warfare project. He and associates developed novel instruments to measure wind speed and gas concentrations in air. They used these instruments to study temperature inversions and gas travel in the Central Valley of California and on the side of Mount Shasta. Also, the instruments played a prominent role in the field tests in Florida and in Panama.

In response to Dugway's request for knowledge about phosgene toxicity, Ruben's idea was to carry out the photosynthesis procedure, but to use rats instead of plants. Sam and his group made carbon-11 monoxide, converted it to carbon-11 phosgene, exposed a rat to it, killed the rat, cut the animal up to see where the carbon-11 went in the body, extracted various fluids from tissues, and chemically analyzed the fluids.

They carried out three such experiments and solved the broad features of the problem. Most of the phosgene decomposed to produce acid in the lungs, but some reacted with proteins to form systemic poisons in the lungs and in the bloodstream. This knowledge was achieved at great cost. In preparing for a different experiment using radioactive phosgene, Sam accidentally broke a tube filled with liquid phosgene. He died the next day on the eighth anniversary of his wedding, and a month before his thirtieth birthday.

INTERVIEW 2: JULY 20, 1999

Tape 3, Side A

Johnston: Back to Caltech graduate studies: While I was away in Florida, my research director, Professor Dickinson, died.

Hughes: Was that unexpected?

Johnston: Colon cancer. It was unexpected until it was diagnosed a few months before.

The first year when I got back as a graduate student at Caltech, I was going to work with Yost, but there was an instructor, Richard Dodson, who came in at the same time. He had also been active in war work, needed graduate students, and so Yost turned me over to him. He was a radiochemist, radioactivity chemist.

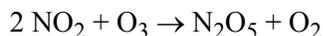
At that time, Pasadena was far from the cyclotrons, far from the center of this type of research, which was at Berkeley. Dodson would bring in a sample of some radioactive isotope and saying, "Quick, do an experiment before it's gone in two weeks." I wasn't getting anywhere. Under that situation, we couldn't compete with Berkeley to come up with anything new. When Dodson left after one year, I worked full time with Professor Yost.

Hughes: What was your project?

Johnston: Yost had me continue the work I was doing on radioactivity. I indicated I wanted another project. He didn't say anything then, but later in the laboratory, when all the graduate students were there together, he came in and delivered a five-inch oscilloscope, some radio tubes, some photomultiplier tubes, and things like that. He had picked them up from the war surplus store. He paid five dollars for the oscilloscope, with his own money. They weren't heavily funded in those days! Yost said, "Chemists should use oscilloscopes and not retorts," and walked out. Yost was answering my question with a challenge, and the challenge was open to everybody in the room.

One graduate student there passed a jolt of current through a thin wire, which exploded, and he looked at the electrical surges on the oscilloscope. I came up with a plan. At any desired time, cause the oscilloscope to sweep only once, and take a time-exposure photograph of the single sweep, which would give the history of the changes occurring in the system during the single sweep. Using lenses and apertures, I formed a narrow beam of light and let it hit the face of the photomultiplier tube, and a rotating disk with slots along its edges chopped the light beam. A time exposure photograph of this chopped light during a single sweep of the oscilloscope showed a square wave all across the picture. I proposed to build a system where I would rapidly flow and rapidly mix together two chemicals that reacted with each other inside a cell with the chopped light beam going through it, and I would suddenly throw a switch that stopped the flow into and out of the cell, and also trigger a single sweep of the oscilloscope beam. If one reactant absorbed the light and the other reactant and the products did not absorb the light, then the time exposure photograph of the oscilloscope screen would reveal a square wave with a steadily increasing amplitude as the absorbing reactant was removed by reaction.

I worked out this idea and carried it to Yost and asked him what he thought about it. Before I went to Yost, I studied the chemical literature and picked out three different reactions that I thought might be interesting. The first one concerned some reactions of permanganate, I think it was, and other highly colored salts in solution. The next one was to study the fast reaction of nitrogen dioxide with ozone. The second reaction had been studied in the literature, but its rate had not been measured, and I forget what the third reaction was. Yost looked at my proposal, didn't say anything, and pointed his finger at the second one [laughs]. Thus I became a gas-phase chemical kineticist with prime interest in the oxides of nitrogen and ozone, which happened to be important in the atmosphere. The reaction was:



NO_2 absorbed the light; ozone and the products did not absorb the light.

Hughes: Were you trying to process all on your own?

Johnston: Yost recommended then that I go talk to research Professor Oliver Wulf. Oliver Wulf was an upper atmospheric chemist—ionosphere. I talked to him about how I could get ozone. Well, he knew all about that: Pass a silent electrical discharge through a stream of pure oxygen. He showed me how to build an ozonizer—the glass shop made it up—and how to analyze for ozone. Professor Yost bought a used 15,000 volt transformer of the sort used to power neon signs. From \$20 of my own money, I bought a used 35-mm camera. I had lots of help from Wulf, and Yost would answer any question I brought to him.

I made nitrogen dioxide by heating and decomposing certain solid chemicals. You can buy nitrogen dioxide these days in stainless steel tanks, but then we couldn't do it that way. Nitrogen dioxide is a liquid, but it has quite a tendency to vaporize. It's the brown gas seen when copper is dissolved in nitric acid.

Professor Wulf also taught me how to make a compact saturator, which the glass shop built. It included a folded 20-mm glass tube mounted in a horizontal plane with liquid on the bottom and air flowing over it, without bubbling. I mounted it in a thermostat and controlled the concentration in the gas stream by controlling the temperature of the thermostat. (There are complications with formation of N_2O_4 , which we took care of but do not need to be discussed here.) The glass shop made the ozonizer, the saturator, and a fast-mixing device. I had learned enough glassblowing to put the system together.

It was the late spring of 1947; I still didn't have any results. Then one night I finally had set my system set up. I flowed one stream of oxygen gas through the silent electrical discharge to make a dilute solution of ozone. I flowed the other stream through the all-glass saturator filled with liquid nitrogen dioxide at a carefully controlled temperature. The gases mixed in a fancy glass thing that looked like a flattened spider; it rapidly mixed the two streams of gas and passed the mixture out into a cylindrical reaction cell. The chopped beam of light went down the middle of the reaction cell. I rapidly, simultaneously stopped the flow of both streams of gas, an action that initiated one sweep of the oscilloscope beam, which the camera captured. When I developed the films and saw that the width of the square waves got wider toward the end, I said to

myself, "I got a thesis!" I worked twenty-four hours a day, every other day for a week. It included three full nights. I needed to work at night in a dark room to avoid stray light from reaching the phototube. I had enough experimental data for a thesis. This method was about a thousand times faster than the fastest method being used for gas-phase studies up to that time. I spent the summer of 1947 interpreting the data and writing the thesis. I started work at Stanford in the fall of 1947, and formally received the Ph.D. degree from Caltech in the spring of 1948.

In one sense of the word, I kicked off the fast reaction race. My method gave results in the millisecond time scale. But fairly soon people with flash photolysis and shock tubes reached the microsecond time scale. Now with lasers and some tricky optics, chemical reaction rates are studied in the femtosecond range, which is a million-billionths of a second! Such rates are a million million times faster than my results. So I didn't go very far in the fast reaction race, but for two or three years I had a new experimental method that could explore a time range not covered before. I did, what was to me, interesting chemistry.¹

Hughes: That was a post-World War II discovery? I ask that because some of the instrumentation which became so useful in the fifties came out of wartime development.

Johnston: My fast reaction instrument did not directly come from the war; that was a new formulation. But we used a war-surplus oscilloscope and optics, so in that sense it came out of the war effort.

Hughes: Was any compensation made for students whose work had been displaced by the war effort? You were obviously slowed down in getting your Ph.D.

Johnston: Well, after the war was over, some government agency gave \$500 a year for any veteran to go to college, but NDRC workers got no recognition or extra pay .

Hughes: And was that enough for tuition in most places?

Johnston: Yes. Before that, the tuition had been less than \$500. In a very short time, the tuition became \$500! There was a flood of GIs returning to college. I taught the freshman chemistry at Stanford. It was overflowing.

Hughes: If the war had not come along and you had not done that poison gas work, do you think you would have ended up where you ended up?

Johnston: No. The war work served me more heavily in problems concerning supersonic aircraft and stratospheric reactions after 1971. The principles involving temperature inversions and air motions came in strongly in the later work.

Hughes: Before the war, you were already interested in the kinetics of gases, is that true?

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

Johnston: Before the war? Well, I was interested in rates of reactions, whether gases or in solution. I was going to do rates of reactions with Dickinson.

Hughes: Maybe I'm trying make too close a connection between the war work and what came afterward.

Johnston: The connections are mostly my getting a job so easily. And I had grown up a lot.

Hughes: Chemistry is a very diverse field.

Johnston: Correct.

Hughes: Yet, during and after the war, you were dealing with gases and reactions. I guess I'm still struggling with how formative that war work actually was on the direction your career took.

Johnston: Well, it certainly had some effect, but I think my studies as a graduate student at Caltech had greater effect.

I was accepted in Stanford before I had my glorious week of getting results on the fast reaction system. I stayed at Caltech all summer working on the data, and I had the data interpreted and an article ready to submit. Well, almost. I went to Stanford in the fall of 1947 and set up the fast reaction system there. The graduate students coming in from the war were excellent.

Hughes: Say a bit about the chemistry department at Stanford at this time. Who was there and what was its reputation?

Johnston: When I arrived there, I was given a little room in the basement, which had a small window high on the back wall. It had no hood. Looking through the glass window on the door, I could see the room to be quite handsome. Nice wooden cabinets on the walls. When I opened the door there was a terrible stink. Previously, some kind of biochemical animal work had been done in there. So before school started in the fall of 1947, I took soap and water and a ladder and scrubbed every surface in the room, floor, walls, wooden cabinets, drawers, and ceiling. That fixed the odor.

In the freshman chemistry laboratory, a hood had been provided by having a big smokestack up through the top of the building with little gas flame in the chimney, so the heat from the flame would suck the air out of the laboratory and up the stack. But the earthquake in 1906 broke the chimney, and they never had a hood since.

Hughes: But there was no fume extraction mechanism.

Johnston: No. Except, we could open the windows.

Hughes: Were there safety codes?

Johnston: No! [laughs] And Berkeley was worse; recall Sam Ruben. He worked in a room with no hood. But safety was a serious consideration at Caltech.

Hughes: Why do you think there was a difference in attitude?

Johnston: Pauling had consideration for people who worked under him, and Dickinson did, too. They were both very humane people.

Hughes: What does that say about Berkeley and Stanford?

Johnston: It appears to me that at Berkeley, people were so excited about Ernest Lawrence's cyclotrons and all the wonderful things happening there that they didn't worry about safety. Their attitude seemed to be that students and workers should take care of themselves. Stanford was dirt poor at that time. They didn't have enough money to install safety features, or to pay much in the way of faculty salaries. My salary was \$3,000 a year for three years, and that was on the low side then, even for an instructor. And there was some inflation already. Stanford also didn't have any money to support research.

The head of the department when I got there was Philip Leighton. He was a fine scientist, co-author of a classic book on photochemistry, and served as lieutenant colonel during the war at Dugway Proving Ground. But after I had been at Stanford for one year, he resigned as head but remained as professor.

The one who took over as department head was Professor George Parks. He was an old-timer; he hadn't done significant research for a long time. But he did have one ideal, and that was to save money for Stanford University.

At the last session we talked about Stanford?

Hughes: We talked mostly about infrastructure. We didn't talk much about research. So I think that's where we should begin.

Johnston: All right. I again set up my new experimental method, but I was more interested in conceptual problems than the fast reaction feature.

Hughes: Give me an example of what you would consider to be an interesting conceptual problem.

Johnston: Okay. First I'll talk briefly about a very interesting person who solved a very interesting conceptual problem, and then I'll talk about the problem.

One member of the Dickinson's war research group, Bob Mills, was a graduate student at Caltech in 1947. He was the kind of guy that everybody likes. He followed me to Stanford and was my first graduate student there.

There's an interesting phenomenon in chemistry called unimolecular reaction. A bimolecular reaction is where two molecules collide with each other and change into products. Now, in a unimolecular reaction, an isolated molecule breaks apart into two products. A unimolecular chemical reaction involves three types of reactions at the molecular level. I have to give these three reactions to clarify the discussion. Call the reactant A and call any gaseous molecule M. M could be the reactant A, or argon Ar, or

nitrogen N_2 , or carbon dioxide CO_2 , or any other molecule. In the first process (1), an ordinary reactant molecule A collides with some molecule M to form activated A^*



where the square brackets represent molecular concentration. The activated molecule can either (2) be de-activated by collision with an M, or (3) fall apart to products, call them B and C.



After a small amount of algebra, the rate expression becomes:

$$\text{rate} = - \frac{d[A]}{dt} = \frac{k_a k_c [A][M]}{k_b [M] + k_c}$$

At high pressures, that is, high concentration of M, this expression becomes

$$\text{rate} = (k_a k_c / k_b) [A]$$

so the rate is linear with concentration of reactant A and independent of the concentration of the energy-transfer molecules M. The reaction is said to be “first order.” At low total pressure or low concentration of M, the rate of reaction is

$$\text{rate} = k_a \times [A][M]$$

which is the rate of activation of molecule A by the collision partner M. This rate expression is “second order.”

If one plots the first-order rate constant against total pressure over a range of about five orders of magnitude, the reaction would be first order at the high-pressure end, and it would become second order at the low-pressure end, that is, it would be proportional to the concentration of inert gas as well as proportional to the reactant.

All right. The thermal decomposition of nitrogen pentoxide, N_2O_5 . Nitrogen pentoxide is not quite the right name, but it's okay. It has two nitrogens, so some people call it dinitrogen pentoxide. Now, let me go beyond that. In the late 1920s, the concept of a unimolecular reaction was thought about by some great people. The algebra I give above is the simplest form of the theory. The quantities k_a , k_b , and k_c depend on molecular mass, moments of inertia, vibrational frequencies, and electric quantum states.

Now, the theory was worked out by some brilliant and outstanding chemists and physicists in the late 1920s and early 1930s. The thermal decomposition of N_2O_5 was a famous reaction from earlier German literature. It was found that N_2O_5 showed first-

order kinetics. And so when this theory was developed, people realized that N_2O_5 ought to show the second-order behavior at low pressures.

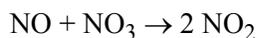
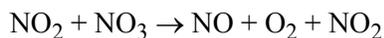
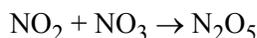
Richard Tolman, an outstanding member of the Caltech chemistry department, respected this theory and in fact contributed to formulating it. It was based on sound physics. Before the war, Tolman had some graduate students measure the rate of this reaction over a wide range of pressure. At one atmosphere pressure, it was already first order. So he went to extremely low pressures. The measured rate did change from first order to second order, but it did so at utterly different pressures from that expected by the theory. They had to go a factor of a hundred below the pressure where the theory predicted it would happen. Tolman wasn't the only one; a number of other people tried it, and only one or two covered as wide a pressure range as he did. So the measurements were okay. People who were aware of the theory were sure it should be correct. It was at that stage that Tolman shifted from chemistry to astrophysics, because, he said, "Chemistry is hard." These elegant reproducible experiments and fundamentally based theory disagreed in a major way.

Hughes: Did you know that?

Johnston: I was aware of that history. In the first year I was at Stanford, a little article came out by Farrington Daniels and one of his bright graduate students, J.H. Smith, who studied the bimolecular reaction between nitric oxide NO and N_2O_5 . NO plus N_2O_5 produces three NO_2 's. There are things about the article that seemed queer, but they published this article, not quite understanding what was going on.



Well, I realized what might really be happening. When N_2O_5 fell apart, it formed NO_2 and NO_3 , and the NO_3 would react with NO and go away, or NO_3 would react with NO_2 to form N_2O_5 again. The unimolecular decomposition of N_2O_5 goes by way of a four-step mechanism:



If NO is added to N_2O_5 , the nitric oxide would snatch the NO_3 as soon as it was formed, and the observed rate would be that of the elementary decomposition:



Hughes: Did you have any help with this research?

Johnston: My first graduate student was Robert Mills, who was very active on Dickinson's war project. He came with me to Stanford instead of staying there at Caltech. He's a really outstanding person. We developed three different apparatuses. One would be to study the high-pressure range, using our fast reaction method. This is all at one temperature. Another studied hundred-fold change of lower pressures, and this was done by a modified fast-flow reaction but it didn't have to be very fast. And another was a 22-liter glass bulb to study the reaction at low pressures.

But this time the results were totally different than Tolman's. The fall-off pressure came at a pressure about a hundred-fold higher. A plot of our data against the previous theory showed excellent agreement. So the theory had been right, and Tolman's experiments had been right, but Tolman was measuring something different from what he thought he was measuring. Bob Mills' thesis solved a major mystery that had plagued some of the best chemists for about twenty years.

Hughes: Did anybody else have this instrumentation that you developed at Stanford?

Johnston: Well, people picked it up, but we were two or three years ahead at least. What happened next was Norman Davidson at Caltech--this is beside the point--made a big leap from the millisecond time scale to a microsecond time scale, using a shock tube. That's another story.

Hughes: It seems to me that it's a very technology-driven area of chemistry, that you simply can't do refined experiments until you have the instruments to dissect the reaction.

Johnston: Yes, that's right. The N_2O_5 work showed that the phenomenon of unimolecular reactions was interesting, and I looked around at certain other ones. In the literature, some outstanding German physical chemists, Schumacher and Spenger, had studied the unimolecular decomposition of NO_2Cl , nitryl chloride. It was a first order and unimolecular, but they didn't study a very wide range of pressures. So we took the nitryl chloride reaction, and another graduate student studied it over a wide range of pressure, and it showed the various falloff behaviors.

Now, the rate of a unimolecular reaction at very low pressures depends somewhat on which gas is causing the thermal excitation. CO_2 causes the reaction to go faster than argon, because CO_2 carries more internal energy. It's a measure of the efficiency of energy transfer. At low pressures, we measured energy transfer upon molecular collision, an interesting conceptual problem.

Tape 5, Side B

Hughes: Now, at this stage, you were interested in these experiments mainly for their theoretical basis. You wanted to understand how fast reactions work, looking at as many stages in the reaction as you could, rather than hoping to get some applied use out of this information?

Johnston: Yes. We couldn't see any applied use at all, but rather soon practical applications turned

up.¹

Hughes: Were people supplementing their salaries by consulting with industry?

Johnston: I think the answer is yes, and I can give you my experience there. When our papers began to come out on fast reactions involving the oxides of nitrogen and similar things, a representative from M. W. Kellogg Co. looked me up and explained one of their problems. They had a promising hypergolic rocket fuel. In an internal combustion engine, the fuel and air come together, and a spark ignites them. In a hypergolic engine, the fuel and oxidant ignite upon contact. Each one is relatively stable by itself. That's not going to send a rocket to the moon, but once the rocket gets in orbit, their hypergolic booster could be useful for fine-control steering.

Red fuming nitric acid and hydrazine self-ignited upon mixing and released a large amount of energy, which gave a good, high thrust to the rocket. But in the combustion chamber, there were mini-explosions and rough burning. It was so much of a problem that they were afraid they might have to give it up. They asked if I could do anything in my research that might help Kellogg. Well, we came up with the idea that we would study the unimolecular decomposition of nitric acid, just as if it were a pure chemistry problem, and we would see if the new scientific information gave any hints about the problem. For doing this, they paid my summer salary. But it was exactly the kind of thing I was most interested in.

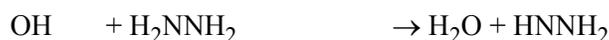
Hughes: What results did you get?

Johnston: We studied the unimolecular decomposition of nitric acid, figured out the mechanism, the steps by which it occurred, which were:

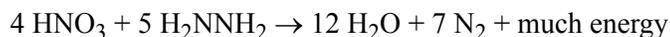
Nitric acid plus energy breaks down to give hydroxyl radical plus nitrogen dioxide



Hydroxyl radical plus hydrazine rapidly react to form water and hydrazine free radical



In a series of fast steps, hydrazine free radicals react with nitrogen dioxide to form water and molecular nitrogen, thereby releasing a large amount of energy. The net reaction of these many steps is:



We did no work with hydrazine. We just studied the unimolecular decomposition of nitric acid. We showed there was a high activation energy barrier to the decomposition of nitric acid. Energy was required to start the reaction, but the energy had to come from the last stages of the reaction. There were delayed feedbacks between fuel combustion

1. Please see Dr. Johnston's bibliography in the appendix to this volume for all references to his papers.

and fuel ignition, which caused the mini-explosions and rough burning. Red fuming nitric acid is nitric acid with a large amount of nitrogen dioxide dissolved in it. I discussed with Dr. Messerly why they used red fuming acid, and together we concluded they should omit the nitric acid entirely and use just nitrogen dioxide as oxidant. They tried this experiment, nitrogen dioxide and hydrazine were hypergolic, and the combustion was smooth and fast. That problem was solved.

Hughes: So they had been reading your papers, and Kellogg thought your work might apply to some of their problems.

Johnston: But they had no idea how it might apply, nor how much it would apply.

Hughes: Were you unusual in having industrial support?

Johnston: No. To keep research alive in those days, we had to have support from industry, or from the Office of Naval Research, or have a National Research Council Fellowship, because the National Science Foundation wasn't started until late in 1950, I believe. Anyhow, this was a convenient arrangement. They paid my summer salary, and they paid the undergraduate students, and we got to study another unimolecular reaction.

INTERVIEW 3: JULY 27, 1999

Tape 5, Side A

Hughes: Tell me how you met Dudley Herschbach.

Johnston: I was advisor for freshman students who thought they might major in chemistry. I met them as a group early in the fall quarter, met with them individually in my office, and, as a minimum, I signed their list of courses each quarter. By appointment, a student could talk with me anytime. Before instruction started in the fall quarter of 1950, I met with the new group in a small classroom. I gave a short talk and then we had a general discussion. A student on the back row asked notably good questions. He obviously understood everything I was saying. Later, during his appointment with me in my office, I found that he was a pre-medical student, majoring in chemistry. We went through what courses he should take during the year. He emphasized he wanted to take some fairly difficult courses in physics and math. We reviewed the required courses he should take for him to meet the pre-medical requirements and to be a chemistry major, in order to find how many vacancies were in his schedule during which he could take extra courses.

At Stanford the standard load was fifteen units per quarter, the maximum number of units was twenty, but these limits could be modified with the advisor's signed consent. I talked to Dudley once or twice during the quarter, and at the end of the first quarter, he came to my office. We finished the scheduling questions for the next quarter, he stood around and didn't go away, and I thought he might have something to say. I asked him, "How'd you make out this quarter?" Well, he finally confessed he'd made all A's.

Dudley had been a star football player in high school, and he was courted here at Berkeley to come in as a freshman. He recalls Glenn Seaborg took him out to dinner, introduced him to some of the great people here, urged him to come to Berkeley, and offered him a good football scholarship. Dudley also applied to Caltech and to Stanford. He decided he wanted to go to Stanford. It was fairly close to his home, which was only thirty miles away. Stanford also offered him a football scholarship. When the Stanford admission office saw his record from high school, they gave him an academic scholarship. So it's a good story that he entered on a football scholarship, but it's not quite true! He was offered one, but he turned it down to accept the academic one. Even so, he was on the freshman football team the first year.

Sometime in the year, Dudley decided he did not want to go into medicine; he wanted to major in chemistry. After his first quarter, he took twenty or more units each quarter. He kept taking more and more advanced courses as he worked his way up through physics and math courses. Of course, he took all the required chemistry courses. And he swept through with A's every time, except once.

He went all the way through Stanford and made only one B. Why did he make that B? Well, he took a course from a professor that I won't name, who was so drunk at the time the finals came in, he just couldn't grade them. So he figured, he would give everybody a B: nobody who has a C or less would complain, and A students got a B occasionally. The professor never graded the finals at all.

At the end of his first year at Stanford, Dudley went to his coach and said he wasn't going to continue in football; he wanted to spend all his time on his academic work. The coach was terribly upset. He said, "You're making a big mistake. If you stay with me, boy, I can get you a job." A job as a football player, of course. Dudley figured he could get a job somewhere else.

Hughes: When did you get to know him?

Johnston: During the year that I was his freshman advisor, we got to be friends, and so he came around and talked to me occasionally in the second year. In the third year, I hired him as an undergraduate student in my laboratory. I had some funds from the Office of Naval Research. Doing research during the summer, he studied the rate of reaction of nitric oxide with fluorine at low pressures and discovered that the reaction emitted light.

Dudley finished his four years at Stanford with enough courses to major in chemistry or physics or math, and he took his bachelor's degree in mathematics. During his senior year, he applied to Harvard for graduate study in chemistry. I told him that graduating seniors applied to more than one place. If you don't get in one place, you'll get in another. No, he said, he'd like to go to Harvard. He thought it through, and he knew about the people there, and he wanted to go to Harvard. He didn't apply anywhere else.

He had to take the Graduate Record Examination. I remember when he came out after taking it, he was just all laughs. "What stupid questions they asked! You could just see right through them." He went through the examination quickly, turned it in, and flunked it; he flunked the Graduate Record Examination! As we found out much later, when his application appeared at Harvard, it was screened by the secretaries at the front desk; the application of anybody who flunks the Graduate Record Examination was rejected automatically. The secretaries didn't pay any attention to all A's and high recommendations from the Stanford people, and the professors never saw his academic record. So Dudley was denied admission to Harvard graduate school. Dudley stayed on with me and got his master's in chemistry.

Hughes: I see.

Johnston: I gave him a theoretical problem. To use the methods, newly organized and presented in a book by Wilson, Decius, and Cross, to carry out a more advanced calculation of the pre-exponential factors A for a list I had prepared of twelve elementary bimolecular reactions. We had recently made the first measurement of the rate of many of these reactions.

Hughes: A very unusual problem for an undergraduate, right?

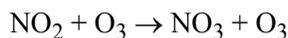
Johnston: Yes! It wasn't unusual to have undergraduates in the research lab in the summer. But it was unusual for anybody to flourish the way Dudley did.

There was a long-standing theory called activated-complex theory or transition-state theory. The basis for this theory was set by a great physicist, Fritz London. Within a couple of years after quantum mechanics was discovered, he formulated a theory of the simplest bimolecular reaction, where a hydrogen atom hits a hydrogen molecule and knocks out a hydrogen atom.

London's theory was picked up by chemists, notably by Henry Eyring, who did outstanding, well-known work in the field. If two molecules are going to react and change into something else, they must get together and swap things off somehow. The point where they are colliding and swapping things off is the transition state or activated-complex, whichever name you prefer. London spelled out the concepts of the theory without actually calculating the numbers. Some very difficult experiments were done by others who measured the hydrogen rates, which confirmed the idea, and Eyring generalized the theory for chemical applications. In developing activated-complex theory, Henry Eyring went from pure, high quality physics to practical chemical problems, and he made a number of simplifications. He generalized activated-complex theory—perhaps further than it deserves.¹

Hughes: What is an example of an elementary bimolecular reaction?

Johnston: For my Ph.D. thesis, I measured the rate of the reaction of ozone with nitrogen dioxide to form nitrogen trioxide and oxygen



Nitrogen dioxide and ozone collide at high relative velocities, and nitrogen dioxide removes one atom of oxygen from ozone. There are subsequent reactions of NO_3 , but this two-molecule reaction is interpreted to be an elementary bimolecular chemical reaction.

Bimolecular reactions are second order, as can be demonstrated by experiment. The observed rate of a second-order reaction is directly proportional to the product of the concentration of a molecule times the concentration of a molecule.

$$\text{Rate} = k \times [\text{concentration of a molecule}] \times [\text{concentration of a molecule}]$$

where the two molecules may be the same or different. From experiment, I found that the rate divided by the concentration of nitrogen dioxide and divided by the concentration of ozone was the same for all values for these two reactants, which was the value of k , the rate constant or better the rate coefficient:

$$\text{Rate observed} \div \{[\text{NO}_2][\text{O}_3]\} = k$$

From simple reaction-rate theory, the coefficient k is a product of two terms

$$k = A e^{-E/RT}$$

where E is called the "activation energy," and A is called the "pre-exponential factor." R is a universal constant and T is absolute temperature. By measuring how the rate

1. F. London, "Probleme der modernen Physik," Sommerfeld Festschrift, 1928.
E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations*, McGraw-Hill Book Co., Inc., New York (1955).
H. Glasstone, K. J. Laidler, and H. Eyring *The Theory of Rate Processes*, McGraw-Hill Book Company, Inc., New York (1941).

coefficient changes with temperature, we evaluated the activation energy, E , and the pre-exponential factor, A . Simple theory interprets E to be the energy barrier that separates reactants and products of reaction.

Using our fast-reaction methods, we directly measured rates of reaction in a region that had been inaccessible. So once we collected a fair number of reactions and their rates, we asked how well do our newly measured reaction rates agree with activated-complex theory? I had made up a list of twelve bimolecular reactions, many of them we had measured by our fast-reaction methods.

I taught summer school here at Berkeley sometime in the early 1950s, when I was at Stanford, and so I became aware of some of the things that Richard Powell was interested in up here and also met Ken Pitzer. He was extremely outstanding in all kinds of things. One of his many his interests was in molecular vibrations, and so I had Dudley come up, when we had reached a fairly advanced stage, to talk to Powell and Pitzer about the sort of thing we were doing. We got some ideas, especially from Powell, and advice from Pitzer, and came out with a little paper. In hindsight, that was a fairly interesting collection of authors. And it was a good paper. It was the seed from which my textbook grew.

In 1955, Wilson, Decius, and Cross published a book that gave a general elegant method of calculating the normal coordinates of polyatomic molecules and the frequencies of molecular vibrations. They broke down the motions of molecules into their independent components: vibrations, rotations, and moving through space. Dudley Herschbach, David J. Wilson, and I studied that book, and we wanted to use their methods and principles to estimate the properties of activated complexes. Some people at some times had used the vibrational frequencies of the activated complex as adjustable parameters, but in that case the theory can explain anything but predict nothing. We developed a procedure for obtaining all needed parameters from observed molecular spectroscopy and molecular structure.

In order to calculate pre-exponential factors A for bimolecular reactions, we needed to know, both for reactants and the activated complex, the molecular weight, moments of inertia for over-all rotation, moments of inertia for internal rotation, barriers to internal rotation, all vibration frequencies and electronic degeneracy. We, like others, obtained these data for the reactants from spectroscopy. We assumed that the excitation energy of the reactants has gone into the potential energy of a single separable reaction coordinate, so that the rest of the activated complex is like a normal molecule. Thus, except for the reaction coordinate, we made heavy use of analogy with ordinary molecules. For single, double, or triple bonds we used the tables in Pauling's *Nature of the Chemical Bond*. However, for the H_3 complex or for methyl radical abstracting a hydrogen from an organic compound, the bonds were taken to be "half bonds." We used Pauling's rule for the length of a bond of any order:

$$R_1 - R = 0.30 \log_{10} n$$

where R is the bond radius in angstrom units, R_1 is the radius of the corresponding single bond, and n is the order of the bond. Long-standing arguments justified a linear complex for H_3 , and this structure was assigned to the C-H-C links in methyl radical

reactions. We assigned stretching force constants for the activated complex from Badger's rule, and bending force constants from the bifluoride ion.

David Wilson and I applied this procedure to ten reactions from the literature, and nine out of ten agreed well with theory, but the observed A factor for one reaction was 100,000 times larger than the theoretical one. We argued that the reported measured rate was not that of an elementary reaction, but was the rate of a complex set of reactions.¹

Hughes: What happened to Herschbach?

Johnston: After he didn't get into Harvard, we called up acquaintances and friends there and asked, "Why in the world didn't you take this guy?" The Harvard professors found that secretaries had tossed out his application when they saw that he flunked the Graduate Record Examination. And so the next year he applied just to Harvard, and this time we telephoned in advance that everybody should watch for him; he was the best graduate we had ever seen. And so he was admitted. Professor E. B. Wilson, Jr., of Harvard visited Stanford early the next year. I asked him, "Well, how's Dudley doing?" "He seems to be doing all right." He was out a few months later and Professor Wilson said, "He's head and shoulders above all the rest of them." [laughs] Dudley worked with E. B. Wilson, Jr., who was the co-author with Pauling of their famous book on quantum mechanics.

Now let's run ahead with Dudley and then drop back. At Stanford he got an AB degree in math; at Harvard he received a master's degree in physics and a Ph.D. degree in chemistry. As soon as he finished his doctoral degree at Harvard, he was made a junior fellow. Do you know about these?

Hughes: No.

Johnston: It's for people immediately after they get their Ph.D. degrees, real high-ranking scholars, to do research of their choice, with full support from Harvard for a year or two.

Hughes: Why did you leave Stanford?

Johnston: I regarded Caltech as the best. When Pauling came up to Stanford and asked me to accept an associate professorship there, I felt highly complimented. That was really the reason number one, the chance to get back there, the chance to get into the big league, because Stanford then was small time.

Money was part of it. There was quite a problem at Stanford at that time in faculty salary.

1. "Theoretical Pre-exponential Factors for Hydrogen Atom Abstraction Reactions." David Wilson and Harold Johnston, *J. Am. Chem. Soc.*, **79**, 29-32 (1957).
 E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations*, McGraw-Hill Book Co., Inc., New York (1955).
 L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.
 L. Pauling, *Jour. Am. Chem. Soc.*, **69**, 542 (1947).
 R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1933), **8**, 710 (1934).

I had also a very serious problem with research space and facilities. I had first one and then two quite small rooms in the basement of the old chemistry building, and the only ventilation they had were little windows high on one side—no hoods and no forced-air circulation of any kind. In this room we were working with all kinds of poisonous things: ozone, nitrogen dioxide, and fluorine. It seemed rather hopeless to get better facilities. In fact, we did have an accident in one of the rooms. A small tank of phosphorus trifluoride was released by accident into the small room. People had to get out of the room and close the door. The door had a glass window. From the smoke produced, we could see only a foot or two into the room,

Hughes: Was that pretty true of Stanford as a whole at that period?

Johnston: Yes, but not so extreme in some departments. As I say, the head of the department really had the idea of saving Stanford money, by not providing salary and facilities for the professors. Chemistry was worse off than physics.

Hughes: Did that parsimony impact on the quality of the people that would come or stay there? And on science that was being done?

Johnston: There certainly was low morale among the junior faculty in the mid-1950s.

Hughes: When you were at Stanford, biochemistry was part of chemistry; there was not a free-standing biochemistry department.

Johnston: That is correct. As I recall, biochemistry consisted of J. Murray Luck and one or two others. Professor Luck was said to have received an outside offer at a salary substantially greater than he was getting at Stanford. He went to the department chairman, or maybe it was the dean, and said he would have to accept the offer unless Stanford could, more or less, match it. The chairman congratulated Professor Luck and wished him success at his new position. But Professor Luck liked it so well in Palo Alto that he didn't want to leave. He had to back down, and then he never got any raise at all. To support his research and his family, he founded the *Annual Reviews of Biochemistry* and later *Annual Reviews* of many other scientific fields. There was a big biology building down the street from the chemistry building, but as I recall it was mostly botany and other natural history types of biology.

Hughes: You missed by a few years the renovation of Stanford biomedicine.

Johnston: Right.

Hughes: Nobel Prize winners were brought in—

Johnston: Yes, that's right. I think I was there for the first Nobel Prize winner at Stanford.

Hughes: Was that Joshua Lederberg?

Johnston: No, the magnetic resonance man. Felix Bloch did his great work at Stanford. Of course, there were very good scholars at Stanford. Just after I left, Stanford worked out a plan. The university had thousands of acres, but a stipulation of the will giving land to them said they couldn't sell it. So here they were, a poor, struggling, almost starving

university with gorgeous land all around them, and they couldn't sell it. They come up with the idea of ninety-nine-year leases. Stanford Industrial Park was one of the big steps on the way to Silicon Valley. It has Lockheed, and all kinds of big buildings were put up. They had a ninety-nine-year lease. That helped Stanford as much as if they had sold it. So that made Stanford prosperous enough to bring in more good people.

There was a physics professor, Leonard Schiff, who was young and had recently been brought in, who spearheaded getting more appointments for physics and chemistry. After I left, chemistry got a new building. Over the years, they've built up to be really a magnificent place in chemistry—and in many other fields. But it was the shot in the arm from leasing the land. They may have leased it on an income basis instead of one shot.

Hughes: Do you remember when that might have been?

Johnston: Oh, after 1956.

Yes, I didn't get into the boom at Stanford, but I got in on the boom at Berkeley and have been very much better off here than I would have been there. Here, if a problem comes up in almost any field, somebody around will provide help or even give the answer, just like that, off the top of the head. So when I got here, I enjoyed great support from fellow faculty members.

Hughes: Is that collegiality a function of the people here, or is it something to do with the fact that this is a college of chemistry?

Johnston: Yes, well, and it also had something to do with the small departmental size. The department is so big now that I hardly know what a lot of the faculty are doing. Some of them I don't even recognize, that have come in not too long ago. There was a small enough group—they'd invite each other out to dinner and things like that. It's still true that you can get lots and lots of help from the faculty members, but we've lost some collegiality by being big.

Hughes: Do you think that there is a greater spirit of cooperation here at Berkeley than was true of Stanford?

Johnston: At Stanford there were four or five of us who cooperated in our poverty [laughs] and who complained about it and didn't get anywhere. At Caltech, there was certainly a lot of collegiality. It didn't have all the variety that's here. It's bigger now, of course.

Hughes: Well, I don't want to do Stanford in, but I'm very aware of the strong history of chemistry at both Caltech and at Berkeley, but I don't have an awareness of really strong individuals at Stanford at that time.

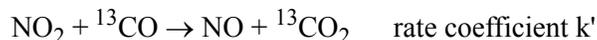
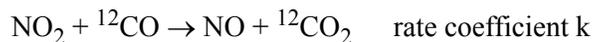
Johnston: I think that's correct. Phil Leighton was on the way to being one, and I don't know what his trouble was with the faculty, but he got discouraged.

Hughes: Did he go to another institution?

Johnston: No, he quit as chairman. He stayed at Stanford as professor.

- Hughes: Dr. Johnston, I believe you want to make a comment about our discussion last time?
- Johnston: Yes. We were discussing last time the reason that I left Stanford to go to Caltech.
- Hughes: Had you been in touch with Pauling?
- Johnston: No. He had a need for someone to teach freshman chemistry. He gave a large number of the lectures, but he was away much of the time. So I gave the lectures when he was away, and I was in full charge of the laboratories, which was not a bad assignment at all. It was very interesting.
- Hughes: You mean the student laboratories?
- Johnston: Undergraduate student laboratories.
- Hughes: Why did you find that interesting?
- Johnston: Well, certainly the students were interesting. Most of them liked to learn. Another side point here: at Stanford the freshman chemistry met in a fairly large, high-ceilinged room. They had no forced ventilation, no fume hoods, and even the freshman chemistry dealt with pretty bad things in those days. But that was hazardous on the students. At Caltech, every pair of freshman students had a down-draft mini hood and sink located down the middle of the laboratory bench, which removed liquids and fumes.
- Hughes: Which of those two cases was the more usual in chemistry labs in the 1950s?
- Johnston: I only knew three places: Berkeley, Stanford, and Caltech. Berkeley had a three-story old wooden shack about where Pimentel Hall is now. It was devoted to the freshman chemistry laboratory. They had no fume hoods, no air circulation, but each lab had a narrow open porch on its far side. Students would take their most obnoxious things outside. I guess Stanford was the worst because their only ventilation was to open the windows.
- The freshmen in those days heavily used hydrogen sulfide, H_2S , which is the essence of the odor of rotten eggs. But hydrogen sulfide is even more toxic than hydrogen cyanide.
- Hughes: Was there any regulation?
- Johnston: No. Well, I shouldn't jump to say none. What do you mean by regulation?
- Hughes: Well, some exterior agency.
- Johnston: No. Of course, the agency that should have been controlling these things, and I think they were at Caltech, were the chemistry professors and administrators.
- During my last year at Stanford, Professor William Bonner showed me an article in the literature where an organic reaction showed an extremely large kinetic isotope effect, and he asked if I could explain it. We planned an experiment to study the kinetic isotope

effect on a much simpler reaction as an interesting case and to educate us on the practice and theory of such reactions.



I acquired a fifteen-liter Vycor (fused quartz) bulb mounted in a high temperature furnace, and with my graduate student David Wilson, we studied the rate and kinetic isotope effect at 550 to 725 K. The experimental quantity is the ratio, k/k' ; the theoretical expression involves a tricky double difference.

Hughes: Is it too complicated to outline?

Johnston: Well, probably not. I'll try. A bimolecular reaction can be written abstractly as



The rate expression involves ratios and differences between the activated complex X and the reactants A and B

$$k = \kappa \frac{Q(\text{X})}{Q(\text{A}) Q(\text{B})} \exp - \Delta E/RT$$

where Q refers to partition function, κ is a tunneling correction, ΔE is the energy difference between activated complex and the reactants, R is the universal gas constant, and T is temperature Kelvins. The partition function Q involves molecular mass M, moments of inertia I, and vibrational frequencies ν :

$$Q = f(M, I, \nu)$$

If one of the reactants occurs as two isotopes, A and A', the rate expression involves double ratios and double differences:

$$\frac{k}{k'} = \frac{\kappa}{\kappa'} \frac{\frac{Q(\text{X})}{Q(\text{A}) Q(\text{B})}}{\frac{Q(\text{X}')}{Q(\text{A}') Q(\text{B})}} \exp - \Delta' \Delta E/RT$$

Using the same methods and references as in Article 29, we defined the activated complex, evaluated all the partition functions and solved for the kinetic isotope effect, that is, the ratio of the two rate coefficients, which was in excellent agreement with what we observed.

As a part of this study, we also calculated the kinetic isotope effect by Jake Bigeleisen's method, which used a formula almost totally different from the partition function method. It involved the reduced mass along the reaction coordinate, vibrational frequencies, and zero-point energies. My new graduate student, Donald Rapp, and I

worked on the question of how could one quantify k/k' , depending on molar mass and moments of inertia in the standard formula, but not depend on these quantities in another formula. There must be some implicit cancellation of molar mass and moments of inertia in the partition function. We worked out the algebra of where this cancellation occurred for simple cases involving only three of four atoms in the activated complex, and we presented this to Dudley Herschbach as an interesting problem. Dudley came up with a completely different way of calculating partition functions. Instead of doing it through one set of variables, he did it through another set of variables. Dudley's method was a big contribution to the theory of statistical mechanics.

Hughes: In 1956 you moved to Caltech?

Johnston: Pauling was head of the Chemistry and Chemical Engineering Division at Caltech. In the summer of 1956, he came up to Stanford and talked and visited around. I think he came to our house for dinner. When he got back, I got an invitation to join the faculty at Caltech as an associate professor, and I was to teach freshman chemistry. I did it for a year. That was '56-'57. Now, Caltech was great when I was there, and there were still a lot of great people. I still thought it was the greatest place there was.

Pauling asked me to collaborate with him in rewriting his book, *The Nature of the Chemical Bond*. That's a famous book. It has a h-u-u-ge amount of chemistry in it, and applying quantum mechanics to chemistry. I realized if I did that, it would take full time for several years. The research that I wanted to do on fast reactions, unimolecular reactions, theory of reactions would be blocked. It was as bad as an administrative job. When Pauling really wanted me to do it, I called Ken Pitzer at Berkeley and asked if there was there any chance for an opening here.

Hughes: So you could escape.

Johnston: I'm not criticizing Pauling for that. That's a fairly common thing, to have a great man let the young man rewrite his book. But I would have to do an enormous amount of work just to get up to date on the book that he wrote. Plus there was a lot of organic chemistry in there, which I did not know much about. And an enormous amount of work in that field had been done since the book was written.

Hughes: It would have been politically inexpedient to say no to Pauling and stay at Caltech?

Johnston: Yes. Well, if the head of the department thinks you're a shirker [laughs]—

Hughes: It would not be very good.

Johnston: When I came to Berkeley, I continued for several years to work on the activated-complex, bimolecular-reaction problems, and especially on the kinetic isotope problems. And we found some new things about the language of it that Eyring hadn't gotten to. The dominant effect in the kinetic isotope effect is the quantum-mechanical correction for the different zero-point energies, and for hydrogen transfer problems a major problem is quantum mechanical tunneling. Hydrogen vibrating at absolute zero vibrates faster than deuterium does at absolute zero. We know those frequencies fairly well and can correct for the zero-point energy difference.

Hughes: And that was known?

Johnston: It was known. We studied quite a few kinetic-isotope effects, including the reaction, $\text{CF}_3 + \text{CHD}_3$ over a wide range of temperature. Transition state theory, as used in ordinary reactions, works quite well at high temperatures. But at lower and lower temperatures, it deviates substantially, and the rate is faster than that expected from these molecular properties. Well, that had been suspected and something known about it for a long time. It's called quantum-mechanical tunneling.

Hughes: How does that occur?

Johnston: It's a matter of the quantum-mechanical uncertainty principle. For a free atom of mass m and velocity v , the de Broglie wavelength λ is:

$$\lambda = h / mv$$

and all points within this length are indistinguishable. For a free atom at temperature T , the thermally averaged unit of uncertainty is the de Broglie wavelength:

$$\Lambda = h / (2\pi mkT)^{1/2}$$

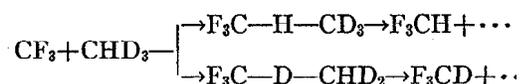
where h is Planck's constant. I prepared a contour map of the potential surface for a hydrogen-transfer reaction including reactants, transition state, and products, a standard thing to do. At the position of the transition state I inscribed a rectangle with length of one thermally averaged de Broglie wavelength along the reaction coordinate and width of a de Broglie wavelength at right angles to the reaction coordinate. All points inside this rectangle are indistinguishable. The procedures of Wilson, Decius, and Cross are based on small excursions about potential energy minima or flat areas. In the vicinity of the transition state of hydrogen-transfer reactions, the de Broglie wavelengths are large compared to the curvature of the potential energy diagram. Tunneling is often interpreted as a particle penetrating a barrier along the reaction coordinate, but I think it is just as well to think of it as the barrier height fluctuating according to the uncertainty principle. If we use barrier-penetrating interpretations, we should think of multiple directions of tunneling and consider side-wall repulsion in limiting the range of tunneling.

Hughes: Anybody who knew quantum mechanics would be aware of that phenomenon?

Johnston: So far as I know, my 1960 article was the first to point out these features. Shortly thereafter, theoreticians took up these considerations and provided elegant solutions.

We did a series of kinetic-isotope studies in the early 1960s, both experimental and theoretical. We examined different methods of calculating quantum-mechanical tunneling, including tunneling through the barrier in directions other than along the reaction coordinate and effects of side-wall repulsion around the transition state.

One of our best articles was the study of the reaction of $\text{CF}_3 + \text{CHD}_3$ over a wide range of temperature:



The free radical CF_3 was made from a stable molecule. When it reacted with CHD_3 , it reacted with an H or with one of the three D's. Each case had the same reactants and the same energy barrier. They have the same potential energy function. Many things canceled. And where they differed was just in mass along the reaction coordinate, in the zero-point energy in the potential energy function, and in the degree of tunneling. Terry Sharp and I measured the rate and isotope effect of this reaction between 300 and 700 K, and we combined our data with that of two other investigations to span the range of 300 to 1800 K. Without tunneling corrections, the observed and calculated isotope effects agreed only above 1000 K. With the full nine-atom model and tunneling function of Johnston and Rapp, there was good agreement above 500K, and the observed points lay only slightly above the calculated curve between 500 and 300 K.

Tape 6, Side A

Hughes: What was your involvement?

Johnston: Christopher Parr and I made one stab at trying to calculate the activation energies for bimolecular reactions in which a hydrogen atom is transferred from one molecule to another. Various investigators had found empirical relations among molecular bond lengths, bond orders, bond force constants, and bond energies:

(1) Carbon-carbon bonds provide a good illustration of the meaning of bond order: acetylene has a triple bond and thus bond order three; ethylene has a double bond, bond order two; ethane has a single bond, bond order one. Pauling (1947) gave a simple general relation between bond length R and bond order n .

(2) Based on infrared spectroscopy Badger (1934) found a relation between bond-stretching force constants F and bond length R , and later Herschbach and Laurie (1961) found a simpler and more general expression for the relation between force constants and bond lengths.

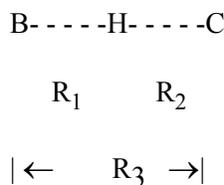
(3) Hirschfelder, Curtiss, and Bird (1954) measured and tabulated the properties of weakly bound pairs of noble gases in terms of the Lennard-Jones potential energy function:

$$V = 4 \epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right]$$

the bond length is $2^{1/6}\sigma$, the bond energy is 4ϵ , and the stretching force constant is $72\epsilon / 2^{1/3} \sigma^2$.

I (1964) extended Herschbach and Laurie's relation from molecular bonds to the weakly bound noble gases in Lennard-Jones pairs. Christopher Parr and I (1963) presented a relation between bond energy and bond order that included regular bonded molecules and weakly bound noble gas pairs.

The simplest hydrogen-transfer reaction is $H + H-H \leftrightarrow H- \cdots H- \cdots H \rightarrow H-H + H$, and we used its quantum mechanical properties to generate theorems for the general hydrogen-transfer reaction: $B + H-C \leftrightarrow B- \cdots H- \cdots C \rightarrow B-H + C$, where B and C are either atoms or radicals. Label features of the transition state:



We assumed that the bond order of reactants, transition state, and products have value one throughout the reaction; the CH bond weakens as the BH bond forms:

$$n_1 + n_2 = 1.0$$

We used our bond-energy bond-order (BEBO) relation to evaluate the energy of the R_1 and R_2 bonds as n_1 goes from 0 to 1 and n_2 goes from 1 to 0. We used Pauling's relation to find the order of the anti-bonding R_3 bond, and we used Sato's formula (1955) for the repulsive energy put up by this anti-bonding. In this way we calculated the activation energies for thirteen reactions, which agreed with measured values within plus or minus two kilocalories per mole. However, we concluded, "The success of the method is regarded not to reflect validity on the assumptions used."

Hughes: How did Herschbach get to Berkeley?

Johnston: At my strong recommendation, Professor Robert Connick, dean of the College of Chemistry at Berkeley, offered Dudley Herschbach an assistant professor appointment, and he accepted.

Hughes: When was this, more or less?

Johnston: He came here probably in 1960. He was a junior fellow at Harvard for either two or three years. I know he was not yet here in 1959 and was here in 1961.

Professor George Kistiakowsky at Harvard was an extremely outstanding physical chemist and public affairs man. He had the idea of doing molecular beams a few years before Dudley. He and his students built the best molecular-beam system they could, and they tried and tried, but nobody ever got any results. So finally George went in with an ax or ax handle and smashed up his machine. [laughter] Total waste of time.

When Dudley came to Berkeley, he designed a molecular beam machine in full detail, had it built in the College of Chemistry shop, and with his graduate students as assistants he carried out successful experiments where atoms or molecules in one molecular beam collided with atoms or molecules in a crossed molecular beam. He had a detector that was highly sensitive to alkali metal atoms, for examples, sodium and potassium. He could measure the velocity of both beams and the angle of deflection after a collision. He immediately discovered significant new things with his new

method. The best physical chemistry graduate students who came to Berkeley in those years worked with Dudley.

Harvard liked to send their Ph.D. graduates off to other universities or other jobs until they were successful, and the ones that are really successful, Harvard invited to come back. Despite all Berkeley could do to keep him here, Dudley went back to Harvard in about 1965. He had a continuing successful career there. As you know, in 1986 the Nobel Prize in chemistry was divided three ways: to Dudley Herschbach, Yuan Lee, and John Polanyi in Toronto for their fundamental work in chemical dynamics. The student they wouldn't admit to Harvard as a graduate student came back to Harvard as an honored full professor and won the Nobel Prize.

Yuan Lee came here as a graduate student, and obtained his Ph.D. at Berkeley working with Professor Bruce Mahan. He worked with Dudley at Harvard as a postdoctoral fellow and developed a high-sensitivity universal detector. With his detector he could measure almost anything with equal sensitivity as Dudley could with his alkali atoms. He became assistant professor—maybe associate professor—at the University of Chicago. Berkeley brought Yuan Lee back from the University of Chicago; I don't know whether as associate professor or full professor. Lee started from the fundamental beginning and worked up. Using collisions in crossed molecular beams, he derived the potential energy functions between pairs of noble gas atoms and worked up from there. One by one he did collisional excitations of small molecules by noble gas atoms, and later he studied chemical reactions in the crossed molecular beams. He was able to contribute to and solve a wide variety of conceptual problems.

Hughes: In the preface of your book, you said: "There is strong reason to believe that we stand at the threshold of a new era in kinetics."

Johnston: That's right. Dudley Herschbach and Yuan Lee and others.

Hughes: That's exactly who you were thinking of then?

Johnston: Yes.

Hughes: What precisely were you expecting them to contribute?

Johnston: They were carrying out collisions in crossed molecular beams under completely controlled conditions and measuring the chemical and physical properties of the products of collision. And that was direct evidence for understanding chemical reactions in a fundamental way.

Hughes: I have the idea that you don't consider yourself to be a theoretical chemist. And yet you gave me a folder labeled "theory."

Johnston: Yes. I'm a chemist who uses theory to understand what I've been doing. The only contributions I made to theory was inspiring Dudley to come out with our 1959 paper on molecular partition functions from local properties. I got him interested in the problem.

Let's be careful about that word theory. To some chemists, theory is what can be found from solving quantum mechanical equations. Schrödinger equation, you know about that?

Hughes: Yes.

Johnston: A complicated molecule is almost as difficult a problem as smog is—not quite.

Theory in the sense of using fundamental quantum mechanics to explain everything is the highest level of chemical theory. I've had three papers at that level of theory. That's when we got a theoretician interested in one of our problems, and one of my graduate students worked with Professor Fritz Schaefer when he was here, another with Professor Bill Lester. So I've had graduate students use fundamental theory, but it's only in collaboration with a theorist in the department.

Some people wouldn't regard activated complex calculations as theory. We've taken activated complex theory and made an occasional step forward. There's theory involved in what we do, but I'm not a theorist. Our showing that the size of the uncertainty principle was larger than the structure of an activated complex was meaningful. I think that woke several theorists to have an interest in the problem. They provided elegant and excellent solutions. So no, I've never had enough mathematics to really be a theorist in the true sense of the word.

Hughes: Could you comment on what being at the University of California at Berkeley meant to your work in terms of colleagues and facilities and institutional support?

Johnston: I have certainly had great support from colleagues in chemistry. The faculty at Berkeley is one of its great resources and advantages. If I ever needed personal or chemical advice, I'd talk to Ken Pitzer. But then I've worked with several other people, some briefly and some at length.

Hughes: What was usually the motivation to bring somebody else in?

Johnston: When I was interested in a problem that I couldn't solve, but it overlapped the expertise of somebody else.

Hughes: I see. So you were seeking expertise.

Johnston: Yes, and perhaps more than that. People in the department come around and talk to me too. There's a way of giving back. No, this is a terrific place from that point of view.

Hughes: It's a collegial department?

Johnston: Yes.

Hughes: As a result, you didn't feel the need of going to colleagues elsewhere?

Johnston: I think that's almost true. I've had graduate students leave here, and we've had follow-up collaborations, but that usually doesn't last too long. They need to get their name on the paper first and only their name on the paper. I certainly collaborated with the

National Bureau of Standards for a couple of summers. I spent nine months in Brussels with Professor Paul Goldfinger. I spent six months in 1984 at the National Center for Atmospheric Research in Boulder. It was good interaction there too.

Hughes: Did those associations lead to further research?

Johnston: Yes. You used the word “networking”. What did you have in mind there?

Hughes: An information-gathering system through colleagues. I’m trying to get a feel for how the information that you used in your work got to you. What mechanisms did you use to acquire it?

Johnston: Most of the data we used we generated ourselves, that is, my graduate students did.

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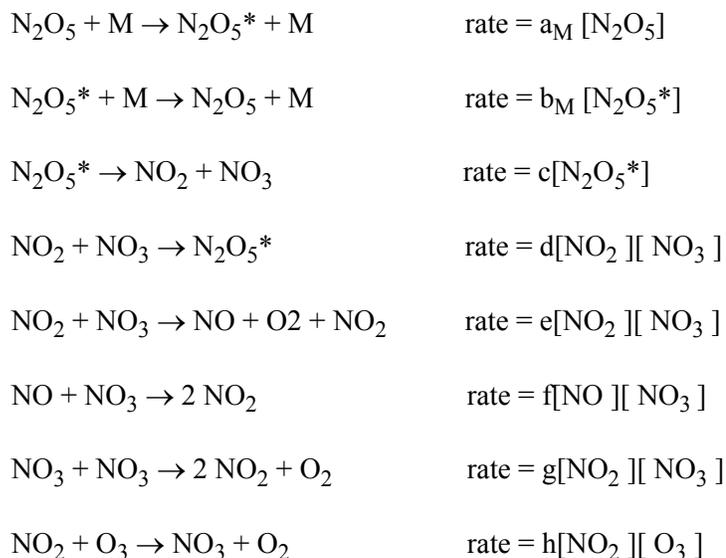
Tape 7, Side A

Hughes: Dr. Johnston, we're going to concentrate next on the stratospheric work, but I thought before we plunge into it, that you might pick up some of the work in the 1950s that link to what came later.

Johnston: All right. There are several lines of work I did between 1950 and 1970 that were useful after I started working on the stratosphere in 1971.

We used the fairly fast—for the day—reaction technique, published in 1949, to cover lots of ground that had been too fast to handle before. The most convenient set of cases involved the oxides of nitrogen. Each of nitric oxide (NO), nitrogen dioxide (NO₂), and nitrogen trioxide (NO₃) has an odd number of electrons, which makes them “free radicals,” by definition. Their reactions are usually rapid, they illustrate a number of chemical principles, and as I found later they are important in the atmosphere. My first ten publications all involve the oxides of nitrogen. Later all of these reactions were found to be important in the chemistry of the stratosphere.

The question here is: What set of elementary chemical reactions are important in a complicated chemical or photochemical system? My earliest example of this was an article in 1951, where I showed that “the mechanisms of four kinetic systems involving nitrogen pentoxide can be expressed in terms of eight reactions which are believed to be elementary steps.” The eight elementary reactions are:



where square brackets indicate concentration of specie enclosed.

The four reaction systems, their mechanisms, and their rate expressions are:

(1) Thermal decomposition of nitrogen pentoxide:



mechanism reactions a, b, c, d, e, f;

derived rate agrees with observations by six investigators over thousand-fold range of pressures.

(2) Decomposition of nitrogen pentoxide in the presence of added nitric oxide:



mechanism reactions a, b, c, d, f;

derived rate agrees with observations over hundred-thousand-fold range of pressures.

(3) Decomposition of ozone catalyzed by nitrogen pentoxide



mechanism reactions a, b, c, d, h, g;

derived rate agrees with observations with the strange fractional exponents, 2/3 twice.

(4) Formation of nitrogen pentoxide from ozone and nitrogen dioxide



mechanism reactions h, d, c, b;

derived rate agrees with observations with rate that of the elementary reaction h.

Hughes: When did you return to your interest in smog?

Johnston: Early in the 1960s, I became interested again in smog chemistry. An important element in this chemistry is the photochemical production of free radicals in the atmosphere and the reactions of these radicals with oxygen. I worked out a plan to solve some of the

mysteries of this system; I would start with the methyl CH_3 radical, measure the rate of loss of all reactants, and measure the rate of formation of every product. Next, we would carry out similarly detailed measurements on the ethyl radical CH_3CH_2 , and then oxygen atom-containing radicals, HCO and CH_3O . In the case involving the oxides of nitrogen, I had been able to characterize eight elementary reactions by the studying the rates of all reactants and products in four systems, and I was optimistic about doing the same for oxidation of simple organic free radicals, and perhaps building up to larger radicals.

In a project funded by the U.S. Public Health Service, I bought a Bendix time-of-flight mass spectrometer, fitted it with a quartz reaction cell with quartz windows, passed a chopped beam of ultraviolet light along its axis, and rapidly flowed a gas stream through it. Julian Heicklen and I planned to measure the decay of reactants and the buildup of all reaction products in order infer all the free radicals in the reaction and find the full chemical mechanism. In a stream of flowing air, we produced methyl radicals (CH_3) by photolysis of methyl iodide and ethyl radicals (C_2H_5) by photolysis of ethyl iodide. We also produced CH_3CO radicals by direct photolysis of acetone and HCO radicals by direct photolysis of acetaldehyde.

We measured initial rates, steady-state rates, and the full curve of product buildup as a function of time. In the first two articles, we tried to establish which free radicals were present in significant amounts, what were the elementary reactions, and to evaluate the ratios of certain rate coefficients. In the last two articles, we emphasized how many free radicals could be in our system and how many elementary reactions could be occurring, all consistent with our observations. A quotation from our article on the photochemical oxidation of acetone: "From identified products at least 14 free radicals are inferred to be intermediates in this system. An exhaustive and impartial examination ... exclude a large number of possible reactions but 140 reactions could still be occurring Thus this method cannot give a complete mechanism, nor can any method that simply analyzes all molecular products."

Hughes: I read about an uncertainty principle associated with your name.

Johnston: Franco Cramarossa and I identified an "uncertainty principle" with respect to the mechanism of reactions with free-radical intermediates: "In a kinetic or photochemical system involving three or more free-radical intermediates, one can never deduce the mechanism by any method that merely analyzes for all the final products and the reactants ... there are simply more elementary reactions than observed products."

Molecules contain an even number of electrons, examples are N_2 , H_2O , O_3 , CH_4 , $\text{C}_2\text{H}_5\text{OH}$, HNO_3 , N_2O_5 , and there are millions more. Free radicals have an odd number of electrons; examples are H , OH , HOO , CH_3 , CH_3OO , CH_3O , NO , NO_2 , NO_3 , Cl , ClO , Br , BrO . From these odd and even properties, we defined "free-radical arithmetic." A molecule may dissociate into two molecules in only two ways:

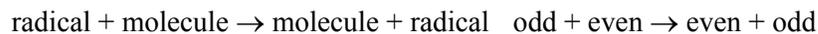
molecule \rightarrow molecule + molecule even \rightarrow even + even

molecule \rightarrow radical + radical even \rightarrow odd + odd

A radical decomposition always produces at least one radical:



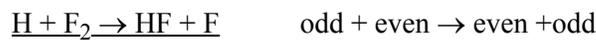
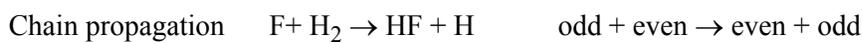
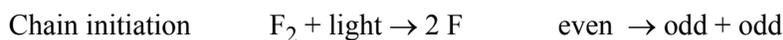
Bimolecular reactions of radicals with molecules usually have the form:



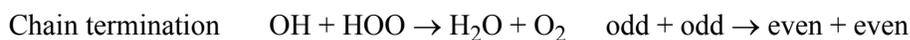
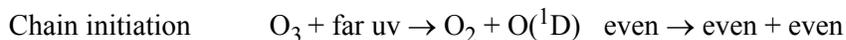
Radical-radical reactions typically have the forms:



Both in the laboratory and in the atmosphere, chain reactions can be initiated by a molecule absorbing visible or ultraviolet light (molecule + light \rightarrow radical + radical), for which the free radical arithmetic has the form:



An example in the atmosphere is ozone destruction catalyzed by free radicals based on water:



The chain length is the rate of chain propagation divided by the rate of chain termination. If the rate of termination is greater than the rate of propagation, there is no chain reaction. If the rate of propagation is large compared to the rate of termination, the chain length is long, and free radicals in trace amounts can change the concentrations of species present in large amounts.

For a wide range of light intensity, chain propagation rate coefficients, reactant concentrations, and temperature, Cramarossa and I derived algebraic formulae, constructed tables of values, and presented figures for:

- (1) Chain length
- (2) Steady-state radical concentration
- (3) Half-life of radicals in the system

In our tables and figures, we emphasized the boundary between conditions that give long chains and give essentially no chains.

Now, we haven't talked about the molecular modulation effect?

Hughes: No.

Johnston: The realization that we couldn't get the mechanism of a reaction with three or more free-radical intermediates unless we separately measured the rates of all important elementary reactions in the system was the motivation for our developing what's called the molecular modulation method.

Hughes: Did you give it that name?

Johnston: Yes. But the system wasn't as productive as we hoped it to be. Better methods came along a few years later. But the idea there is: if a free radical absorbs light in a certain region and if we shine light through that region, the light will be absorbed to some extent. We pick conditions so some of the light gets through and some doesn't. Now, if we make this free radical by turning the light on and off—see, we are making free radicals by breaking some molecules down with light, and we would like to see which they are, state by state. If we just send a direct current light, it would be very hard to separate out what's going on. But if we chop the light, 100, 200, 300 times a second, then the molecule itself is modulated. The free radical that's produced goes down and builds up, goes down and builds up. We can come up with the spectra of certain free radicals.

One of the most interesting spectrum we did was that of the HOO free radical, the peroxy free radical. We studied chlorine in the presence of carbon monoxide and formed a spectrum that we couldn't identify. Too bad we didn't, because in the years later, this turned out to be a dimer of ClO, ClOCl, which is very important in the chlorine atmospheric chemistry. We saw it and didn't know it.

The big change here was in 1966 I became dean of the College of Chemistry, a job for which I was terribly unsuited. [laughs]

- Hughes: Why?
- Johnston: I'm just not the type.
- Hughes: You don't like administration?
- Johnston: No! It takes a very large amount of time; it takes time away from research. A partial solution was the fact that we had in 1958 bought some property in Sonoma County near Healdsburg, up in the hills. It had some Russian River frontage. We built a house there in 1966. So to get away from it all, I would take research problems there and work on them in the summer.

But what was really nice was the National Bureau of Standards [NBS] was collecting critical data on reaction rates in the 1950s. The first time they went through it, they did it completely the wrong way; just put all the empirical rates down without any understanding of the elementary steps. David Garwin and I pushed the idea that we ought to be tabulating the elementary steps. So NBS paid my salary for two summers—not the whole summer, a month or two—to spend the hot hours of the day in our nice beautiful country spot studying and going through a huge stack of reprints involving ozone, atomic oxygen, chlorine, hydroxyl radicals, and oxides of nitrogen.

In the time available, I was able only to do a good fraction of my goal, not all, but I was able to complete a critical study of all the elementary reactions in the system of O_3 , O_2 , and O , just with each other, and did a fair amount of work in the literature on that. I plotted up all the measurements anybody had made and tried to decide which was high quality. In one of the reactions, I found that every measurement that had ever been recorded was on the same straight line, with some scatter of course, going back to 1909. The earliest paper there was 1909, and even with results from the newest methods, the old and new measurements agreed. In another reaction the previous workers didn't agree at all. I had to really think where people might have done something wrong and come up with a recommendation as to which measurement seemed to be best.

I was working on the same project, concentrating on the oxides of nitrogen, when time ran out in the summers. We couldn't publish critical tables and only have done half of them. I intended to get back to it during the school year, but I didn't make it. You'll see later why I got interrupted.

During World War II, the atmosphere in Los Angeles was gorgeous. We could see the mountains nearly every day, and the clean ocean breeze blew in every afternoon. It was the paradise Los Angeles used to advertise. There was gas rationing. The government limited civilian use of gasoline. I observed the beautiful air because at that time we were outside measuring it.

After the war was over, the air got dirty very rapidly. By 1948, it was pretty bad. We sort of understood what was happening insofar as the inversions were concerned, but didn't know what the chemistry was. I was busy trying to finish my thesis.

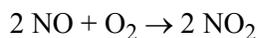
Airie J. Haagen-Smit was a professor at Caltech. He was a biochemical microchemist. Microchemistry is analytical chemistry measuring accurately very small amounts of

stuff. He was Dutch, a very precise man, and a bit astringent to deal with. His specialty was in accurately measuring chemicals of various sorts. The people at the Riverside citrus station—

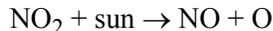
Hughes: Connected with Caltech?

Johnston: No, with the statewide University of California. At Riverside, they detected a new disease among the plants. The flowering plants and spinach and other plants were dying. A new disease had appeared. In about 1950 they asked Haagen-Smit if he, as a biochemist, had any thought what it might be? I don't know what genius-like steps went through his mind, but he solved the problem.

People were thinking smog came from factory smoke, and there was talk about applying some controls for smokestacks. Haagen-Smit made ozone in the laboratory and exposed some plants to it and reproduced the damage caused by the suspected disease. Where did the ozone come from? He came up with the following mechanism: nitric oxide, NO, comes out of the tailpipes of cars in large amounts. Max Bodenstein, a major physical chemist in Germany, accurately measured the rate of the reaction of nitric oxide with molecular oxygen back in 1918 and 1920:



It was well known in 1950 that near ultraviolet sunlight broke nitrogen dioxide into nitric oxide and an atom of oxygen:



Atomic oxygen adds to molecular oxygen to produce ozone:



The net reaction is:



It was known in organic chemistry that ozone rapidly reacts with double bonds to make ozonides and all kinds of products. Haagen-Smit's theory was that the nitric oxide alone in air and in sunlight generated ozone, and the ozone reacted with unburned hydrocarbons to make smog. We had done Bodenstein's reaction in our laboratory many times. We often used that reaction in the laboratory as a test of our apparatus. We measured the rate at high pressures in our fast reaction system, and it reacted at the millisecond time scale. We measured the rate at low pressures in our 22-liter bulb, and it required many days to show a significant degree of reaction.

At Stanford, I was in a seminar where the speaker was presenting Haagen-Smit's mechanism for smog production from automobile exhaust. The nitric oxide in a smoggy atmosphere was less than a part per million. I knew that the rate of Bodenstein's reaction was very slow under these conditions. During the discussion period after the

talk, I said that the reaction would be slow and could not explain the rapid buildup of ozone observed during the morning.

Hughes: Is this what you worked out?

Johnston: No. The only thing I did in 1951 was to point out to Haagen-Smit that Bodenstein's reaction was too slow to be an important source of ozone in the atmosphere.

Hughes: You were noticing a diminishing of air quality after the war?

Johnston: Yes.

Hughes: Was that a common observation?

Johnston: It was in the newspapers, frequently.

Hughes: How did the public explain it?

Johnston: Smokestacks. Industry putting out smoke.

Hughes: Do you include car exhaust?

Johnston: Haagen-Smit was the first to propose that. One of the points is that all of a sudden, instead of having a few industries with smokestacks, the villains are the car manufacturers, the gasoline makers, and the public! The public couldn't defend itself very much, but the big companies viciously opposed Haagen-Smit.

Hughes: Was Haagen-Smit hoping to explain the atmospheric conditions through these reactions? Was that his point?

Johnston: Yes. His first mechanism was the sequence including Bodenstein's reaction to form ozone, and the ozone rapidly attacks organic compounds in a variety of ways, including damage to vegetables and flowers.

Hughes: Were you alone in thinking that the Bodenstein reaction was too slow?

Johnston: It hadn't been brought to anybody else's attention. Bodenstein's reaction was well known. It's in many physical chemistry textbooks. There was no argument about the reaction itself nor of Bodenstein's reported rates.

Hughes: I thought one of your points was that the Bodenstein reaction was too slow.

Johnston: Correct. It was too slow under atmospheric conditions, including smog.

Hughes: Was that a common realization?

Johnston: No.

Hughes: Was that your contribution?

Johnston: That was my contribution. I sent Haagen-Smit a letter explaining the problem of the rate, and he took Bodenstein's reaction out of his mechanism.

As I told already, at seminar given at Stanford, a speaker presented Haagen-Smit's chemistry of smog. I stood up at the meeting and politely pointed out that Haagen-Smit's first reaction was too slow to produce the observed build up of ozone every day.

Vance Jenkins was sitting in the back row—I think I remember his name. He didn't say a thing. He was a representative of the oil and gas industry. SRI [Stanford Research Institute] had large projects studying smog, supported by oil and gas companies. Jemkins went to people at SRI and said in effect, "Hey, this brash young guy stood up and said Haagen-Smit's mechanism is wrong. Why don't you hire him and find out what he's talking about?" So I was hired as a consultant to SRI, they invited me to present an informal talk to their board of directors, and they hinted that I might get funds for my research. Especially the oil people were vociferous that Haagen-Smit was all wrong, that he was only a publicity-seeker. Automobiles and gasoline couldn't have anything to do with it. They really opposed him on a personal level. He was a shy man and was very much upset.

I hadn't really studied Haagen-Smit's mechanism beyond just hearing this seminar. SRI brought me in and told me that in this seminar I had said that Haagen-Smit was wrong, and they were much interested in that. Would I explain what happened? I told them, "No, I didn't say he was wrong all the way. I just said he was wrong in one particular reaction." They said, "We'll, pay you for studying the literature here and coming back to explain what you found." They said terrible things about Haagen-Smit. So I was given the job of disproving the theory of this quirky, perhaps dishonest, scientist. I was given the job of overthrowing his theory entirely.

In sunlight and volatile organic compounds, several reactions occur to produce the hydroxyl free radical, OH, which rapidly reacts with almost any organic compound: So I went to work on his published articles and abstracts of his talks to see what he'd actually said. I rapidly concluded that Haagen-Smit was a genius! Everything he said was based on experiments he had carried out, and his techniques seemed to be sound. I told them it seemed to me that he was right, across the board. I presented a modification to Haagen-Smit's mechanism:



I postulated the reaction of peroxy radicals with oxygen to make ozone.

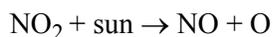
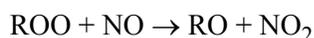
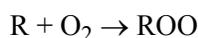
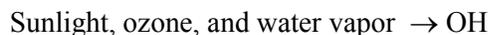


Then the ozone goes on to have further reactions as worked out by Haagen-Smit.

The manager said, "Oh, this is important, this is very important, but we must be careful. We have to do more research before we can bring this out." They postponed my appointment with the board of directors. They made no more reading assignments, and

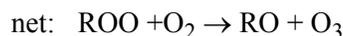
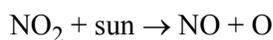
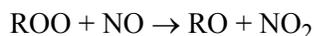
my consultantship lapsed. Before I left SRI, Dick Cadle and I published one article in 1952, in which I gave a modified version of Haagen-Smit's mechanism.

The mechanism that finally developed in the period 1960 to 1970 is that free radicals R are produced in the slow photochemical combustion of hydrocarbons. These free radicals add molecular oxygen to produce ROO, and it reacts with nitric oxide to form NO₂, which sunlight breaks down to form atomic oxygen and then ozone. Haagen-Smit correctly got the phenomenology right, but the detailed mechanism took years to get straight. A brief form of the mechanism goes like this:



The essence of smog is slow photochemical combustion of organic gases in the sunlit atmosphere in a process that is cyclic in OH and HOO, cyclic in NO and NO₂, consumptive of volatile organic compounds, and produces ozone.

The net effect of three reactions in this mechanism is equal to my postulated reaction in 1952. I had the overall process right, but my mechanism was wrong:



Hughes: What was the scientific community saying about Haagen-Smit's findings?

Johnston: In 1952, there weren't many people, frankly, in a position to really understand it. From the chemical warfare research I had done and the specialization I had in oxides of nitrogen, I could understand it. Phil Leighton, Francis Blacet, and W.A. Noyes, Jr., would understand it. But there were few people interested in or expert in this corner of the field. It involved photochemistry out-of-doors.

Hughes: "The field" was atmospheric chemistry?

Johnston: Yes. Well, the field work I did in chemical warfare did not concern reactions in gases. It was where the gases went. But there was some overlap. Haagen-Smit developed the mechanism to a very advanced stage. But it wasn't till later that this mechanism with organic peroxy-free radicals was worked out.

As I left Stanford in 1956, Professor Philip Leighton and I had a long conversation about his and my future plans. He proposed that he and I collaborate on a full book developing the ideas about smog chemistry, but I told him that I had no further interest in the subject, and I suggested that he write the book himself, which he did.¹

This book gave an excellent account of the science of photochemical air pollution as of 1960.

In 1970, the statewide administration of the University of California with seven different campuses went to the legislature and proposed that they provide a certain amount of funds, and the university would use them to bring together experts from all the different campuses and all the different disciplines that were applicable, and they would try to issue a definitive report up to that date on smog, chemistry, health effects, economic effects, and all aspects. I think they only had an appropriation for one year, and enough people were working on it from enough different points of view that they were able to publish seven volumes when the contract expired.

Hughes: Remarkable!

Johnston: Yes. Well, lots of capable people were working on it simultaneously. I was co-chair (with Jim Pitts) of Task Force 7, "Atmospheric Chemistry and Physics." I taught a course in physical chemistry in the spring of 1970 and offered the students in the class—not the whole class, but students I thought could do it—summer employment if they would pitch in and help me comb through the literature to come up with this chapter. That was a very good investment.

Hughes: They were undergraduates?

Johnston: Yes, twenty-one in all.

Hughes: How were you paying them?

Johnston: I received some Project Clean Air money.

We tabulated measured rate coefficients at 27 degrees Celcius for five classes of reactions with hydrocarbons, involving 76 reactions:

Atomic oxygen O plus unsaturated hydrocarbons, 15 cases

Atomic oxygen O plus saturated hydrocarbons, 21 cases

1. *Photochemistry of Air Pollution*, Philip Leighton, Academic Press, New York and London, 1961.

Atomic oxygen O plus oxygenated compounds, 5 cases

Ozone O₃ plus unsaturated hydrocarbons, 30 cases

Hydroxyl radicals OH plus saturated hydrocarbons, 5 cases

Using my large stack of reprints of articles provided by the National Bureau of Standards and the output of the undergraduate students during one summer, I prepared a critical review of twenty-four elementary reactions among inorganic species, sixteen of which involved the oxides of nitrogen, nine reactions of free radicals derived from water, five involved atomic oxygen, five ozone, and six chemical reactions of singlet oxygen. I listed rate coefficients for all the authors who had reported measurements, and I gave a preferred value for each reaction. We cited 179 articles from the literature.

I wrote a twenty-five-page review of tropospheric reactions of nitrogen oxides, free radicals derived from water, without and with sunlight, without and then with added organic compounds. I used free radical arithmetic on all the reactions, derived rates and steady-state concentrations, of ozone and many free radicals. The operation was an effort to update Haagen-Smit's work.

Haagen-Smit demonstrated this overall mechanism: almost any organic compound, plus NO₂, plus sunlight, generates ozone. But that's leaving out literally hundreds, maybe thousands, of free radical steps and so forth in between. He also demonstrated that just the exhaust gases from a car, exposed to sunlight, generates ozone. He characterized the general features of these reactions in a considerable amount of detail.

Hughes: When was it?

Johnston: Early 1950s.

Hughes: Were you in personal communication with him?

Johnston: Not in the beginning, but later, yes.

My chapter in 1970 concerned the free-radical reactions that interact with the oxides of nitrogen to enable it to produce ozone. There's another byproduct of smog, the particulate matter, the blue haze, as it was called at first. And then there's the eye irritant. We didn't go into that; we were just trying to get the chemistry in my big chapter. So I had several different people working, especially people at Riverside.

Hughes: They were collecting data?

Johnston: They were interpreting the literature. No, there wasn't time to carry out more experiments. We only had one year. But they did a systematic study of all aspects that were published.

Hughes: Was there already quite an extensive body of information?

Johnston: By 1960, there was a substantial amount. That's when Phil Leighton wrote a book on the chemistry of air pollution. Only a small number of reactions were really known for sure at that time. They had to say over and over and over again, "This is probably what's happening but hasn't been shown yet." And then there was a large amount of work between 1960 and 1970, and the seven volumes of Project Clean Air was trying to pull that all together.

An interesting sidelight of 1970 was that graduate students in physics were in a depression. They couldn't get jobs, or it was difficult to get jobs. Tom Mottershead had just finished his Ph.D. in physics at Berkeley and couldn't find anything. I forget all the preliminaries, but he was on the project in my task force, and I gave him the problem of studying particulates that are formed by smog. He went at it from a physics, fundamental point of view, and he didn't have any results at all after one month, and he only had two months. But then he finally built up to the point that he understood it, and I understood it, and he contributed a valuable section of that chapter.

Hughes: How did his work differ from what a chemist might have done?

Johnston: A large number of chemists could have done the same thing; high mathematics wasn't involved. I think physicists get a more fundamental training in their field than chemists. Chemists are anxious to show off their fireworks to the freshmen—that's not completely true. But in physics, they start out with the dull things and then work up step by step by step. I'm not really trying to criticize chemistry teaching. A lot of chemists could have done it, but they weren't available. Chemists who just got their Ph.D. degree didn't want only two months of work at that time.

Now, for future reference, let me mention one of the reactions of oxides of nitrogen that I had reviewed. There was a reaction of nitrogen dioxide and water, NO_2 plus H_2O , that had been studied by three different groups, and they got extremely different results. I'm pretty sure we understood why. They were measuring a surface reaction in their apparatus, not a gas-phase reaction. We figured that out, and that was listed in our set of recommendations. In fact, one of them was in error was a factor of about 1,000.

[Tape 8, side A]

Hughes: You mentioned molecular modulation, but you didn't explain what that allowed you to do, and you might want to say how that particular technology was very soon replaced by the laser.

Johnston: All right. Without going into technical details, the method is designed to measure the spectrum of free radical intermediates in photochemical reactions and through a phase shift to measure lifetimes or rates of the free radical. Especially in Great Britain, the method was adopted and proven, and it was used, not widely, but in a few studies.

Hughes: For what period was the molecular modulation method used?

Johnston: As I remember, our first article was in 1966, and I think our last article was '72 or '73. So just five or six years.

- Hughes: It was picked up by a specific laboratory group in Britain?
- Johnston: A couple of laboratories used it and got good results.
- Hughes: They were looking at complex interactions?
- Johnston: Yes, looking at free radicals and other systems.
- Hughes: Is that the only general application that molecular modulation could be used for?
- Johnston: It was fairly narrow in its capabilities. Jumping very far ahead, Professor Richard Saykally in this department used, in effect, molecular modulation—he didn't call it that—at very high frequencies in recent years. The technique is so far removed from what we did that it shouldn't really be called molecular modulation. The way we were doing it was really cumbersome—big equipment and limited results.
- During and after the 1970s, Dudley Herschbach, Yuan Lee, and others built molecular beam machines with highly sensitive detectors and studied molecular collisions in crossed molecular beams. They sometimes crossed a molecular beam with a laser beam, or crossed one beam of the two crossed molecular beams, or used two or more lasers with molecular beams. Also in the 1980s and 1990s, laboratory chemical kineticists used lasers without molecular beams to obtain the rate coefficients of many elementary reactions. The power and specificity of the crossed molecular beams and lasers are much greater than molecular modulation, so we dropped doing it after about 1972 or '73.
- Hughes: You've been implying all along, but I thought for clarity I would ask you: in these kinetic and photochemical systems that you were studying, you were trying to go beyond the products and the reactants to work out the intermediate substances.
- Johnston: Yes.
- Hughes: Why was knowing this sequence of events in detail of interest?
- Johnston: Elementary reactions are the elements of real-world chemical reactions. The rate coefficients of an elementary can be measured in the laboratory and transferred to a complex system, such as the atmosphere. Chemical reaction rate theory is applicable to elementary chemical reactions. The list of elementary reactions to be included in a model must include the reactions of free radical and other intermediates.

Let me cite two books in this context.

The first book consists of tables that list: the sequence number, a chemical equation for a reaction, the solvent, concentrations of reactants, concentrations of any added ingredients, temperature, empirical rate coefficients in terms of arbitrarily assumed rate law, comments, and references. The book has approximately 300 pages. These data are limited to the specific conditions of the measurements. They are not transferable to other conditions, and they cannot be tested by reaction rate theory. I contributed reviews for this book, but it was under protest. I said we should be measuring and tabulating rates for elementary reactions only.

The second book is about the same size. It tabulates only what are thought to be elementary chemical reactions (except in a few cases where the products were unknown). The tables include the rate coefficients: A , $E/R \pm$ uncertainty estimate, $k(298\text{ K})$, estimated uncertainty factor for k , and references to extensive critical notes. There are about 750 elementary reactions tabulated in this book and about two thousand references to published articles. This book gives the sort of data that I advocated since the early 1950s. I certainly don't claim credit for getting this work done; physical chemists were naturally and independently doing chemical kinetics in this way for a long time. These data are confidently transferred to atmospheric conditions and used in numerical models.

Hughes: Meaning that you have data for—

Johnston: For all the reactions in the book. But we still have to worry that there may be some species that we haven't recognized, or there may be reactions that we have not yet thought about. So we have to be careful.

Hughes: The only ones missing are those that haven't been conceived?

Johnston: Correct, that haven't been thought of. Now, we have these days many observations in the stratosphere, and people test their observations against the set of elementary reactions—they make a model using the elementary reactions that apply to that system. There's a lot of good agreement between measurements and models.

Hughes: Is Haagen-Smit perhaps the beginning of this movement?

Johnston: No. It was a logical physical chemical development. Haagen-Smit came out with an explanation of what goes in and what comes out in photochemical smog, although he gave some thought to the reactions. Let me say this: There are other publications that tabulate the reactions of volatile organic compounds in the troposphere, but even so, there are still many more reactions occurring in photochemical smog than the known pertinent elementary reactions.

Hughes: And that is because of—

Johnston: The complexity of the system.

Hughes: You don't know it well enough to model it?

Johnston: Well, people do model urban and regional smog processes, but we know we don't know it all. Upon reaction, most organic compounds give more than one set of products, four or five or six in some cases. Almost at every stage, the reaction can go in two or three different ways. So the complexity cascades down.

Hughes: And that doesn't keep you awake at night?

Johnston: No, why should it keep me awake at night?

Hughes: Because you collectively know that the model you have proposed has lacunae in it.

- Johnston: Nobody has gotten around to making all those measurements.
- Hughes: And the large amount that you do know brings you close enough to verify the theory to everybody's satisfaction?
- Johnston: No, not to everybody's.
- Hughes: So not knowing all the steps leaves the results more flexible to interpretation?
- Johnston: Sure, yes, that's one way of putting it. Well, there are many problems that are so complex that we can't solve them on computers.
- Hughes: But it seems to an outsider, which I certainly am, that you're in danger of building a house of cards. If here and there you are quite aware that the data is incomplete, doesn't the synthesis stand on very shifting sands?
- Johnston: I think I see what our difference is. Many people interpret events and actions in a bipolar manner, for example:

Pole		Opposite pole
Win	or	Lose
Right	or	Wrong
True	or	False
If you are not for me,		you are against me.
Proven	or	Unproved

Some things in the world are like this, but not everything. Scientists see the world in a different way. They seek to find the most probable value V of something according to current knowledge and to find the recognized uncertainty of the value $\pm U$. If the uncertainty is caused by multiple random actions, the uncertainty has the gaussian distribution, sometimes called the "bell curve." I think there is some measurable physical constant, I forget which it is, that is known out to the seven significant figures, symbolized as

$$V = a.bcd\text{efgh} \pm 0.000000U$$

where the lower case letters are integers. Even this best of all known physical constants is uncertain in the seventh decimal place.

A measured scientific value is neither right or wrong, true or false. If the value of the quantity hurts the interests of some industry or the agenda of some politician, the industry or politician often accuses the scientist of being "against" them, of being their enemy, of being a publicity seeker, of their trying to assure their financing for the next year, et cetera. If the quantity is stated to have uncertainty, that does not make it wrong

or false or unproved. Every quantitative thing in science—and in life—is uncertain to some degree.

Hughes: Are those decimal places in atmospheric chemistry sufficient to make you relatively content with the data that you work with?

Johnston: Chemistry of the stratosphere is now a mature science, but some research continues in an effort to get improved data. Our understanding of stratospheric chemistry is vastly better than it was thirty years ago, when I got into it, and much better than ten years ago. Our understanding of the chemistry is much better than our understanding of stratospheric motions. Atmospheric chemistry of photochemical smog is vastly more complicated than chemistry of the stratosphere, but a new generation of atmospheric chemists, for example Ron Cohen of this department, is busy in learning more about the system, and they are making significant progress.

[End of session]

.INTERVIEW 5: AUGUST 9, 1999

Tape 9, Side A

Hughes: In the late 1960s, the U.S. government proposed building a fleet of supersonic transports. Why did that idea arise at that time?

Johnston: Before we get started, let me give you this list of technical terms that need to be defined:

Mixing ratio of X, the number of molecules of X in some volume of air divided by the total number of molecules of air in that volume.

Concentration of X, the number of molecules of X in unit volume, for example, molecules of X per cubic meter.

Emission index of X, the number of grams of X in an engine exhaust divided by the number of kilograms of fuel burned.

Mach number, the speed of an aircraft divided by the speed of sound.

I guess anybody who has flown across the Pacific would like to have a faster airplane. The only way to go fast enough to cut that drudgery down would be with supersonic planes. The military had developed supersonic aircraft, and I think it was John Kennedy who initiated the civil supersonic aircraft program. The United States government proposed to work with the industry and build two prototypes. That's no big fleet, but it would be quite expensive.

The government put out a competition for design, and several companies submitted proposals. Boeing got the contract, partly because it proposed a fancy wing-in, wing-out design so it could fly comfortably at subsonic speeds as well as supersonic. (Later, Boeing had to drop this moving-wing feature.) Supersonic aircraft make a strong sonic boom. They experimented—now I'm jumping in time—over a couple of cities in the Midwest by having military planes deliberately generate sonic booms over the cities, and the people almost went wild. It led to a powerful anti-sonic-boom campaign. William Shurcliff in the Boston area became the leader of it. There was considerable opposition on the basis of the sonic boom. I think his group was Citizens' League Against the Sonic Boom. That was a major environmental issue through the 1970s.

Hughes: It was the noise, not the pollutants.

Johnston: It was both and more. Simultaneously, many economists who analyzed the supersonic transport [SST] program said it wasn't economically practical.

Hughes: Do you remember the basis of their argument?

Johnston: Yes, at least part of it. With the designs they came up with, the SST couldn't fly all the way across the Pacific. It would have to come down at least once, maybe twice, and these stops would slow down the trip. Economists said it would not be competitive with wide-body long-range subsonic aircraft. A liberal point of view was that government money should be spent in alleviating problems in Watts instead of paying manufacturers for doing what should be their job of developing a new product. There was a big fury in the 1970s about these points.

I have several filing-cabinet drawers which contain primary documents of that period. Newspapers had big headlines about what somebody said and what somebody didn't say and about the noise. Congress passed a law that any supersonic passenger aircraft had to do their supersonic flight over water, not over U.S. land.

Hughes: This was an effect of the lobbying by the Shurcliff group?

Johnston: He organized a group and sent out newsletters. He made a big environmental issue out of the noise.

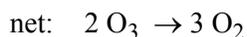
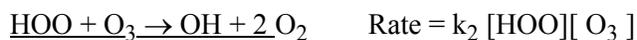
Hughes: But never mentioned pollution?

Johnston: No. The economists said it would be a money-losing operation, and liberals said it was a bad place to put our priorities. So there were raging debates on that in 1970. Now let me give the background to the problem of pollution of the stratosphere.

In 1930 Sydney Chapman published a theory of ozone production and loss in the natural stratosphere. Early calculations agreed with early balloon-borne measurements of the vertical ozone profile in the stratosphere. These calculations were based on an assumption about the amount of ultraviolet radiation the earth receives from the sun. Chapman's postulate was the surface temperature of the sun.¹

When the atmospheric scientists were able to use captured German V-2 rockets to get above the atmosphere and measure the amount of sunlight coming into the atmosphere, ozone as calculated by Chapman was twice as high as that observed. And so the word went out: There's something else in the stratosphere that destroys ozone.

Professor R.G.W. Norrish and his graduate student George Porter discovered flash photolysis a few years earlier. In their laboratory they photolyzed ozone with or without added water vapor. When they added water vapor, ozone was destroyed more rapidly. They explained the fast ozone loss in terms of the free-radical mechanism involving OH and HOO free radicals.



But nobody knew the rate coefficients, k_1 and k_2 , for these two reactions. These reactions hadn't been measured in the laboratory. They were difficult measurements to make.

The first theory of what else might be destroying ozone was presented in a couple of nice papers in 1965 and 1966 by Barry Hunt, who said that Norrish's free-radical chain reaction involving OH and HOO would explain the low observed profiles of ozone, if the rate coefficients had values within a stated range. As his hypothesis, he assigned

1. Chapman, S., A theory of upper atmosphere ozone, Mem. Roy. Met. Soc., **3**, 103-125, 1930.

numerical values to the rate coefficients k_1 and k_2 . This article had nothing to do with supersonic aircraft ; it was a pure science article working toward an understanding of the natural ozone balance.¹

And then in early 1970, atmospheric scientists noted that the exhaust gases from 500 SSTs would increase stratospheric water by 10 percent, and using Barry Hunt's assumed rate coefficients, k_1 and k_2 , they calculated that SST would reduce stratospheric ozone by about 1 percent. Notice the two "ifs" in the analysis: If natural water in the stratosphere has reduced ozone by a factor of two and if 500 SSTs increased stratospheric water by 10 percent, then it was highly reasonable to suspect that 500 SSTs would cause a measurable decrease of total ozone. Other atmospheric scientists carried out simple model calculations and found about a 1 percent reduction of ozone, but they concluded that such a reduction of ozone was no problem, because day-to-day variation in water vapor is much larger than 1 percent, and it would have no effect on the climate.

Early discussions of ozone change did not consider that it might have effects, other than change of climate.

Hughes: Such as what?

Johnston: "Effect on climate" means effect on the global temperature, changing the global heat balance, global warming or cooling, long-term changes in seasonal or regional weather.

A physicist, James McDonald, reasoned behind closed doors before a National Academy of Sciences committee as follows: Atmospheric ozone strongly absorbs solar radiation that damages proteins and DNA, and thus protects the surface of the earth from such radiation. However, a small amount of this damaging radiation reaches the surface of the earth, and it is responsible for causing sunburn, "snow blindness," cataracts, leathery skin, wrinkles, solar keratoses, and skin cancers. He figured that if there was a 1 percent reduction in ozone, because of the way the absorptions go, there would be a 2 percent increase in damaging ultraviolet radiation.

Hughes: And when did that information first come out?

Johnston: It developed in secret in 1970.

Hughes: Why was it kept secret?

Johnston: I think people wanted to be sure about it. During the early or middle of 1970, it was recognized that the water vapor from the SSTs would probably reduce ozone by 1 percent, and that was regarded as negligible. In the fall, James McDonald argued that a one percent decrease in ozone would give a 2 percent increase in the radiation that breaks down DNA.

Hughes: That information was suppressed?

1. Hunt, B.G., Photochemistry of ozone in a moist atmosphere, *J. Geophys. Res.*, **71**, 1385-1398, 1966.

Johnston: No, it was preliminary. It hadn't been reviewed. We aren't supposed to publish our science in newspapers. James McDonald presented this prospect at a National Research Council committee meeting. He was working carefully behind closed doors.

In November or December, 1970, Halstead Harrison, a member of the Boeing chemical research staff, carried out calculations that indicated a 3.8 percent decrease in ozone, and he published it in November 1970 in *Science*. That stirred up the newspapers a little bit, but still the skin cancer theory hadn't come out.¹

Senator William Proxmire, who had been against the SSTs on other grounds, heard about McDonald's skin cancer theory and invited him to come and testify before the Congress, which he did in January 1971. That hit the headlines pretty strongly, because there was a lot of rage in Congress for and against the SST. During McDonald's testimony, it was revealed that McDonald had been interested in and advocated further research on "flying saucers." The SST supporters ridiculed McDonald for believing in flying saucers, and his testimony was discredited. Several weeks later, Professor George Kistiakowsky of Harvard told me that Senator Henry Jackson of Washington state referred on the Senate floor to McDonald as "that kooky scientist."

During March 1971, the Congress was scheduled to vote on approving funds for another year of SST development. Recall the project was to build two prototypes, which were to be tested before the industry would go into manufacturing a fleet of SST.

A great physical chemist, Professor Joe Hirschfelder, was on a Department of Commerce committee studying the SSTs. Apparently, he persuaded the committee to get together a group of scientists covering a wide range of disciplines—biology, atmospheric sciences, chemistry, physics, and engineering—to study the ozone reduction problem to see if something had been omitted. A meeting was set for March 18, 1971, in Boulder, Colorado. Hirschfelder invited me to come to that meeting. I told him, "I'm not interested in the SST." He said, "Well, you should be." He persuaded me to go.

Hughes: Where did he come from?

Johnston: He was from the University of Wisconsin.

Hughes: So he was an academic.

Johnston: He was academic, and very outstanding, very brilliant man.

Hughes: Had you known him?

Johnston: Yes, we knew each other. His field and my field are not exactly the same, but we both knew about each other, had met each other.

The skin-cancer theory was a completely new consideration, which hit the press in the middle of January, more or less. There were pictures on the front page of newspapers.

1. H. Harrison, *Science*, **170**, 734, 1970.

When I reluctantly went to this meeting, I got a requisition from the Department of Commerce paying my way to Boulder, and the document read as if they were buying a ton of steel or something. They paid my way there and back, and lodging there. Before going, I wasn't even sure where the stratosphere was. Was it the third layer or the second layer of the earth's atmosphere? I went to the library and read up—the stratosphere is the second layer—and I learned a fair amount about it. In the stratosphere, there is a temperature inversion top to bottom. When I read that the stratosphere had a temperature inversion and recalling our chemical warfare work, the problem became more interesting, because exhaust gases from the aircraft would take a long time to mix.

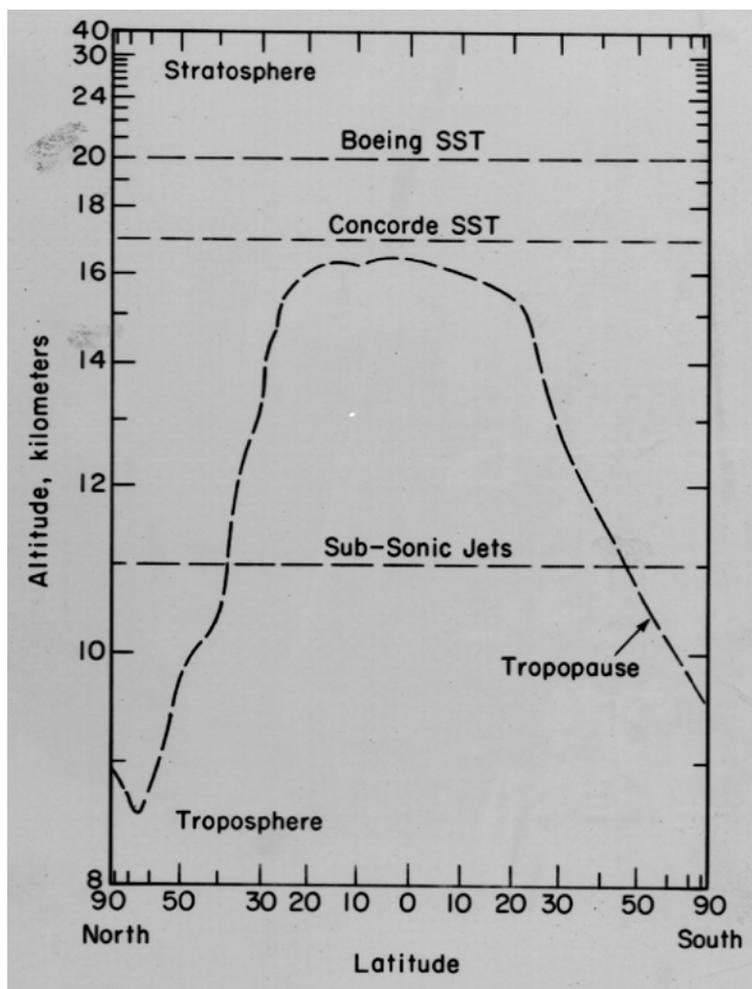


Figure 2. Ed Danielson explained how the stratosphere is not just one thing. It is essential to consider the stratosphere to be in at least two parts. In this figure (based on a figure in an Atomic Energy Commission report), I show features of the troposphere and stratosphere from the north pole through the equator to the south pole. The altitude scale is such that an equal area and shape corresponds, in three dimensions, to the same mass of air. The arching dashed line gives the altitude of the tropopause, the boundary between the top of the troposphere and the bottom of the stratosphere.

The first day at Boulder was spent with presentation of tutorials for the instruction of all the different disciplines. We had a number of informative talks about the stratosphere. Ed Danielson presented a talk that I was particularly interested in and impressed by: the history of the nuclear bomb debris from the atmospheric tests of 1960-61. These bombs threw a lot radioactive particles up into the stratosphere, and they produced gaseous radioactive carbon-14.

The Atomic Energy Commission [AEC] spent huge amounts of money following up where the bomb products went. The problem was extremely important, so no money was spared in carrying out measurements. Spy planes could get up to twenty kilometers altitude, and they carried out measurements over a wide range of latitude and altitude. Balloons were flown at several latitudes every three months, at altitudes up to about thirty-five kilometers. AEC published the record since the tests began in 1955 through 1970.

Because of the spherical shape of earth, tropical regions receive more solar energy per unit area than polar regions. There is a net rise of warm moist air in the tropical region and a net sinking of cold dry air in the polar regions. In the troposphere, air is readily mixed in horizontal and vertical directions; in the stratosphere air is readily mixed and transported in horizontal directions, but strongly inhibited in mixing and transport in the vertical direction, because of the temperature inversion there. Ed Danielson explained in March 1971 that air in the stratosphere below the height of the tropical tropopause readily exchanges air in the troposphere via horizontal motions, but air in the stratosphere above the height of the tropical tropopause must undergo inhibited slow vertical motions to mix with the troposphere. Danielson said that radioactive carbon-14 gas in the lower stratosphere had a residence time of about six months, but air in the stratosphere above the tropical tropopause had observed residence times of two to five years. I added the dashed horizontal lines showing the cruise altitude of long-range subsonic aircraft to be about eleven kilometers, the Concorde SST was about seventeen kilometers, and the proposed Boeing SST would be twenty kilometers. By horizontal motions, exhaust gases from subsonic aircraft in the stratosphere readily move to and mix with tropospheric air. Exhaust gases from the Concorde and especially from the Boeing SST must slowly overcome the temperature inversion to reach and mix with the troposphere.

Tape 10, side A

Ed Danielson summarized this all of this in one technical statement: "Above the height of the tropical tropopause, there are no lines of constant potential temperature connecting the stratosphere and troposphere."

Hughes: Is it for that reason that you wrote in one of your papers later on that the stratosphere was especially vulnerable to pollution?

Johnston: One of the reasons. It's in two parts: All the stratosphere has a temperature inversion that inhibits vertical transport and mixing, and pollutants deposited in the part of the stratosphere above the height of the tropical tropopause have no easy way to get out.

I learned a lot from Danielson's talk, including the importance of the measured radioactive gas behavior. AEC made extensive, long-term measurements and established a number of principles. From these measurements Danielson and others stated that the expected lifetime of SST exhaust in the stratosphere would be about two years.

Hughes: And that was new information?

Johnston: It was new to me. The Atomic Energy people knew about the lifetime of bomb-produced radioactivity, and they published their reports periodically. I went back and looked at these reports. They never said it quite as clearly as Danielson did. I took extensive notes at the Boulder meeting. I didn't know much about the subject, so I wanted to be sure I got everything down and could think about it later.

Joe Hirschfelder presented a short talk on how nitrogen oxides are made from hot air. When hydrocarbons burn in air, they produce large amounts of carbon dioxide and water. If under any circumstance, air is heated to a high temperature and then cooled down rapidly, some nitric oxide [NO] is generated. It depends on how high the temperature and how fast the cooling. At every cycle of an internal combustion engine, air is heated to high local temperatures and rapidly cooled down.

Hirschfelder handed out proof sheets, not then published, of a Study of Critical Environmental Problems—SCEP. These pages from the SCEP report gave fuel consumption by 500 SSTs and amounts of emitted water, carbon dioxide, carbon monoxide, nitrogen oxides, sulfur dioxide, and soot. GE [General Electric] engineers—GE was the major company building the SST engines—were quoted as saying that burning one kilogram of fuel produced 42 grams of nitrogen oxides. SCEP estimated the SSTs would increase the global average nitrogen oxides by 6.8 parts per billion, and up to 68 parts per billion in regions of high SST activity. The SCEP report quoted these figures from official governmental and industrial sources.

Hughes: The summer study was in 1970, and it occurred at MIT.

Johnston: Yes. They had a month-long summer program where they brought together atmospheric scientists and a wide range of other experts. People were beginning to worry about human activities having a global effect, or at least large regional effects.

Hughes: So the SCEP conference wasn't precipitated just by the supersonic transport problem?

Johnston: No.

Hughes: It was a broader problem?

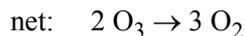
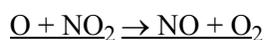
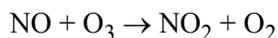
Johnston: Yes, it was a much broader problem, but they had a section on aircraft. The only thing they knew that might reduce the ozone from aircraft exhaust was the effect of water. In the summer 1970 conference, they came to a consensus that water from the SST might reduce ozone about 1 percent and that a 1 percent ozone reduction was negligible.

It's known, they said, that carbon monoxide, CO, and nitrogen oxides are produced from the exhaust of supersonic transport in the atmosphere. But because these

concentrations were so low and the rate coefficients for them were so poorly known, the effect of water would be much bigger. They used these words: “NO_x . . . may be neglected.”

Hughes: Also carbon monoxide.

Johnston: They said carbon monoxide may be neglected and were correct about that. Carbon monoxide has no potential for a cyclic chain reaction, in one step it is irreversibly converted to carbon dioxide, but nitrogen oxides do have a significant chain reaction for ozone destruction, as Crutzen had shown in 1970:



Hughes: Was Paul Crutzen at this meeting?

Johnston: No, he was a graduate student at Oxford. I later found that he had made some unpublished calculations based on Concordes. He wasn't aware of any health hazard. I had never heard of Crutzen until several weeks after that conference. In hindsight, the thing neglected at that meeting was the fact that Paul Crutzen the year before had proposed nitrogen oxide reactions as the explanation for the natural global ozone balance. He suggested that it was the major contributor rather than free radicals derived from water. Crutzen's work wasn't mentioned at this meeting, but his basic equations were used in London's calculation. Crutzen wasn't referred to in the 1970 summer SCEP report. And his article came out in early 1970. He wasn't referred to in the March 1971 conference. I don't remember hearing his name mentioned, but I wouldn't have recognized it if it had been.

Hughes: He had data by the time of this SCEP conference?

Johnston: Yes. But Crutzen first mentioned supersonic transports in a short paragraph toward the end of his article of October 1971, my *Science* article came out in August 1971, and the meeting was in March 1971.

In the afternoon of the first day, James McDonald gave his talk. He presented his calculations and logic very clearly and definitely: if the SSTs reduced ozone by 1 percent, as some atmospheric scientists had recently calculated (SCEP, London and Park), this ozone reduction would increase the damaging ultraviolet radiation that reached the earth's surface by about 2 percent. McDonald didn't do any calculations of ozone reduction; he used the results given by others. He presented data that showed the damaging wavelengths of radiation from the sun are more intense in the tropics than they are in other regions. Atmospheric ozone, which is mostly in the stratosphere, is the primary filter that cuts out biologically damaging solar ultraviolet radiation. The overhead ozone is least in the tropics, greater in mid-latitude regions, and, on the

average, greatest in polar regions. McDonald pointed out that the incidence of skin cancers among white people was a strong function of latitude. In northern Australia, where people from British people had settled, skin cancers are epidemic. Across the United States, incidence of skin cancers increases with latitude, for example, by quite a big factor between Florida and Oregon.

Now, throughout McDonald's talk, he was dignified and scientific about it, but he was viciously attacked and interrupted in the middle of his talk over and over again by Arnold Goldberg, a scientist from Boeing. What he presented was logical and made good scientific sense, and still does. The vicious treatment he was given in trying to make his talk generated some hostility and suspicion on my part. McDonald considered factors about differing lifestyle and people wearing more clothes in the northern climates than southern climates and so forth. For the United States, McDonald estimated that 1 percent systematic reduction of ozone would cause a 2 percent increase of damaging ultraviolet radiation and a 1 percent increase of skin cancer. McDonald estimated there were 500,000 cases of skin cancer a year in the United States. (The most recent estimate that I've seen is a million.) So a 1 percent increase in 500,000 would be 5,000 additional cases of skin cancer per year in the United States, more in some regions of the world and less in others.

Hughes: Had you come to this conference with a suspicion that there was a political agenda?

Johnston: No. I knew there was politics involving economics and sonic boom. I reviewed last year's newspapers and January's newspapers.

McDonald gave this statement of a 1 percent decrease in ozone on the average causing a 2 percent increase in skin cancer. Some of the objections to using that as an argument for not reducing ozone was, well, if everybody moved north in the northern hemisphere by about fifty miles or whatever, it would counteract this effect. The amount of skin cancer varies with latitude, so if people were worried about this, just move everybody north. Well, think about that.

Hughes: Was that a serious suggestion?

Johnston: It's been made over and over again. It sounds good in politics. All you've got to do, they say, is move north fifty miles and we'll be as safe as ever. Can't you just see everybody in the northern hemisphere packing up and moving north by fifty miles?

Now, let's keep the books balanced. There have been environmentalists who pictured ozone reductions as causing monsters to be generated, and ozone reduction as scorching the earth. It was not just the pro-Boeing people who said scientifically outrageous things to maintain their case; some environmentalists were equally outrageous a little later.

Hughes: The fact that you had gone over the newspaper articles indicates that you were clued into the political ramifications of the scientific problem. But did it surprise you at this meeting that the political dimensions were so extreme?

Johnston: Yes.

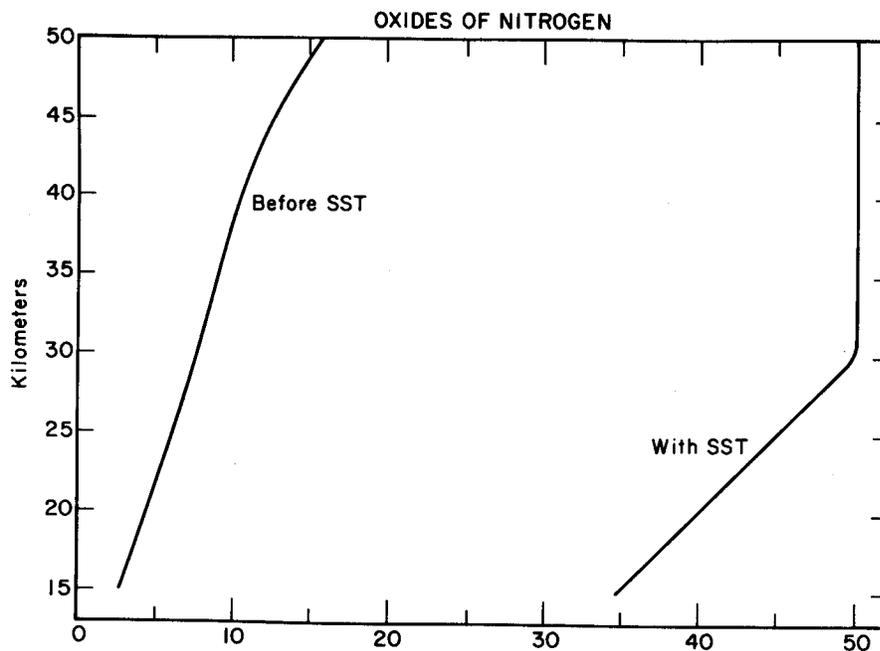
- Hughes: If you had known that it was going to be such a political affair, would you have been even more reluctant to attend this meeting?
- Johnston: I think I was reluctant because I had other scientific work I wanted to do.
- Hughes: Your reluctance to attend was not based on politics; it was based on your other scientific commitments.
- Johnston: Right. I think I would have gone anyhow. I might have been inclined to go if it looked like my field was going to be important in the discussion. I wouldn't have known quite what a hornet nest I would be getting into. So I think yes, I would have gone. I went aware of the bitterness of what the economists were saying about each other, and the sonic boom stories that had been in the headlines for a year.

A talk was given by Julius London from Boulder, Colorado. In Boulder there is the National Center for Atmospheric Research [NCAR], the National Oceanic and Atmospheric Agency [NOAA], and the university. He is a professor in atmospheric sciences at the university. London passed out an "extended abstract" of the talk he was about to give. The abstract was eight pages long; it contained three figures and numerous chemical equations involving ozone, water, and oxides of nitrogen.¹

London set up an "equilibrium" model, that is, it included no atmospheric motions. He ran calculations through a computer, and he estimated both the effect of water and the effect of oxides of nitrogen. He showed the amount of NO_x before supersonic aircraft, and the amount after. I still have copies of those curves. He calculated that water would reduce ozone by about 1 percent, and the oxides of nitrogen would reduce ozone by 1.8 percent. He had very large amounts of nitric oxide produced, and on hindsight, it wasn't a realistic basis for a global average.

- Hughes: What was he basing this on?
- Johnston: He was on the SCEP study committee, and they had gathered information in the summer of 1970.

1. Jae Park and Julius London, "The Photochemical Relation Between Water Vapor and Ozone in the Stratosphere," unpublished article, 8-page abstract.



NO_y PARTS PER BILLION (Park & London, March 1971)

Figure 3. London's vertical distributions of nitrogen oxides before and after long-term operation of five hundred Boeing-type supersonic transports. Just after the Boulder meeting, I inscribed lines at every kilometer altitude on Park and London's plot, and measured their amount of nitrogen oxides for each case. I replotted these data to construct this figure.

During London's talk, I made a simple calculation with rate coefficients and some tables out of a book I brought with me [Project Clean Air, Volume 4, Task Force 7, Section 2, University of California, September 1970]. I calculated the rate of ozone destruction locally by the ozone-oxygen reactions (Chapman's reaction, $O + O_3 \rightarrow 2 O_2$) relative to the rate of ozone destruction by nitrogen oxides ($O + NO_2 \rightarrow NO + O_2$).

$$\text{Rate ratio} = k_2[O][NO_2] / k_1[O][O_3] = k_2[NO_2] / k_1[O_3]$$

The rate coefficients k_1 and k_2 were in my tables from Project Clean Air; London gave concentrations of ozone and nitrogen oxides; and the unknown concentrations of atomic oxygen canceled out. So just from simple order-of-magnitude calculations by slide rule, I could see that NO_x would contribute a big effect.

At the end of London's talk, I stood up, and said, "I made a calculation here. It seems to me that the NO_x would have a much bigger effect than that." He said, as a put-down, "I did my calculations on the computer." [laughter]

At intermission, some people came up to me and said the estimate of the nitric oxide emissions from the engines was way too high. I got several different estimates. Some people said the quoted number was three times too high, five times, a hundred times. Other individuals said that natural nitric oxides in the stratosphere were much greater than the increase to be expected from the SSTs. Nitrogen oxides had never been

measured in the stratosphere, but they were said to be much greater, because in the ionosphere they're greater. So I was hotly challenged for even saying anything about the effect of nitrogen oxides.

London had the mistaken understanding that natural nitrogen oxides in the stratosphere came down from the ionosphere into the stratosphere. I asked London: "What logic did you use to reach the conclusion that NO_x may be neglected?" And he said they were cruising around in the Boston Harbor where they were having the summer study, and somebody came up to him and said that SSTs produced a stated amount of NO_x . "Do you think it would have any effect?" London thought a minute, and the increase in nitrogen oxides from SSTs they were talking about was small compared to the relative amount of NO_x in the ionosphere. So without making any calculations, just his own recollections, he said, "No, I think it would be negligible." So that's how it got into the report.

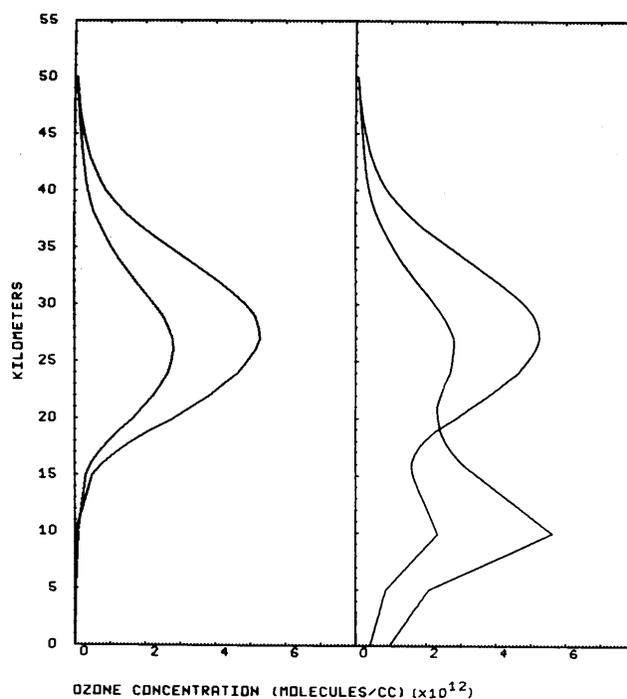


Figure 4. Right-hand-side. London's calculated vertical distribution of ozone without NO_x from the SSTs showed a maximum at about 26 kilometers in the stratosphere and another smaller peak at 10 kilometers in the troposphere. London's calculated vertical distribution of ozone with added NO_x from the SSTs show a greatly reduced ozone concentration at 26 kilometers in the stratosphere and a greatly increased peak at 10 kilometers in the troposphere. Calculated ozone column reduction: 1.8%

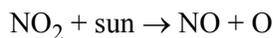
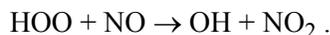
Figure 5. Left-hand-side: Johnston's calculated ozone (molecules cm^{-3}) $\times 10^{12}$ using correct value for rate of $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$.

Ozone column reduction: 40%

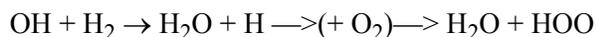
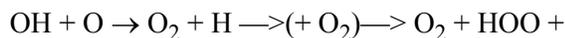
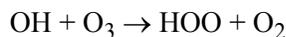
That night I worked on the problem of nitrogen oxides and SSTs. I literally stayed up all night. I picked up one of London's handouts including his calculations. It had curves that he drew of the oxides of nitrogen before and after the SSTs. I pulled out my Project Clean Air table of rate coefficients.

London gave his full mechanism; I remember it was around forty reactions, maybe it was more. And he showed in his calculations that the nitrogen oxides decreased ozone quite remarkably in the middle stratosphere, but increased ozone in the troposphere to such an extent that the net effect was a 1.8 percent ozone reduction.

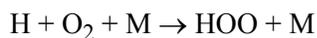
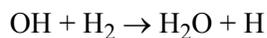
Ozone production happens in smog; I was familiar with that. I thought, well, he's making ozone from smog. But I looked at London's mechanism, and there was no carbon monoxide, no methane, and no volatile organic compounds of any kind. You don't make smog without a fuel. Sometimes people incorrectly say that these reactions significantly produce ozone:

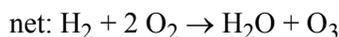
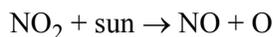
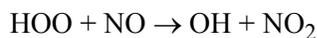


but this process is limited by the amount of HOO present, which is about a million times lower than that of ozone. This process produces ozone only if there is some reaction which converts OH back into HOO, without loss of ozone or atomic oxygen. I went through London's list of reactions, and there are three reactions that convert OH to HOO:



The first two reactions consume ozone or atomic oxygen, and added to the three reactions starting with $\text{HOO} + \text{NO}$, each of these completes a "null cycle," a cycle with no net chemical change. The reaction of OH with hydrogen gives a cycle that forms ozone,





This process is cyclic with oxides of nitrogen, cyclic with respect to free radicals based on water, but consumptive of hydrogen. The only source of hydrogen in London's model is its formation from hydrogen atoms produced in the photochemical system, and the amount is less than one part of hydrogen in a thousand parts of ozone. Thus smog reactions could not have caused the large increase in ozone that London showed at ten kilometers.

In the atmospheric problem, there are two classes of the evenness and oddness, even and odd electrons and even and odd number of oxygen atoms. The number of electrons are even in molecules and odd in free radicals. Each of atomic oxygen, O, molecular oxygen, O₂, and ozone, O₃, has an even number of electrons. Atomic oxygen and ozone have an odd number of oxygen atoms. Molecular oxygen, O₂, has an even number of oxygen atoms. From general considerations of the addition of real positive counting numbers,¹ I concluded that the ozone peak in the troposphere could not be generated by London's chemical mechanism, but it was a mistake of some kind.

I knew from SCEP how much nitrogen oxides per year are emitted at twenty kilometers. How high and how low would this spread? Well, that's a tough problem in atmospheric motions. When I taught the course in physical chemistry, we derived the Gaussian distribution from the random walk of the "drunken sailor." During the meeting that day, Danielson gave "the vertical turbulent diffusion coefficient, Kz." From this value I calculated the standard deviation to be ±2.5 kilometers after two years of random walk, that is, the vertical spread would be five kilometers. I uniformly distributed the two-year accumulation of nitrogen oxides from the exhaust into a vertical shell five kilometers thick and all around the globe, which gave a uniform mixing ratio (mole fraction) of 6.7 parts per billion of nitrogen oxides. I calculated the rate of ozone destruction by nitrogen oxides to be about a hundred times faster than the rate of ozone destruction by the Chapman reactions, and the steady-state half time of ozone destruction by nitrogen oxides would be about seven months. A two-year stratospheric residence time for exhaust gases and a seven-month half-destruction time implied serious ozone loss in the five kilometer thick shell in the region of maximum ozone concentration. I acknowledged a factor of ten uncertainty in the numbers, but I considered this simple calculation of ratios and reaction times proved that nitrogen oxides from SSTs could not be ignored.

Hughes: You came up with that information after your night of calculation?

1. Project Clean Air, Volume 4, Task Force 7, Section 3.1.6, University of California, September 1970.

Johnston: Yes. Part of that night was spent writing up a fourteen-page handwritten report (I still have the original copy of this report).

I got up early and had my handwritten report reproduced. I was given a special slot first thing in the day to present this. When I told Hirschfelder I had something interesting, he said all right, he'd give me five or ten minutes.

SCEP had said that nitrogen oxides, plural, with no specification of amount, all the nitrogen oxide in the stratosphere could be neglected. Well, if I was going to disprove that all of it can be neglected, all I had to do was to show one case where it's important. So that was the logic I used. Nitrogen oxides shouldn't be neglected, because under conditions given that day, nitrogen oxides from the SSTs would destroy ozone much faster than natural destructive processes and at a reaction time comparable to the stratospheric residence time.

When I presented my arguments the next morning, I got scorn from the audience. Almost nobody met me, gears engaged with what I said. They said, "There's so much nitrogen oxide up there naturally, this added amount would have no effect." Nobody ever measured anything up there naturally, but that was what they said.

Another said, "You didn't consider atmospheric motions." Well, in a way, I did. Atmospheric motions spread the exhaust gases all around the globe and up and down five kilometers, on the average. Julius London had not included atmospheric motions in his model, but he was not attacked with scorn and hostile questions.

"If that's so, how can you explain what happens in the polar regions?" and so forth.

Hughes: Were people approaching this from a scientific standpoint?

Johnston: No, these statements were hostile attacks that paid no attention to what I said.

Hughes: Why was that?

Johnston: The logic I gave was: they say "all may be neglected," and I say, "here's a case where some may not be neglected." That disproves the point that all may be neglected. They dodged that logic by demanding that I solve all the problems of the stratosphere. What about this that you didn't consider? I got only these hostile questions. They were acting like lawyers, not like scientists.

Hughes: Also, in the context of this meeting, people were saying, if there's a problem with the supersonic transport at all, it's in terms of water vapor.

Johnston: That's what they were saying, and some said there was no ozone reduction by water.

Hughes: And you were saying, if there's a problem at all, it's NO_x, right? Because it's a much bigger problem than any water vapor problem.

Johnston: Certainly from what was known at that time, NO_x was more important than water vapor. If enough new measurements are made, it might lead to discovery of new compounds in the atmosphere or new reactions never known to occur.

Hughes: In the context of the meeting at MIT in 1970, it seems to me from what you've told me and what I've read that participants were trying to decide: Should we allow this program on supersonic transports to go forward, and if we do, what are the problems involved? And the argument was, if there's a problem, it's a water vapor problem.

Johnston: The MIT study was *Man's Impact on the Global Environment*. They were a scientific fact-finding group. They dug up facts and considered a number of possible global impacts. They published official facts about SST emissions and other properties, but they spent only about 5 percent of the book on SSTs.

Only the Congress could decide whether the supersonic transport program should go forward.

I was confident that nitrogen oxides were an important problem, not that my numbers were exactly right. But the nitrogen oxides could not be neglected just because somebody on the boat said he thought they would be unimportant. All of the opposition came with the accusation that I hadn't explained everything.¹

After my presentation, Arthur Westenberg, quite a well-known physical chemist and kineticist, very scholarly and dignified man, presented some calculations he had made. He calculated the ozone reduction that would occur if one added X micromoles of NO_x per milliliter of air, and he gave several values of X. Westenberg showed in his calculations that there were some amounts of NO_x that would reduce ozone by a very large fraction. He didn't say a thing about the SSTs; he didn't say a thing about the stratosphere even. He just showed these results, that under stratospheric conditions of temperature, pressure, and solar radiation—he did say that much about the stratosphere—abstractly added various amounts of NO_x give a calculated ozone reduction that varies with the amount you add, and it builds up to a very large value with a high value of micromoles per milliliter.

Westenberg also got some hostile questions: "You haven't considered atmospheric motion." Well, he wasn't talking about atmospheric motion. He was talking about just the pure abstract chemistry of it. "Why didn't you consider—?" completely missing the mark of the talk. But anything presented, good science or not, if it seemed to be unfavorable to the SST, led to cutting counterattack by the pro-SST people.

Hughes: Who did these people represent?

Johnston: There were government employees, employees of big research laboratories, a substantial number of aircraft industry representatives, and a few academics.

1. C.L. Williams, Director, *Study of Critical Environmental Problems (SCEP), Man's Impact on the Global Environment*, MIT Press, Cambridge, MA, 1971.

- Hughes: There were reasons, other than science, why people were resistant to Westenberg's and your data?
- Johnston: Yes, politics. Westenberg made his calculations before coming to the meeting. I guess there had even been some talk about nitrogen oxides. Over a wide range of variables, he showed calculated-ozone reductions from negligible to serious. Westenberg apparently felt it was up to other people to say where the SST would fall in that range. He submitted his article for publication, I was one of the referees, and I praised it highly and said it should be published. One of the other referees said no, and criticized it so much it was never published.
- Hughes: Was it eventually published?
- Johnston: Just as a lab report.
- Hughes: There were only two reviewers?
- Johnston: Yes, that's what *Science* does. I guess many more people submit papers to *Science* than they accept. With one negative and one positive review, they rejected the article. I've always wondered who the negative reviewer was, and apparently he was very negative.
- Hughes: One substantial negative review can trump a positive review?
- Johnston: It's up to the editors to decide. Generally, it would go out for a third reviewer.
- Hughes: Was the fact that Westenberg's data didn't get published in a mainstream publication an impediment?
- Johnston: If two of us had come out in public on the same thing, there would have been reinforcement. But he was cut off and dismissed. Nobody ever spoke of his calculations again that I know of. The atmosphere wasn't his field; he was shut out.
- Hughes: The episode points out, does it not, the criticality of the peer review system?
- Johnston: Yes. It indicates that politics can get in its blows through the peer review system. Peer reviewers can be prejudiced or have their own axes to grind.
- Hughes: You had done these calculations overnight. Did you have any doubts about your data?
- Johnston: I had no doubts that nitrogen oxides should not be neglected in stratospheric ozone chemistry.
- Hughes: Significant data were presented at this conference, and seeing it all in juxtaposition and perhaps hearing the pros and cons, you got an immediate picture of where the problem was, and you immediately did something about it?
- Johnston: I discovered that they had overlooked an important feature, the oxides of nitrogen.
- Let me tell you one more quick thing. On the morning of the second day, while the meeting was going on, somebody came into the meeting room and handed the speaker a

little slip of paper. The moderator read it to the group. “The House of Representatives has just voted 215 to 204 to cut off federal funds for the SST as of March 30, 1971.” Then the moderator said, “The Senate votes next week. I think we should pay no attention to this and proceed as we had planned.”

Hughes: Do you remember why the House had turned it down?

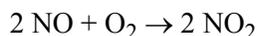
Johnston: Well, there had been a large amount of debate—economics, sonic boom, priorities. The water vapor and skin cancer considerations were buried by the flying saucer accusations. The NO_x problem was completely unknown to the Congress at this time.

Toward the end of the afternoon, I got up and made a motion to the meeting of the entire group : “We recommend that the oxides of nitrogen be regarded as potentially an important variable in problems concerning stratospheric photochemistry.” And members of the group said things like: “The nitrogen oxides emissions are going to be X times lower than GE said it was.” “This problem is so dominated by air motions that chemistry is unimportant.” And so forth. Somebody stood up and said, “I don’t think we are in position to make firm conclusions at this time. I move that the motion be tabled.” By a large majority, that motion was tabled. Now, I have in my writings somewhere the exact wording. I recommended only that this meeting go on record as saying NO_x was a significant variable in the SST/ozone problem.

Hughes: And the meeting wouldn’t endorse that.

Johnston: No, they turned it down. The assembled group of experts in atmospheric sciences formally supported the assertion that in problems of the stratosphere, the oxides of nitrogen could be neglected.

When I got back to Berkeley, I studied the two handouts that London had passed out. One of them included Bodenstein’s reaction and one didn’t.



The handout that I had studied overnight in Boulder was the one that didn’t include nitrogen oxides in the typescript, but three NO_x reactions were written in by hand. Park and London had thought about Bodenstein’s reaction, I guess, or somebody reminded them of it, and they had added it in. But by mistake, London had put in the rate coefficient 13,000 times too great.

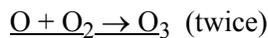
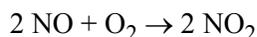
Hughes: How could he have done that?

Johnston: He misread something in the literature. He had copied it off a rate table. He gave a reference, but I never could find that reference. If that reaction went 13,000 times faster than it does, then this would be a very potent source of global ozone.

Hughes: Did you know right off that that was an impossibility?

Johnston: Yes. Bodenstein measured the rate coefficient carefully over a wide range of temperatures and a wide range of pressures. Many others had studied this reaction and

confirmed Bodenstein's values. If that rate were 13,000 times bigger than the value Bodenstein had measured, then this catalytic chain reaction would be a major natural source of ozone in the troposphere:



Later at Berkeley I took London's two distributions of NO_x before and after SSTs (Figure 3) and calculated them with and without the mistake in the Bodenstein constant. I included the so-called "self healing effect." I found that his two distributions gave a calculated 40 percent global ozone reduction. (See the left-hand-side of Figure 4.) The peak in the mid-troposphere was caused by his wrong value of Bodenstein's rate coefficient.

To summarize: In March 1971, Park and London assigned a plausible vertical distribution of natural NO_x and a distribution of NO_x upon operation of a large fleet of SST (Figure 3). They calculated 1.8 percent ozone reduction produced by this large injection of NO_x (Figure 4). They found large ozone reduction above 25 kilometers and large ozone increase below 20 kilometers. In early April 1971, I discovered that Park and London had used a rate constant for the reaction, $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ that was larger than that observed by a factor of 13,000. Upon redoing Park and London's calculation using the correct rate coefficient, I found an ozone reduction of 40 percent (Figure 5). An article containing Figures 3, 4, and 5 was accepted for publication in 1972 and finally published in 1974.

INTERVIEW 6: AUGUST 24, 1999

Tape 12, side A

Hughes: Please continue with your account of the SST problem.

Johnston: Within one week, I'd written up a first draft of this idea. When I developed it that far, I wrote a preliminary paper that extended the overnight version. In the overnight version, I just considered only five kilometers as vertical spread of exhaust gases. I next considered other vertical spreads.

I called up the President's Science Advisory Committee and spoke to one member of the committee, Dr. Russell Drew. I told him about the Boulder meeting, about my calculations, and that NO_x certainly could not be neglected in this problem, and we should pay some attention to it. He was uninterested. Yawn, yawn. That was the day the Senate voted it down. He said, "SST was voted down by the Senate, it's a dead issue. What are you worried about?"

I wrote a moderately intemperate statement about environmental effects. Now, the environmental effect I knew of so far as ultraviolet was concerned was snowblindness and blindness. In the laboratory, we were working with ultraviolet light, and we knew and were strongly urged as students to protect our eyes. Ultraviolet light is invisible, and an undetectable exposure could blind an eye. So I mentioned that feature.

I sent a copy of this to the President's Science Advisory Committee, to Hirschfelder, to London, and a copy to four wise professors on this campus: Leo Brewer, Melvin Calvin, Jack Hollander, and George Pimentel.

Hughes: How did these four people respond?

Johnston: I didn't get a written response from any of them.

Let's go to May 1971. The House of Representatives was going to appropriate money to have an orderly close-down of the SST program and pay Boeing off for closing costs. Gerald Ford all of a sudden proposed that instead of phasing SST out with that money, the money should be used to extend the lifetime of the project another six months. It passed the House, although the House and Senate terminated the SST program in March.

Hughes: Now, was he being pressured by the industry?

Johnston: I don't know, but they're so tied together, I don't know. Gerald Ford was the Speaker of the House of Representatives at that time. Although the House and Senate had cut off the funds at the end of March, in May they said, "Let's don't cut them off, let's use them to extend the program." Of course, at the end of the program they'd have to appropriate close-out funds anyhow. The House voted to reinstate the SST project for at least six months, and the Senate voted a week later.

Hughes: Were you upset?

Johnston: No. I never was against the SSTs; I was against their making self-serving errors in chemistry. But then something happened that really did upset me. A small, I would say yellow, newspaper called the *Newhall Tribune* —have you heard of it?

Hughes: No.

Johnston: Somehow got hold of my early April correspondence, things I sent confidentially to five people only.

Hughes: You mean a draft of the first paper?

Johnston: The first draft. Very unfinished draft, including the note at the bottom that tried to wake up people who said NO_x was totally unimportant. Well, Newhall got hold of a copy, and he came out with blazing headlines, that Professor Johnston says that the SST will cut ozone in half. Of course, what I really was saying in that paper was that at certain altitudes, if you didn't replenish the ozone and the nitrogen oxide reactions went on, ozone would be half gone in six months. The "half-life" is a technical chemical term. Newhall picked that up as meaning it would reduce the ozone by a factor of two. I got a call from a public relations office here at the university, and they asked me if I submitted an article to the *Newhall Tribune*. "No," I answered, "I never heard of the *Newhall Tribune*." The public relations officer said I should come there as soon as possible, and that we had a serious problem.

Hughes: Give me a little background on the *Newhall Tribune*.

Johnston: I don't know anything about it.

Hughes: Why do you suppose Newhall picked up on these drafts of yours?

Johnston: Maybe somebody at the university here, or perhaps somebody's secretary, was emotionally involved in the supersonic transport issue. When they made a Xerox copy of my article, it occurred to them to pass it on. I asked Ken Pitzer about the paper, and he knew a little bit about it. It was a small California newspaper with a somewhat liberal bent.

But they got hold of it, and the public relations department here said I should let the press see what I had written, and also write anything I wanted to about it, and I wrote that this paper was very preliminary and not yet our statement on the subject. I didn't respond to any requests from television or radio. So we just rode that one out.

I got a letter from a high-ranking engineer at Boeing, Mr. Walter Swann. and he really cursed me out. He said I had everything wrong. He said my NO_x emission index was way too high, and —

Hughes: Did he give any basis for his criticism?

Johnston: He just claimed to know all these things himself. He obviously had not read my preliminary article; he had read only the newspaper headlines. I used a nitrogen oxides emission index of 23 units. When measurements were made on the Concorde a few

years later, they found the value to be 18; there was no big exaggeration there. He said my only motive was to get my next year's National Science Foundation grant and publicity, and that he was going to go around to the National Academy of Sciences and the National Science Foundation and protest. And he sure did.

Hughes: And what happened?

Johnston: I'll come to that.

Now, almost the same day, I got a letter from a woman in southern California saying, "God bless you for saving the world." She hadn't read the article either. But it sounded like it was a good thing from her point of view. Anybody who does science in public has to not be perturbed by either side.

Hughes: Was that your first real exposure to public opinion?

Johnston: Yes.

Hughes: How did you react?

Johnston: Well, probably not wisely. [laughs] It sort of put me in a position of I'd caught a tiger by the tail and there's no letting go.

Walter Sullivan, the *New York Times* science editor, had a copy of my paper, and he had a very sensible explanation of what it really said. He started out saying, "Sorry, folks, but there's something else to be said about the SST." He went through things and gave essentially the ideas I was trying to get across.

Hughes: Had you been talking with him?

Johnston: No.

Hughes: Had he been reading your publication?

Johnston: Only this one.

Now, in talking to the atmospheric scientists, I hadn't gotten a favorable response when I presented things from a statistical mechanical point of view. Many —and reasonably so —are in love with models. Modeling is a very important part of science. But a lot of people seem not to believe anything unless presented in a model, and others don't believe any "computer model" results.

So I realized I had to use a model if I was going to talk to anybody else. I set up a photochemical equilibrium model similar to what Julius London used. I solved it by a method of successive approximations, similar to what we use in freshman chemistry. I used an old Monroe electro-mechanical calculator, and spent a full week calculating the ozone steady state at seven altitudes, equally spaced from 15 to 45 kilometers. I assigned five values of nitrogen oxides: 0.0, 2.4, 6.8, 24, and 68 parts per billion [ppb]. SCEP gave 6.8 ppb NO_x as global average and 68 ppb NO_x as worst local case along

the northern hemisphere flight corridor, and SCEP said that these values of nitrogen oxides “may be neglected.” I reduced the SCEP values of NO_x input by the factor of 2.8 to get 2.4 and 24 ppb. I submitted this first version of my article to *Science* in May 1971.

Shortly after I sent the article to *Science*, I realized that I had omitted an important feature. If ozone decreases, then short wavelength radiation no longer absorbed by the lost ozone goes to lower altitude and produces some ozone there. I hadn’t accounted for that. To do so would require much more computation time, far too much for our old Monroe calculator.

I teamed up with computer people at the Berkeley laboratory —

Hughes: At Lawrence Berkeley?

Johnston: Yes, Lawrence Berkeley. The physicist Andy Sessler was head of it then. He came in and talked to me and offered me the services of a computer programmer there if I wanted to go into it. We agreed, and I was given the full-time services of a brilliant computer programmer, Mr. Robert Healey. We set up a model at 45 north latitude, spring equinox, from 15 to 50 kilometers in altitude with one kilometer grid height. The calculations were made for every five degrees of solar angle.

We put in the calculation the observed sunlight distribution at 50 kilometers, the top of the stratosphere, and calculated down just one level. Then we had to calculate what the radiation distribution would be left for the lower forty-nine segments, and continue one kilometer at a time down to 15 kilometers. Then we had to go back to the top and repeat until the entire column reached its steady state. It’s called the “self-healing effect” among atmospheric scientists. So by the time the referees’ report came in, we’d redone everything. We assumed 11 widely different non-uniform vertical distributions of natural nitrogen oxides, for each we ran assigned NO_x inputs of 2.4 and 24 ppb, and we assigned six vertical spreads of the SST exhaust: 20-21, 19-23, 18-25, 17-27, 16-31 kilometers. For the addition of 2.4 ppb of NO_x the calculated ozone reduction varied from 3 to 23 percent, depending on the vertical spread of SST exhaust; and for the high traffic corridor giving 24 ppb of added nitrogen oxides, the calculated ozone reduction varied from 3 to 50 percent, depending on the vertical spread of SST exhaust.

The reviews came back with a letter from one of the editors that reviewers had what he thought were significant comments, and he hoped I would revise the paper, acknowledge Crutzen’s article, and return my report to *Science*. The editor sent me a copy of Crutzen’s 1970 article, and that was quite a revelation. I thought that I’d made these discoveries about nitrogen oxides, but Crutzen had published them a year sooner. Crutzen put some things down that certainly should have been mentioned in the SCEP report and in that March meeting. But he wasn’t given any credit for it in either case.

Hughes: What had he worked out?

Johnston: As a problem in pure atmospheric science, Crutzen pointed out that natural oxides of nitrogen go through their catalytic cycle and would reduce ozone. The problem all during the sixties was that the calculated vertical distribution of ozone based on current

knowledge gave two times too much ozone. So there must be “something else” destroying ozone. In the middle 1960s, Barry Hunt (1966) proposed that the free radicals based on water, which destroy ozone, might be the explanation. But Hunt didn’t know two rate coefficients, and he postulated values that gave the observed ozone column. Crutzen disagreed with Hunt’s model, and in 1970 he suggested the oxides of nitrogen, which also destroy ozone, would explain the excess calculated ozone if the amount of nitrogen oxides in the atmosphere had his postulated magnitude. At that time there were no measurements of the NO_x vertical profiles in the stratosphere.

Tape 12, side B

Johnston: By the time we resubmitted the paper on June 7th, we had made a large number of calculations where we assumed a wide range of natural vertical profiles of nitrogen oxides. I compiled the results in a 107-page laboratory report and condensed it to the four-page *Science* article, published August 1971. Since very few people have ever read the lab report, I would like to submit a written portion of the lab report here:

INTRODUCTION

“This report is aimed at a fairly broad scientific group. Part IA is a detailed, elementary discussion of chemical reactions and catalytic cycles. The only stratospheric data used are taken from a handbook, and the presentation is exclusively from a chemist’s point of view. Part IA is designed as a classroom lecture to undergraduate students. Part IB, on the other hand, is a research article on the relative effect of ozone, oxides of nitrogen, and free radicals based on water with respect to destruction of odd oxygen [ozone]. Part IIA presents a simplified method of calculating the steady-state ozone profile as a function of added oxides of nitrogen. Equations are derived and quantities are tabulated so that anyone, including students as a homework problem, can carry out these calculations and verify the arguments presented. Part IIB presents a very detailed method of recalculating the distribution of ultraviolet radiation throughout the stratosphere for every change of any variable. Such a detailed computation is required if large changes of ozone are to be considered. This method averages the solar intensity over 24 hours (or 12 hours for some purposes) instead of considering a single solar angle. With this method, steady state profiles of ozone are calculated for a large range of uniform and non-uniform distributions of oxides of nitrogen in the stratosphere. Part III compares some observed quantities with those calculated by the photochemical theory, on a world-wide basis. Some complexities of the real stratosphere are considered in Part III, and the report ends with a list of conclusions.

CONCLUSIONS

“(1) If NO and NO_2 , as such, build up in the stratosphere to the expected concentrations from SST operation, the ozone shield would be reduced by a large amount, about a factor of two.

“(2) If NO and NO_2 are converted to HNO_3 (or other inert molecules) at rate faster than is indicated by present knowledge, then the effect of

NO from SST exhaust would be less than expected in (1) above. The chemistry of the stratosphere is sufficiently complicated that one should look for new, unexpected chemical reactions.

“(3) A large reduction in stratospheric ozone would be expected to change the temperature, structure, and dynamics of the stratosphere, which may modify the quantitative aspects of conclusion (1). These effects are outside the scope of this report.

“(4) In the reduction of ozone, the oxides of nitrogen at low concentrations exhibit a threshold effect, and at high concentrations the oxides of nitrogen reduce ozone according to the square root of NO_x .

“(5) Transport by air motions has a major effect in shaping the vertical profile of ozone in the lower half of the stratosphere; the catalytic chemical action of NO_x in destroying ozone is a large effect under all conditions of temperature, pressure, composition, and radiation distribution in the lower half of the stratosphere. Transport by air motions is an action that moves the large catalytic effect of NO from one part of the world to another, but it does not cancel this strong catalytic effect.

“(6) In the present stratosphere, oxides of nitrogen act to limit the concentration and partly to shape the distribution of ozone; the indicated mole fraction of NO_x is about 10^{-9} at 20 km increasing to substantially higher values at higher elevations.

“(7) At all levels of the stratosphere water vapor has less effect on ozone than the effect of natural NO on ozone. The most important effect on ozone by water in the stratosphere is its role in converting NO_2 to HNO_3 , not the role of its free radicals (HO_x) in directly destroying ozone. NO_x from SST is a much more serious threat than water vapor with respect to reducing the ozone shield.

“(8) Further experimental studies, especially chemical analyses in the stratosphere and photochemical and kinetic studies in the laboratory are needed to clear up the uncertainties under (2) above.

“(9) Quantitative physiological studies should be made of what would happen to plants, animals, and people if the ozone shield should be reduced by various amounts up to a full tenfold reduction.

“(10) Even though it may be too complicated for a complete theoretical treatment, the stratosphere is vulnerable to added oxides of nitrogen, and forethought should be given to this hazard before the stratosphere is subjected to heavy use.”

Hughes: Your conclusion to the 1971 paper says: “...if concentrations of NO and NO_2 are increased in the stratosphere by the amounts accepted by the SCEP report and by governmental agencies, then there would be a major reduction in the O_3 [ozone] shield...”

- Johnston: Yes, and that's still true in 1999; key words are NO and NO₂ "as such," not including nitric acid, HNO₃.
- Hughes: In the last sentence, it seems to me that you were hedging your conclusion: "Just as the SCEP report incorrectly discounted NO_X and the SST planners for several years overlooked the catalytic potential of NO_X, it is quite possible (and, in fact, highly probable) that I have overlooked some factors, and the effect of NO_X on the O₃ shield may turn out to be less, or greater, than indicated here."
- Johnston: There are two things here. Look at my "if clauses." If concentrations of NO and NO₂, as such, et cetera. This statement is still true in 1999, but in the article I went beyond that. With a recognizably primitive model, I concluded that major portions of the nitrogen oxides would not be tied up as nitric acid. My disclaimer at the end recognized that much was not known about the stratosphere, and when more would be learned, "the effect of NO_X on the O₃ shield may turn out to be less, or greater, than indicated here." The 1999 state of knowledge is that much more NO_X is tied up as nitric acid than I thought in 1941, and that feature means that "the effect of NO_X on the O₃ shield has turned out to be less, than indicated" in 1971.
- Johnston: I start off that first paragraph of the August 1971 article saying that the SCEP report had said NO_X could be neglected. I took as my project to show that it could not be neglected. Well, if you're trying to prove something cannot be neglected, it's fair to show the worst plausible case. We didn't show just the worst plausible; we showed all the way from 3 percent to 50 percent, and described the different spreads that did that. That was the main content of the August 1971 article.
- Hughes: My memory of what you said last time is that people tended not to take your point —
- Johnston: That's right.
- Hughes: —and criticized you for reasons that you thought were extraneous, at least for that particular paper.
- Johnston: That's right. I guess I've covered some of this before.
- I told you about the summer of 1970, there was an MIT summer study, and they came out with the book *Study of Critical Environmental Problems* SCEP. They're the ones who said NO_X could be neglected in March 1971. That same group, with some additions and subtractions, had a summer meeting in Stockholm in 1971. It was called *Study of Man's Impact on the Climate*, SMIC.
- Hughes: What was this group?
- Johnston: It's a broad group of atmospheric, environmental, and social scientists from universities, foundations, and governmental agencies —very respectable people, high in their field. MIT sponsored it.

Hughes: I think you said last time that it did include industry representatives; it wasn't just academics?

Johnston: Yes, the group included some from industry. SMIC included about the same group that met in the summer of 1970. The meeting was over about mid-August, I guess. A newspaper writer, Claire Sterling—can I have that paper back and read what she said?

Hughes: [hands over 1992 paper]

Johnston: Claire Sterling reviewed the SMIC report and related matters. This article was reprinted in the *Congressional Record*, from which I excerpt the following: “Now that *Science* magazine (in its August issue) has finally decided to publish one expert's chilling view of the matter...it might help to know what others think.... He was challenged sharply at an International Study of Man's Impact on Climate [SMIC] in Stockholm this summer by 30 of the world's most distinguished scientists.... To a man, the scientists at last July elite Stockholm conference refused to accept this. Most of them had attended...SCEP the previous summer.... In the intervening year, they concluded at Stockholm with a pointed snub, ‘no new information has been developed appreciably to alter the SCEP judgment.’” Then Claire talking again: “The trouble with his [Johnston's] findings, according to SMIC scientists, was that all of his work was done in the laboratory. Neither he nor anybody else has done any sampling in the stratosphere.”

Her conclusion:

“To anybody standing above this particular fray, what leaps to mind is not as much one scientist's capacity for error as a kind of neoNeanderthal ignorance of the subject in general. Who would have thought it possible in this age of research and development, with billions of dollars already invested in supersonic transport and both the Concorde and Tupolev very nearly operational, that not a single American, British, French, or Russian scientist has yet gotten off his laboratory stool and gone out and done some relevant sampling in the stratosphere? ... Though any scientist will tell you how urgent such research is...none of the aircraft industries involved, or their sponsoring governments, has yet made a move or put up money. Before we find ourselves groping sightlessly around a lifeless planet, it would be nice to think that at least one of them might.”

[laughs] Beautiful writing.

That's an important link in the chain here. This article was seen by Senator Birch Bayh. He perhaps discussed it around. He and a co-sponsor proposed a program for studying the stratosphere, and in fact money was appropriated for that. It became the Climatic Impact Assessment Program, CIAP. In the *Congressional Record* describing this program, he had added Claire Sterling's full article and a letter from me. He wrote me a letter and asked me what I thought.

The Climatic Impact Assessment Program was to be in the Department of Transportation. I think the original bill was to put it in the Environmental Protection Agency, but it was in the Department of Transportation. Alan Grobecker, who had been

in another governmental agency, Institute for Defense Analysis, was appointed the leader. This was in the fall of 1971.

Money was appropriated and the program was launched January 1, 1972. Grobecker called a first conference. I believe that was in January and held in Boston. So this was an organizing conference. I was one of the invited speakers there. There were a total of four of these conferences over the next few years. One provision in this congressional appropriation was that they had to report to Congress at the end of 1974 with their final report.

CIAP wasn't going to be another agency. It was a focused study. But Grobecker approached it from a broad point of view. He included in his program mechanical engineering, atmospheric physics, chemistry, and biology, economics, and medical aspects. He enlisted independent experts in all those fields.

Hughes: And who was he?

Johnston: Grobecker was an engineer.

Hughes: He'd been assigned the responsibility of government oversight?

Johnston: Alan Grobecker from the Institute of Defense Analysis was appointed head of CIAP. As I remember, he was an engineer in background, and widely respected in IDA, and was brought in to direct this program. I'm not aware of what his previous activities had been.

Hughes: When you say direct a program, which program are you referring to?

Johnston: This is the one Congress had set up.

Hughes: The Climatic Impact Assessment Program.

Johnston: Yes. He went about it, as I say, in a broad way. He was going to cover six different fields, and he proposed from the beginning six different monographs by the summer of 1974, and that included biological and medical effects, economic effects, and so forth, as well as physics and chemistry and engine emissions.

In these four years, Grobecker spent \$21 million. It doesn't sound like much these days. But he enlisted other agencies, as sort of a public service or as an additional service, to do parts of what he needed to have done. The rumor is he got between two and four times as much out of doing that as he spent directly. This program, which started with a definite purpose in January 1972 and terminated on schedule at the end of 1974 with reports written up in 1975, was as I say the first golden age of stratospheric research. Really very little was known before that. CIAP learned many new and significant things.

I received a contract for three years to do laboratory work and interpretation of data as a part of the Climatic Impact Assessment Program.

They measured the amount of nitrogen oxide in the stratosphere as a function of altitude for the first time. They confirmed Crutzen's great 1971 paper, which I deferred to talk about until now. In that paper, Crutzen figured out what the natural source of nitrogen oxides in the stratosphere would be. Now, before that, it was known that nitrogen oxides were generated in the ionosphere, way high and they were certainly destroyed at the ground. So they assumed that it came by air transport from above.

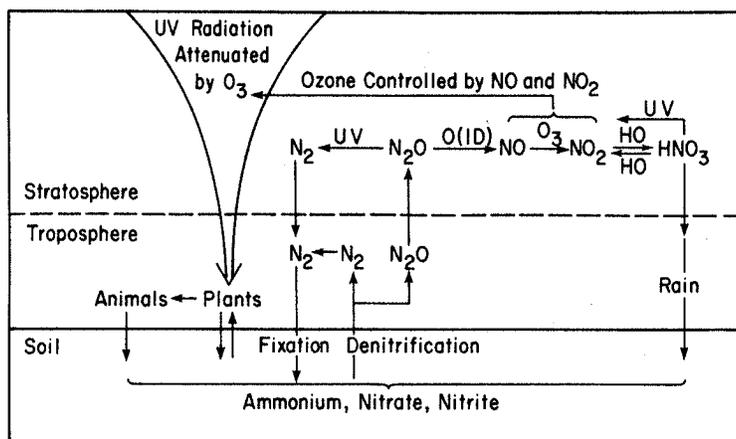


Figure 6. Pictorial representation by HSJ 1972 of Crutzen's new global nitrogen cycle, published in October 1971.¹

But Crutzen showed that stratospheric nitric oxide did not come from the ionosphere, but, as shown in Figure 6, it is formed in a newly recognized sub-cycle of the global nitrogen cycle. Some atmospheric nitrogen is fixed into soil and water by special bacteria and plants, which nourishes plants; animals eat plants; eventually animals and plants mix into the soil. Nitrogen undergoes a large number of chemical transformations in the soil. In one of the transformations, nitrogen gas is returned to the atmosphere, and a small amount of nitrous oxide, N_2O , also goes into the atmosphere. Nitrous oxide, well known as laughing gas, has the same structure as carbon dioxide and is even more inert chemically. It doesn't dissolve in water and doesn't react in the troposphere. In 1971, its estimated lifetime in the atmosphere was seventy years. I think now it's a little more than that. It's a very inert substance, and it gets slowly transported up into the stratosphere. Big thunderstorms in the tropics bump into the bottom of the stratosphere, and because of rising, the tops of these clouds are extremely cold, and they take some water out of the stratosphere and inject some nitrous into the stratosphere. In the middle stratosphere nitrous oxide is broken apart by far ultraviolet radiation, but a small fraction of it undergoes chemical reactions.

Atomic oxygen has two forms of importance in the stratosphere, O and O^1D . The second form, called "O singlet D," is much more reactive than regular atomic oxygen. Singlet D oxygen atoms react with nitrous oxide to make nitric oxide, which enters the NO_x ozone-reduction cycle. The reaction cycle is stopped when nitrogen dioxide reacts

1. Crutzen, P.J., Ozone production rates in an oxygen, hydrogen, nitrogen-oxide atmosphere, *J. Geophys. Res.*, **76**, 7311-7327, 1971.

with the hydroxyl radical to form nitric acid. Nitrogen oxides are removed from the stratosphere in the form of nitric acid, which is rained out of the troposphere. The NO_x catalytic cycle is the most important cause of ozone loss in the natural stratosphere, and it is important in determining the amount of global ozone. Ozone is vital in screening out biologically damaging solar radiation. Thus biological activities in the soils and waters play a strong role in determining how much dangerous solar radiation reaches the surface of the earth. Figure 6 shows all these features of Crutzen's newly recognized global nitrogen cycle.

Tape 13, side A

Johnston: Now that I've made one digression from the Climatic Impact Assessment Program, I'll quickly make another one. I was a national Sigma Xi lecturer for '72 or '73, maybe both. I was invited to give lots of lectures at universities and groups. In every one of these, I presented Figure 6, Crutzen's beautiful example of global ecology. So I spread the word very widely about that. In particular, Sherry Rowland saw this slide and heard my lecture three times during 1972 and 1973.

Back to Grobecker: The Climate Impact Assessment Program sponsored development of mathematical models, and they included atmospheric motions in their models, but in the early days, most of the atmospheric models that could include chemistry were one-dimensional, vertical only, interpreted as global average. Experts said that we must go to two-dimensional models to understand the effects of the global circulation, up in equatorial regions and down in polar zones, and that we should work toward developing three-dimensional model that included chemistry. The computers of that period were not capable of handling three-dimensional models.

Grobecker was very cordial to me. He gave me a research project to study some of these things, and he invited me to give speeches at the four symposia, and I attended a lot of the sub-group meetings. In hindsight, I believe he thought that if we went to two-dimensional models, the calculated ozone reductions by SSTs would greatly decrease. When the first two-dimensional results were obtained by George Widhopf, the calculated ozone reduction was much less than the one-dimensional models gave. Before presenting the results to the CIAP conference underway, George showed these results to Grobecker, who was delighted to see things were turning out as he had expected.

Well, I was at the meeting where Widhopf presented his results. After the talk, George gave me a preprint of his paper, and I found he'd made a mistake—let me see if I can get it right: a CIAP source gave George a statement as to how much nitrogen oxides would be introduced by 500 SSTs. The way the information was given, George understood it to be for the entire globe. He thought he was being given a global input, but he was just given a local slice of it. When he redid his calculations including the correct global input, he got about the same answers as the one-dimensional models. It was mistake in communication. If I had not caught the mistake, I think it might never have been found.

Of course, Grobecker knew I caught the mistake, and toward the last third or half of CIAP, I felt he distrusted me. He came to feel, I think, that anything I proposed would

be selected or slanted to make the SST look bad, and Grobecker decided that he'd better do the opposite. I proposed three things that were reacted to in that way. I think I'll jump ahead a little bit and go through them.

One important reaction was how fast hydroxyl radicals react with a hydroperoxyl radicals, OH and HO₂, which make water and oxygen. In 1973 there were two values that had been published in the literature. They differed by a factor of ten. The modelers had thought one of them was probably better than the other, and they had used only that one.

When I read the papers, I couldn't see anything wrong with either one of them, so I advocated that the modelers should calculate it both ways, and if it didn't make any difference, it wouldn't make any difference. If it did make some difference, then the uncertainty in the calculation was at least as large as the difference of the two models. Well, Grobecker fought that. I had a friend in the Lawrence Livermore group making model calculations, and I asked him to follow my suggestion. He said, "No, that calculation had been put off to the post-CIAP period." When the calculation was done in the post-CIAP era, it was found that the value I advocated gave much less calculated ozone reduction than the one that Grobecker insisted we use.

The other thing I proposed that they do: the nuclear bomb tests of 1960-61 had produced a large amount of radioactive carbon-14. The Atomic Energy Commission had measured the vertical distribution of carbon-14 from the ground to about thirty-three kilometer altitude, every three months ever since 1959, before and after the big nuclear tests of 1960-62. This was an enormous body of data following an inert tracer for eight years. I advocated that these data should be used to test the theories about ozone reduction. Somebody wouldn't let that be done. I went to several people, all of them were contractors for CIAP, and Grobecker refused to have the modelers make this calculation, but then that was a simple enough problem that I could do myself with the help of programmers here at Berkeley.

The various atmospheric modelers had to assume a function that gave how things mixed in the vertical direction. From one modeler to another, they came out with radically different functions. I had shown in 1971 already that the calculated ozone reduction was very sensitive to vertical distribution of NO_x. My students and a postdoc and I compared the observed spread carbon-14 with everybody's model of the vertical eddy diffusion function K_z. Most of the models miserably failed the test. Their calculated carbon-14 profiles didn't evolve in the way it was observed. But one and only one model agreed with the observed history of carbon-14. This K_z function was done by a Don Hunten.

Hunten was quite a distinguished atmospheric physicist and an astronomer. He got his theory from talking to a real expert on atmospheric motion, Richard Lindzen of MIT. Lindzen was a conservative scientist in terms of care and not saying things until he was sure. He was shown by the people at Harvard and MIT how the models were using totally different K_z functions, and he was asked for advice. Well, Lindzen thought about it, and came out with a radically different model, and good physics behind it. He told the group later, "I deplore the use of one-dimensional models, but if you insist on using them, you should put some sensible physics into them." Don Hunten reviewed some of

Lindzen's articles and developed a radically different Kz function, and calibrated it against observed vertical profiles of methane, and the calculated carbon-14 vertical profiles agreed with the observations fantastically well with observed carbon-14. These results came out in time to be considered in the final (1974) CIAP program, but it wasn't published until 1976.

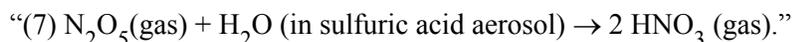
Hughes: Why was there the delay?

Johnston: The refereeing process is slow, and all of us were busy with other things. Anyhow, Hunten's model gave calculated ozone reduction substantially larger than shown by all other models.

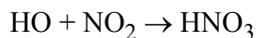
At that time, there was a very important discovery, the reaction of N_2O_5 with water in sulfate aerosols. I had known from laboratory experience that the N_2O_5 violently reacts with water. It's such a strong reactant with water that if you store it in glass, it will extract the water from the silica and form nitric acid slowly over time.

Sulfate aerosols form a thin haze in the lower stratosphere; they consist of very small droplets of sulfuric acid. These are produced naturally by volcanoes and some stuff coming out of the ocean. From laboratory experience, I knew how reactive N_2O_5 was with water and with water on surfaces. These sulfuric acid aerosols contained 20 percent water or more. I argued with Grobecker and insisted that he should sponsor a laboratory study of the rate of reaction with gaseous N_2O_5 with liquid sulfuric acid containing various amounts of dissolved water. I put this topic in at least two letters, and in at least two published articles:

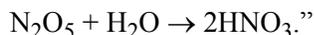
“However, it is conceivable that reaction 7 occurs on the surface of particulate matter in the stratosphere, and until that possibility is quantitatively worked out, it is well to retain reaction 7 as a possibility.



“Nitric acid has been observed in the stratosphere by Murcray, et al. It is presumably formed from hydroxyl radicals and nitrogen dioxide



and it may also be formed by gaseous dinitrogen pentoxide abstracting water from aqueous sulfuric acid droplets



Grobecker held out against it for about a year, and I got very insistent. So Grobecker placed a contract at the Stanford Research Institute [SRI] to study this heterogeneous reaction, but he gave them a short period of time and a limited budget. SRI came back fairly soon with a statement that N_2O_5 reacted with sulfuric acid only once per hundred thousand collisions. At that low rate, the reaction is of no significance in the atmosphere. So I shut up on that one. Almost fifteen years later, Mozurkewich and

Calvert carried out laboratory tests and discovered that N_2O_5 reacts with sulfuric acid aerosols upon one collision out of ten. And when this result was put in the models, the calculated ozone reduction from 500 SSTs cruising at 20 kilometers was greatly reduced.¹ (More later.)

Let's summarize the three cases where I recommended that Grobecker take action, which he did not do or greatly postponed:

<u>I proposed</u>	<u>When done</u>	<u>Effect of my recommendations</u>
Put each of two rates in models	"Post-CIAP"	Smaller calculated ozone reduction
Use obs C-14 to screen Kz	I did it in '74	Larger calculated ozone reduction
N_2O_5 reaction with aerosols	1988	Much less calc. ozone reduction

I believe all my recommendations were based honest scientific considerations, and Grobecker greatly damaged his agenda by believing that I was trying to cheat.

The Climatic Impact Committee [CIC] of the National Academy of Sciences [NAS] had been appointed to work in parallel with the CIAP, to be an independent agency, and to read their reports make their own conclusions. CIC and NAS sponsored a two-week-long meeting at Woods Hole, Massachusetts, July 1974. Several expert guests, including me, were invited. The group discussed and debated the findings of CIAP, as presented in their first three monographs. In general, people calculated about a 10 to 15 percent global ozone reduction.

What was regarded as the best calculation of all was done by people at MIT. They had developed a three-dimensional model for atmospheric motions. That's a big computer calculation right there. They derived their two-dimensional air motions from their three-dimensional model and put in the best chemistry that was known at that time. They considered 500 Boeing SSTs as planned before 1971, but they used as NO_x emission index the value measured on the Concorde. They found a global average ozone reduction of 12 percent, with a local maximum in the northern hemisphere of 25 percent.

The ozone reductions expected by the NAS committee is printed out on this paper^{2 3} (which was given to the moderator):

Northern Hemisphere Ozone Reduction

1. Mozurkewich, M. and J.G. Calvert, Reaction probabilities of N_2O_5 on aqueous aerosols, *J. Geophys. Res.*, **93**, 15889, 1988.

2. D. Cunnold, F.N. Alyea, N. Phillips, and R.G. Prinn, A three dimensional dynamical model of atmospheric ozone, *J. Atmos. Sci.*, **32**, 170-194, 1975.

3. D. Cunnold, F.N. Alyea, and R.G. Prinn, Relative effects on atmospheric ozone of latitude and altitude of supersonic flight, *AIAA Journal*, **15**, 337-345, 1977.

50 Concordes	0.5%
500 Concordes	5%
500 Boeing SSTs	20 to 40%
CIAP fleet for year 1990	15%

Hughes: How did the CIAP respond?

Johnston: Grobecker, Coroniti, and their boss, Robert Cannon, wrote an executive summary to the 551 page report¹ after the 1974 Woods Hole summer meeting. Through the fall of 1974, they presented four successive versions for inspection and comments by CIAP scientists, outside consultants, and the Climatic Impact Committee of the National Academy of Sciences. They called a news conference on January 1975 and presented a brief statement concerning their findings. Let me read their conclusions:

“(1) Operations of present-day aircraft do not create significant perturbation of the environment.

“(2) If the numbers of vehicles in the stratosphere were to increase to meet the projected economic demands of the future, and if 1974 propulsion technology were to be used, the effect of stratospheric pollution would be a potential problem.

“(3) Possible future environmental degradation due to stratospheric pollution can be minimized if proper measures are undertaken in a timely manner. These measures would include: 1) use of new combustors generating low levels of nitrogen oxides; and 2) use of low sulfur fuels, possibly achieved through desulfurization, an application of today’s technology.”

Hughes: That’s all of their report?

Johnston: There was other verbiage in their report. They failed to admit anything about ozone reduction by nitrogen oxides in the SST exhaust. In their press conference in January 1975, they handed out only their executive summary. A few weeks later they released the 550 page *Report of Findings*. Let’s examine their three conclusions.

(1) Nobody ever said that, “Operations of present-day aircraft” would “create significant perturbation of the environment.”

(2) “If ... if ... the effect of stratospheric pollution would be a potential problem.” There is no mention of nitrogen oxides or ozone reduction, and Grobecker gave no numbers, just a weak speculation that there might be a “potential problem.”

1. CIAP, 1974, *Report of Findings: The effects of stratospheric pollution by aircraft*, Climatic Impact Assessment Program , DOT-TST-75-50, edited by A.J. Grobecker, S.C. Coroniti, and R.H. Cannon, Jr., 551 pages, Department of Transportation, Washington, DC. National Technical Information Service, Springfield, Virginia.

(3) He proclaimed assurances that there was a technological fix for the unidentified “potential problem.”

What the newspapers said:

January 22, 1975, *San Francisco Chronicle* headlines “SSTs No Peril Yet, Study Says.”

The Chronicle story began:

“Washington. A three year study concludes that supersonic aircraft now flying will not damage the earth’s protective blanket of ozone, the Department of Transportation said yesterday. Alan J. Grobecker, who directed the study, said a U.S. fleet of high-flying planes would not have weakened the ozone shield either.”

The *New York Times*, page 33 M, headline: “World SST Fleets Said Not To Damage The Ozone Blanket.”

Pittsburgh Press, January 29, 1975:

“Remember the supersonic transport SST? It was rejected in a deluge of ecological righteousness nearly four years ago, partly because environmentalists persuaded Congress that a fleet of faster-than-sound aircraft would fatally deplete the layer of ozone that protects Earth from harmful rays of the sun. . . and now much too late, we learn that the ozone argument was unscientific nonsense.”

Roscoe Drummond, *Christian Science Monitor*, headline, “Scientists Clear the SST,” said in part:

“It must, in retrospect, seem ludicrous that Congress, after long and loud debate, should have halted the SST in midconstruction principally for reasons now proved to be myths. . . Not only unproved but proved to be wrong .”

February 12, *San Francisco Chronicle*, John D. Lofton, Jr., *The SST and the Disaster Lobby*, which included:

“In 1971, when it was decided not to build the supersonic transport, one of the more effective arguments used by the Eco-Freaks and their allies in the Congress was that it would disrupt the upper atmosphere and cause a drastic increase in cancer. . . But now the facts are in. The anti-SST people were wrong. A three-year study released by the Department of Transportation dispels any fears that the present fleet of SSTs will damage the Earth’s protective blanket of ozone

Soon other voices were heard. On January 29, 1975, the U.S. Senate Committee on Aeronautical and Space Sciences conducted a hearing on Planetary Science and the Earth’s Upper Atmosphere. Senator Frank Moss was the presiding chairman. Formal testimony was given by Professor Thomas M. Donahue, chairman, Department of Atmospheric and Oceanic Science, University of Michigan, and others. In his formal testimony, Donahue said:

“A study by the Department of Transportation and by the National Academy of Sciences just completed has shown that a fleet of 500 supersonic transports such as we proposed to build a few years ago would have reduced the ozone content of the stratosphere in the northern hemisphere by perhaps as much as 40 percent . . . One percent decrease in ozone would cause about 2 percent increase in ultraviolet, and about 2 percent increase in the number of skin cancer cases in the United States . . . That would extrapolate to about 350 more deaths and 100,000 new skin cancer cases in the United States every year due to each 100 SSTs and you can do the arithmetic for the rest of the world. So much for the wire service story the other day to the effect that SST’s would not have destroyed the ozone shield.”

Meanwhile, other indignant scientists had been busy behind the scenes. Phil Handler, president of the National Academy of Sciences, received letters from NAS members deploring Grobecker’s tactics and calling for a forthright statement in the upcoming NAS report. I was sent carbon copies of some of these letters. Professor Leo Brewer of the University of California had attended the National Academy of Sciences summer study of 1974 as an expert in thermodynamics. He had heard the National Academy of Sciences presentation. He sent carefully worded letters to Handler, to the *San Francisco Chronicle*, to congressmen, to Professor Henry Booker, and others.

Hughes: I understand that the NAS produced a final report.

Johnston: The National Academy of Sciences Committee on Ozone and Stratospheric Aviation published its final report in 1975, and in that they indicated, as far as the best knowledge of the day was concerned, supersonic transports were calculated to reduce ozone by significant amounts, more or less 10 percent worldwide average. This wasn’t based on my models, but there were some fairly advanced models coming along at that time. MIT had a model where the motions were in three dimensions and the chemistry was in two dimensions. That was a very sophisticated model for that time. They calculated a global average ozone reduction of 12 percent. The National Academy of Sciences report fairly clearly stated the large calculated ozone reductions, and they had a fairly big section on skin cancers and other biological effects.

Hughes: Who was on the National Academy committee?

Johnston: I’d have to look that up. Francis Johnson was the chair.

Hughes: I’m wondering how much overlap, if any, there was between these various committees.

Johnston: The NAS committee were people not active in CIAP.

Hughes: That was deliberate, wasn’t it?

Johnston: Yes, that was the plan.

Francis Johnson made atmospheric contributions by flying captured V2 rockets up above the atmosphere and measuring incoming solar radiation and other things. He had been active in the upper atmosphere research, was a good physicist, and was a no-

nonsense chairman. The way the National Academy of Sciences does things is to take on a controversial subject and try to get a chairman who they can be sure is impartial. They are willing to take witnesses who have an axe to grind provided they can find another witness on the other side, so each will catch the other's errors.

Hughes: They want a balanced committee.

Johnston: They wanted a balanced committee, yes, that's a better word for it.

Kaufman was on the committee. He was a chemical kineticist. He's another one of the fiercely honest people. The final meeting of the Climatic Impact Assessment Program was held after his press release in January 1975. Fred Kaufman stood up at that meeting and strongly rebuked Grobecker for creating a false impression. Grobecker and Cannon published a retraction in *Science*.

I tried to be balanced, but I found myself more skilled at detecting errors by the SST sponsors than by the SST opponents. You can interpret that two ways. One is that more errors were made on this SST side than on the anti-SST side. Or the other is I was biased in my work on this problem. I think if you look at the numbers, there were more errors made on the SST side.

Hughes: Do you have an explanation for why that would be?

Johnston: The people making the pro-SST arguments had all the power of industry and governmental agencies behind them. They didn't control the press as much as they do now, but they controlled what the government said.

Hughes: So there was an overt political spin to all of this.

Johnston: Yes. Especially coming down the home stretch. Back in the early days when they were confident the whole problem would go away when they made their measurements, they were open, very much in a fishbowl, as Cannon said one time.

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Hughes: Now, let's get more into chlorine.

Johnston: In December, 1972, the Department of Transportation SST held a conference in Fort Lauderdale, Florida. The job there was to write technical monographs on all six aspects of the CIAP program. They broke down the work into six quite different categories — emissions, and chemistry, and so forth. Dave Garvin at the National Bureau of Standards and I were co-chairmen of writing one of the big sections.

During that meeting, some of us went for a walk across the street, and we finally broke into small groups. The ocean was just across the street from the hotel, and it was pleasant to walk along the beach there. But there's a busy highway in between. One person out of the group — I didn't know at the time what his name was; I do now — took me aside. He said, "Do you know the space shuttle will reduce ozone maybe as much as the SSTs?" Well, I didn't know that. "How can it do that?" He said, "Well, the space shuttle puts out hydrogen chloride. Its fuel is a mixture of aluminum and perchlorate." The space shuttle burns fuel which has very finely ground aluminum and perchlorate, and a binder, similar to asphalt as fuel and binding. As it burned, it would put a large amount of hydrogen chloride in the atmosphere.

In effect, he was asking me to blow the whistle on the space shuttle. Well, I knew nothing about the space shuttle. I told him, "That's your idea, not mine," but he kept wishing I would do it. I felt it would not be honest for me to take his idea and publish it. I asked him, "Why don't you write it and publish it yourself?" He said, "No, that wouldn't do." I figured it was because he didn't think he knew much chemistry, and I offered, "If you write it up, I'll be very glad to review it for you to be sure your chemistry is right." I offered to sponsor his article to the *Proceedings of the National Academy of Sciences*, but he turned down all of these offers. In hindsight, I realize that he was a medium-level, middle-aged government official, had a family, and was working on the space shuttle. He wanted me to blow the whistle, and I wouldn't do it. I thought we left it at that, but that wasn't what he wanted at all. He'd be fired if he came out with anything critical of the space shuttle. The space shuttle was really the pride of NASA at the time. Well, he left.

Dave Garvin and I were chairmen of the chemistry section of one of the monographs. We'd been accumulating all the chemical reactions we could that were important in the SST atmospheric chemistry. I called him up and told him to look out for reactions involving chlorine, in fact to search the literature and start putting them in the summary, because it's probably going to come up.

In August, 1973 it must have been, I finally got a phone call from an old friend, Larry Anderson at Lockheed of Palo Alto, which had a big CIAP project. Hoshizaki and Anderson had discovered that chlorine from the space shuttle could reduce ozone, and, in fact, they had calculated a very large ozone reduction. They wanted to come out and talk with me and show me their papers. I agreed that one of their reactions would reduce ozone, but another one of their reactions just wasn't going to do it at all. I don't think we'd better go into detail on that one. They'd been invited to come to Washington and talk to high NASA officials about this.

Then I got a call later from Larry Anderson. He said high officials at the Palo Alto Lockheed received a call from high officials at NASA, who said that the space shuttle people at NASA had objected to their coming to Washington. The caller wanted to know if Lockheed was still interested in a big contract coming up, part of the space shuttle. Yes, Lockheed was very much interested. They were told then to keep Hoshizaki and Anderson at home. So the trip to Washington was canceled. They did publish a laboratory report, which nobody paid any attention to. They've never been mentioned as one of the discoverers that chlorine would reduce ozone.

Later I found an eighty-page report by five authors at the University of Michigan. One chapter was "Stratospheric Effects of Space Shuttle Effluents," pages 57-65, which included a discussion of catalytic cycles involving chlorine and ozone. It appears that Richard Stolarski and Ralph Cicerone wrote the section about ozone. So Cicerone and Stolarski had discovered that chlorine would destroy ozone in the stratosphere, and they submitted an article to *Science*, which was rejected. But there was a meeting in Kyoto, Japan, in September 1973, where there were three papers on chlorine. There was the Stolarski and Cicerone paper, and Mike McElroy had a paper, and Paul Crutzen had a paper, all concerning chlorine as a problem. The words "space shuttle" were never mentioned, and it was all discussed in relation to chlorine from volcanoes. If chlorine was produced by volcanoes, that would be an interesting thing, and it should be figured into the overall balance of stratospheric ozone chemistry.^{1 2}

Hughes: How do fluorocarbons come into the story?

Johnston: In November 1973, I gave a seminar at the University of California at Riverside. After the talk, I had a discussion with Norman Hester at the Statewide Air Pollution Research Center, who was engaged in measuring chlorinated hydrocarbons and chlorofluoromethanes in the atmosphere, and he indicated a sense of importance and impending breakthrough. I admitted that I knew relatively little about the subject, and Hester promised to send me some reprints, which arrived on November 28.

The three reprints sent by Hester were all printed in the year 1973, and all concerned measuring tropospheric trace gases, such as methane, carbon monoxide, carbon tetrachloride, chlorofluoromethanes [CFM], methyl iodide, chloroform, trichloroethylene, and tetrachloroethylene. One reported on work done at the Department of Oceanography at the University of Liverpool. Another was from the U.S. Naval Research Laboratory and the Air Resources Laboratory at Idaho Falls. The third paper was by J. E. Lovelock and associates from the Universities of Reading and Southampton, which had been printed in *Nature* on January 19, 1973, and it referred to pioneering work by Lovelock in detecting chlorofluoromethanes in the atmosphere over Ireland in 1970. Hester gave the impression that this subject was highly significant and promised a great breakthrough just around the corner.

1. R. J. Cicerone, D. H. Stedman, R. S. Stolarski, A. N. Dingle, and R. A. Cellarius, University of Michigan, dated June 3, 1973, entitled: "Assessment of Possible Environmental Effects of Space Shuttle Operations," NASA Contractor Report-129003.

2. R. S. Stolarski and R. J. Cicerone, Stratospheric chlorine: A possible sink for ozone. *Canad. J. Chem.* **52**, 1610-1615, 1974.

In late December '73, I got a call from Sherry Rowland, who said that he and Mario Molina had figured that the chlorofluorocarbons were being manufactured and released at such a rate that they could seriously destroy ozone. Rowland asked me: had I heard anything about chlorofluorocarbons reducing ozone? No, I hadn't. I knew that chlorine was understood to reduce ozone, but nobody ever had a source that amounted to anything. They wanted to come up and talk about it, and they came and showed me their preliminary paper. Measurements of chlorofluorocarbons in the environment had recently been financed by the chemical industry for a year or two, and they'd found the chlorofluorocarbons in the troposphere in all kinds of places around the world. R. L. McCarthy, who was head of the freon division at DuPont, revealed, upon request, the rate of manufacture of the chlorofluorocarbons in 1973. Rowland and Molina orally stated that the chlorofluorocarbons released at ground level would act just like nitrous oxide in Crutzen's 1971 paper (refer to Figure 6, page {???}): produced at ground level, carried by air motions up into the stratosphere, encounter the ultraviolet solar radiation, be broken down into chlorine, and the chlorine would reduce ozone by known chemical reactions. The amount released in 1973 was about equal to the amount of nitrogen oxides naturally produced in the stratosphere as recently established by CIAP. They said the amount released in 1973 wouldn't get to the stratosphere for ten or twenty years or more, but then it would more or less double the amount of ozone destruction in the stratosphere. I corrected a minor point or two and gave them a handwritten review that one of my postdocs had just done on the chlorine reactions in general. His name is Bob Watson; he later became a very high person in this field. Rowland and Molina went back and published their article, which came out in June 1974 in *Nature*. People didn't pay much attention to this article.³

Hughes: Why was that?

Johnston: Its implications weren't emphasized. It hadn't received any forceful presentation anywhere. There it was scientifically, and they were saying that the amount of chlorofluorocarbons made now is going to get up there and reduce ozone. They were pretty clear about that.

Hughes: Their paper fell flat in the scientific community as well?

Johnston: Yes. People hadn't had time to wake up to it very much.

Hughes: What did you do about the chlorofluorocarbon problem?

Johnston: The first year or two, I worked to spread the message about the chlorofluorocarbon theory, and gave lots of seminars. In every case, I pointed out the hand-in-glove similarities between Crutzen's nitrous oxide paper of October 1971 and Rowland and Molina's chlorofluorocarbon paper. I emphasized that, whether the computer calculations were correct or not, chlorofluorocarbons were going to more or less double the input rate of ozone destroyers in the upper atmosphere; and it was an important problem, on strong grounds from the beginning. And of course, it had to be verified by chemical measurements and atmospheric measurements and high-quality modeling.

3. M.J. Molina, M. J., and F. S. Rowland, Stratospheric sink for chlorofluoro-methanes: chlorine atom catalyzed destruction of ozone, *Nature*, **249**, 810-814, 1974.

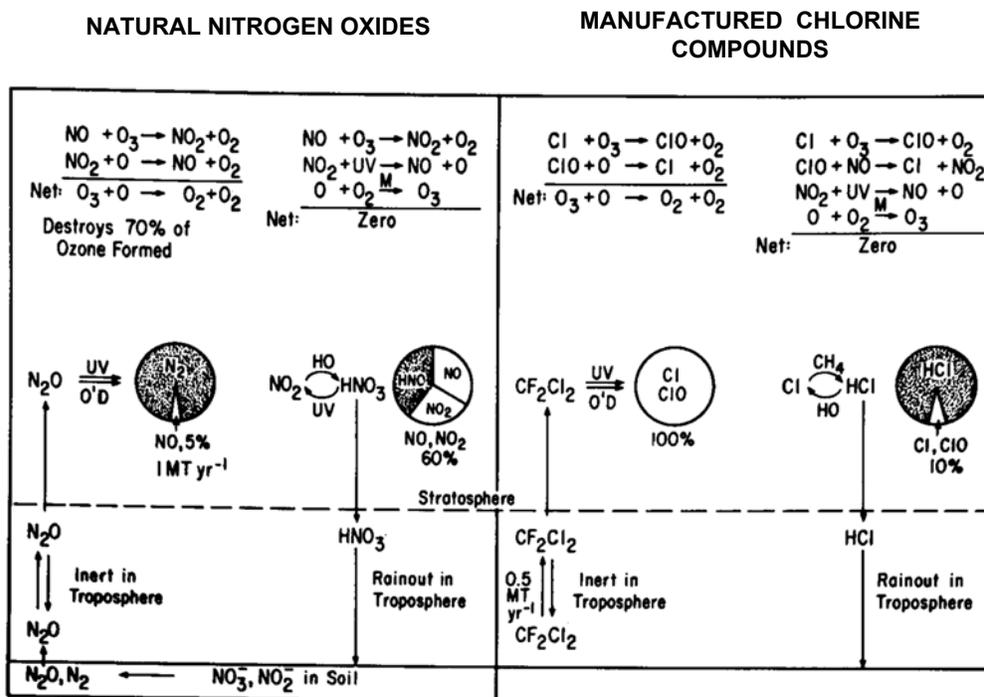


Figure 7. Hand-In-Glove Analogies Between Global Ozone Destruction by Natural Nitrogen Oxides (Crutzen, 1971) and by man-made Chlorofluorocarbons (Molina and Rowland, 1974). Nitrous oxide (N_2O) is naturally formed in soils and waters, and released into the atmosphere. They are broken down to the nitrogen oxides in the stratosphere, which are the major system for natural ozone destruction. Chlorofluorocarbons (CFC) are manufactured, used, and released into the atmosphere. They are broken down to the chlorine radicals in the stratosphere, which are an important system for ozone destruction.

Johnston: High quality quantitative laboratory chemical kinetics measurements were made in several different laboratories, and all the old values were reinvestigated. Many of them were changed by large factors in some cases. The people at Livermore every year made a calculation using then-present knowledge of how much the 500 SSTs at twenty kilometers were calculated to reduce ozone, and how much the chlorofluorocarbons at the 1973 rate of release would reduce ozone. As this new work came in from the laboratory, those curves bounced around very much. I took the Livermore results and plotted them year by year as new results came in from the chemical laboratories, as shown here:

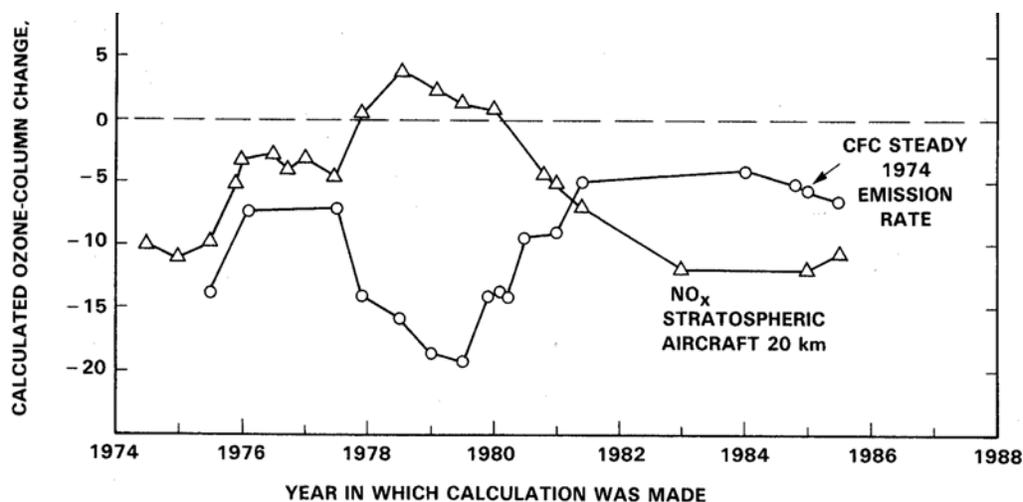


Figure 8. Calculated ozone-column change to steady state for two standard assumed perturbations: (a) 2000 molecules $\text{cm}^{-3} \text{s}^{-1}$ of nitric oxide emitted over one kilometer interval centered at 20 km (originally based on 500 hypothetical supersonic aircraft as planned in 1971); (b) CFC-11 and CFC-12 emitted continuously at 1973 rate. These calculations were made at Lawrence Livermore National Laboratory over this 11-year period using at each time the then current photochemical parameters, eddy diffusion functions, and boundary conditions.

From 1975 to 1978, it was calculated that both SSTs and CFCs would reduce ozone, with CFC being slightly more destructive than SST. During the period of 1978 to 1980, the model for SST found that the oxides of nitrogen would reduce ozone in the middle stratosphere, but it would increase ozone in the upper troposphere and lowest stratosphere, such that the net effect was one of increasing ozone instead of reducing it. But as more information came in, the calculation was that standard 500 SSTs would reduce ozone about 8-10 percent, and the standard chlorofluorocarbons would reduce ozone by 4 or 5 percent. This relation extended out to 1988 in this figure and out to 1990 by later calculations.

Hughes: This is an aside, but in general, have you found in doing science that has political ramifications, that you need a translator, so to speak? You need somebody or an occasion to get the information out of the scientific circle and into the wider society?

Johnston: Yes, it takes more than just a scientific paper to make it have any sort of impact.

For example, to go back to Rowland and Molina, at the meeting of the American Chemical Society in autumn of 1974, Rowland held a forceful press conference and gave out numbers of magnitude of ozone production and emphasized the long delay time. After that, Rowland began to be attacked. The spray-can publication *Aerosol Age* came out with an article in the magazine saying: "When some computer jockeys take their giant machines and feed into them material designed to prove a preconceived idea, they will likely come up with what they want, not what is valid." Robert H. Abplanalp,

inventor of the valve used in most aerosol packages and president of the Precision Valve Company, gave a speech at the Packaging Education Foundation and was quoted by the Ann Arbor, Michigan, *News* on October 10, 1974, as saying: "Extremists in the areas of ecology and consumer protection are today waging a more effective war on American industry than the most capable host of enemy saboteurs." So Rowland and Molina were attacked, just like Haagen-Smit was attacked, and I was attacked.

DuPont wasn't as blatant as the *Aerosol Age* people. They first came out with a big full-page newspaper advertisement that was put in many papers in the country saying how responsible they were and how if this problem was really a problem, they would stop manufacturing chlorofluorocarbons, but so far, there was no proof. It was a reasonable defense. Then somewhat later, they came out with a full-page newspaper advertisement that took quite a different view of things.

Tape 15, side A

Johnston: DuPont took on as its job to discredit Rowland and Molina, and to discredit my work on the supersonic transport studies.

Hughes: DuPont countered through diatribe, not with scientific evidence?

Johnston: Correct. Their point was that nobody had any evidence at all; they did not catch on to the fact that there was an analogy between the observed nitrogen-oxides system and the chlorofluorocarbons. McCarthy, the head of a division at DuPont, testified in both November of 1974 and then again some time in 1975 that there were absolutely no data at all about the problem of chlorofluorocarbons and ozone. It was completely speculation. I stacked up all the publications about the stratosphere that had been published since 1972, the stack was three feet high, and I took pictures of this stack of new evidence. I pointed out that a great deal had been learned about the stratosphere recently, and they should learn about it. Before DuPont took me on as their enemy, I offered to visit them and give them information about what was in that stack of papers. They never answered my offer.

There was quite a bit of letter-writing. Later, I wrote to DuPont some strong letters, and they wrote back evasive responses. By correspondence, I criticized them for attacking us unfairly, by misinterpreting something we'd written, and then attacking the consequences of their misinterpretation.

In a meeting in Utah in 1976, I went to one of my former friends and acquaintances at DuPont and asked him about DuPont's work in this field. He said, "I'm not permitted to discuss that with you." I'd been on some committees with Arthur Kantrowitz, who wanted to set up a formal science court. When there were two sides to a scientific issue, each side would come up and present its case to be judged by blue-ribbon science judges. He asked would I like to submit my work to this process. "Fine. I would be glad to have that opportunity." But as a first step in that direction, he wanted to have a group discussion, where they would discuss the form the court should have and its procedures. He wanted me to be on this panel and among others a friend he had at DuPont. The DuPont man said he refused to sit on any panel with me, and told Kantrowitz that "Johnston was a wild man." [laughs]

- Hughes: Was it not your argument that the aerosol industry had been providing a product, and it deserved some time to see if the theory under which the NAS committee was working was indeed substantiated?
- Johnston: That's the position I certainly took early in the game.
- Hughes: Why did you take that position?
- Johnston: It seemed reasonable. Chlorofluorocarbons were very useful compounds. They're nontoxic, refrigerators are great things to have, and you'd rather have chlorofluorocarbons in your refrigerator than sulfur dioxide, which is highly irritating and toxic. If your refrigerator leaks sulfur dioxide, you're in trouble—more discomfort than fatality. So when it appeared that chlorofluorocarbons might be a severe environmental problem, I thought they should certainly be given a couple of years to understand the problem and organize a response.
- Hughes: Was it in your mind that by taking a tolerant approach you would nudge them into doing research that would come up with alternatives to chlorofluorocarbons?
- Johnston: Well, I never felt I had much influence. No, I was really thinking that they should be given time to understand the scientific problem. I still think that was reasonable. They had been making a good product; all of a sudden it's claimed to be bad.
- Hughes: Did the atmospheric chemistry community then try to test whether indeed chlorofluorocarbons were damaging?
- Johnston: The stratospheric chemists took a great interest in it from the first. The groups that had measured oxides of nitrogen in the stratosphere under the Department of Transportation project shifted to measuring chlorine. The modelers all put chlorine in their models.
- In 1976 the National Academy of Sciences released two reports on chlorofluoromethanes, one by the Panel on Atmospheric Chemistry, chaired by Herbert Gutowsky, and one by the Committee on Impacts of Stratospheric Change, chaired by John Tukey. The NAS committees confirmed every scientific aspect of Rowland and Molina's theory, they pointed out some remaining uncertainties, they recommended selective regulation of CFM, but they recommended that the regulations not take effect for two years.
- Hughes: And the NAS committee indeed was a spur to that work, or would it have happened anyway?
- Johnston: It would have happened anyway. It had already happened in 1976. In the Utah meeting in 1976, Jim Anderson at Harvard, who makes brilliant measurements of trace materials with high-flying balloons and very sophisticated chemical apparatus, had detected both chlorine atoms and chlorine oxide in the stratosphere. The DuPont people had written down what it would take to prove the Rowland-Molina model, and they emphasized that it would require observation of the two radical species that carry the chain in the stratosphere, Cl and ClO, in amounts about equal to model predictions.

When the National Academy of Sciences reports came out, DuPont put out another full-page advertisement, in which, according to the NAS itself, they twisted the facts, and NAS rebuked DuPont. The National Academy of Sciences, signed by the president, formally issued a press release criticizing them and said their action was unworthy of a great institution like DuPont.

Hughes: What was the outcome?

Johnston: Well, when the Department of Transportation project closed on schedule at the end of 1975, Congress officially passed the field of stratospheric research to NASA in 1976. The people in the Department of Transportation were already doing good work and had their equipment going, and they contributed heavily to the progress NASA made. So NASA continued it as partly pure science, and partly one of the assignments they had to understand.

Then 1985 brought in the big change. I was co-chair of one chapter of a large study. Yes, here it is: *Atmospheric Ozone*, 1985, three volumes. [looking through book] There's a whole chapter about assessment models, and then there's a big chapter here about model results. I was co-chairman. Fred Kaufman was the other co-chairman, but he died before the thing was over.

In 1985, two totally different ozone holes were experimentally discovered. An ozone hole is where there's all of a sudden a lot less than there used to be.

Hole number one: People in Antarctica had been measuring the overhead ozone throughout the year--some people spent a cold winter--for about twenty years. For the previous ten years, they kept seeing that in the austral spring, ozone went down, down, down, down. They watched it, and expected it to turn around. You can't call a two- or three-year trend or even a five-year trend real; you can't be sure of it, because things can go along for quite some time, and then go back the other way. But this seemed to be systematic: When the sun came up in the spring, ozone in Antarctica was reduced by quite a large amount. And it kept getting worse over the last ten years. Finally they thought it looked real enough, they had to publish it. So they did, and the article came out in *Nature* in 1985.⁴

Bob Watson, my former postdoc, had risen in NASA; he was a high officer by then. He called a conference in 1985 of all the experts he could think of. He said in effect: Here's a surprise. Here's something totally unpredicted by all the models, and is it real? Could it be instrumental inaccuracy? Do we have any other observations that confirm or deny it? We don't know what caused it; we've got to try to understand it.

There were a lot of ideas floating around. One of the theories was that it might be due to heterogeneous reactions on the polar stratospheric clouds, PSCs. One group said, "It's not chemistry at all; it's just air motions." Air motions mostly in the winter carry material down at the polar regions and carry air up in the tropical regions. For some reason they had — [telephone interruption]

4. J. C. Farman, B.G. Gardiner and J.D. Shanklin, Large losses of total ozone in Antarctica reveal seasonal ClOx/NOx interaction, *Nature*, **315**, 201, 1985.

Advocates of the atmospheric motions theory say it's cold in the Antarctic winter and air has been compressed by the low temperatures, but when the spring comes, it warms up the cold airmass, which expands and lifts troposphere air up. Ozone is not really being reduced, it is just being displaced upward with troposphere air, which doesn't have much ozone in it. I was never convinced.

Hughes: Did the detection of the hole take you by complete surprise?

Johnston: Yes.

Hughes: Looking back, were there any signs that it was appearing?

Johnston: It should have been detected by NASA satellite. Since 1978, there's been a satellite going around the world in a circumpolar orbit. It goes around the world, the world rotates, and the satellite takes measurements. The net effect is that the satellite measures total ozone and its vertical distribution throughout the sunlit atmosphere every day. NASA had archived an enormous amount of data since 1978, right through this period. They realized that not all the data had been interpreted. I think Bob Watson told them to interpret and publish the data for the period of the growth of the ozone hole.

They wouldn't have had observations in the polar night, because ozone was measured by scattered sunlight, but they would have had observations in the spring. NASA scientists went back to the data and returned and stated that there was no observed ozone hole. Somebody realized that this satellite and its computer algorithm had a statement—well, in taking measurements, sometimes crazy numbers come through—if anything comes through below 200 standard units, just save it but ignore it. Nowhere on earth has it ever been that low. I guess somebody noticed the record that had documented ozone was absolutely constant there for quite a number of days, and turned out later that was when it was below 200, which is of course already very low. When they redid their calculations including the data that had been set aside, they observed the ozone hole right off—it was a very conspicuous thing. There was confirmation that the ozone hole was real.

Watson set up an expedition, like a war expedition almost, in 1986 for scientists to go down to Antarctica with airplanes and measuring devices to see what was going on. The head of the exhibition was one of my former graduate students, Susan Solomon. She is extraordinarily brilliant. She quickly learned everything I knew about the atmosphere and we arranged for her to go to the National Center for Atmospheric Research in Boulder to do her thesis with some top people there, which she did. Her specialty was theory of atmospheric motions. She took on the job of being manager of this measurements program and did a marvelous job.

Airplanes took off from New Zealand and flew down to Antarctica and then back, making measurements on the way.

An ER2 spy plane loaded with instruments measured things up to twenty kilometers altitude. A large DC-8 airplane, also loaded with instruments, took measurements at a lower cruise altitude. The expedition came back with a large amount of data, certainly confirming there was a hole, but not really answering what caused it. From what they learned in 1986, they set up a larger measurement campaign with Susan Solomon in

charge again in 1987, and they knew what questions to ask of the measuring devices. In that session, Jim Anderson simultaneously measured chlorine atoms, chlorine oxide (ClO), and ozone as the aircraft flew inside and outside the Antarctic air mass. Where ozone was very low in the hole, the ClO was high, and where ozone was high outside the hole, ClO was extremely low.

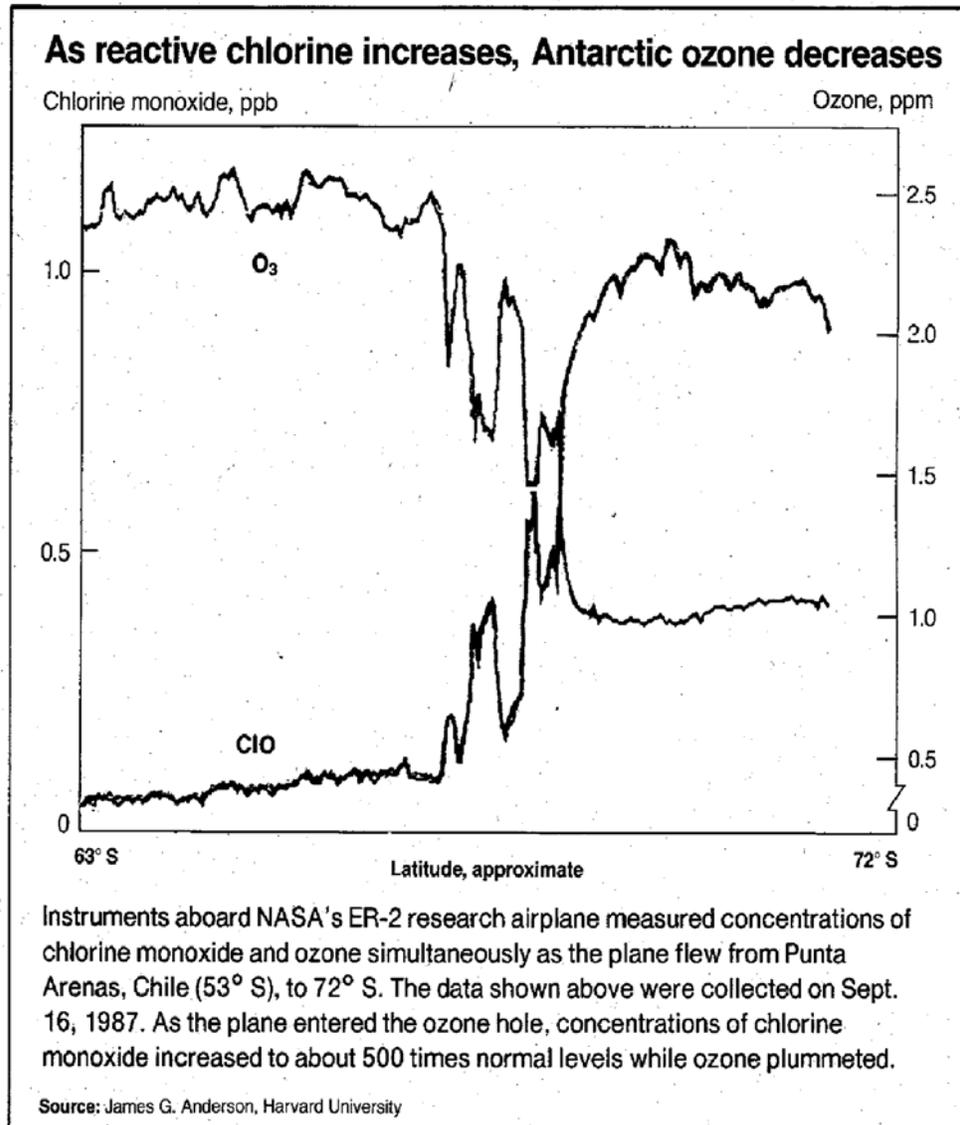


Figure 9. Proof beyond reasonable doubt that the Antarctic ozone hole was caused by chlorine radicals (Cl and ClO).

These observations and supporting theory were broadly recognized as the “smoking gun” that proved beyond reasonable doubt that the Antarctic ozone hole was caused by chlorine radicals (Cl and ClO), which came from manufactured chlorofluorocarbons.

The data were taken in 1987; it took a year or two to interpret the data, because there was such a large amount. It was really 1988 or 1989 before the definitive papers came out. The investigators had been sworn to secrecy until they were able to publish the whole thing. They didn't want people running to call press conferences with this and

that little piece of it. They stuck to that very well. When the articles began coming out they were utterly conclusive. Even DuPont surrendered and said they would stop manufacturing chlorofluorocarbons and look for substitutes.

Hughes: What was the government's reaction to these findings?

Johnston: They responded positively. I forget just when the various laws were passed, but first the spray cans were outlawed and later there were unprecedented international agreements to phase out chlorofluorocarbons.

Hughes: Did the aerosol industry have ground to stand on?

Johnston: They had no ground to stand on. There were big international conferences which negotiated chlorofluorocarbon phase-out, and there was a lot of ozone diplomacy. The Montreal protocol is the word they used, and then later it was modified. The international agreement was that all of it had to be phased out, even from refrigerators, by a future deadline. There are still a lot of refrigerators with CFCs in them. Nobody's going to break them open and put in substitutes, but new machines must use substitutes for chlorofluorocarbons.

Hole number two: Now, let's talk about the other ozone hole. Since 1978 up to 1986, a NASA satellite, traveling in a circumpolar orbit around the earth, measured the vertical profile of ozone by means of Solar Backscattered Ultraviolet [SBUV]. The satellite traveled in a fixed orbit, and the rotating earth presented a different section of the atmosphere to each succeeding pass of the satellite. Every day the SBUV measured the ozone vertical profile of ozone at every place on the globe where there was sunlight. The data were pouring in, and Don Heath, who was in charge of one line of data interpretation, noticed that nearly all over the world, ozone around fifty kilometers altitude was decreasing. I can show you some examples of the measurements.^{5 6} [gets out papers] The satellite instrument shows that ozone around fifty kilometers altitude was going down with a 25 percent reduction over a period of seven years. You wouldn't argue with that.

Hughes: Right.

5. Chandra, J.S., Recent trends in stratospheric ozone inferred from Nimbus SBUV spectrometer, National Workshop on Ozone, April 13-15, 1987, pp.33-44, National Physical Laboratory, New Delhi, 1988.

6. WMO, *Final Report of the International Ozone Trends Panel 1988*, World Meteorological Organization Global Ozone Research and Monitoring Project — Report No. 18.

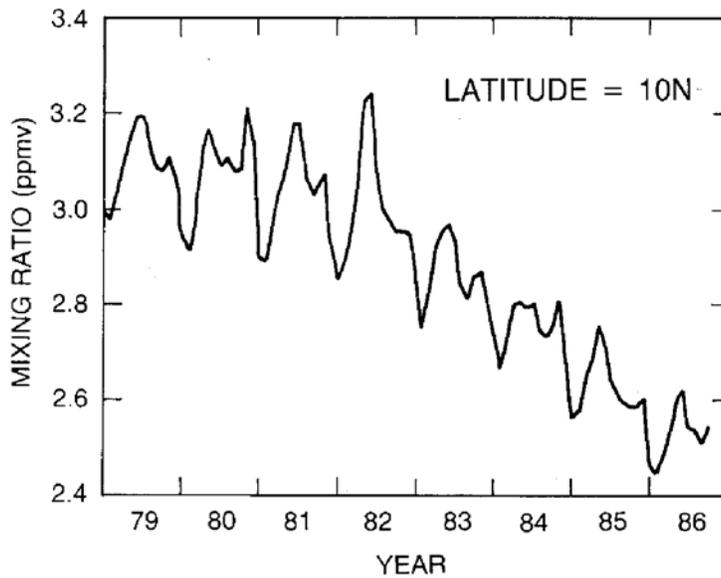


Figure 10. The SBUV weekly mean mixing ratios at 1.0 mb pressure, at 50 km altitude, at latitude 10°N.

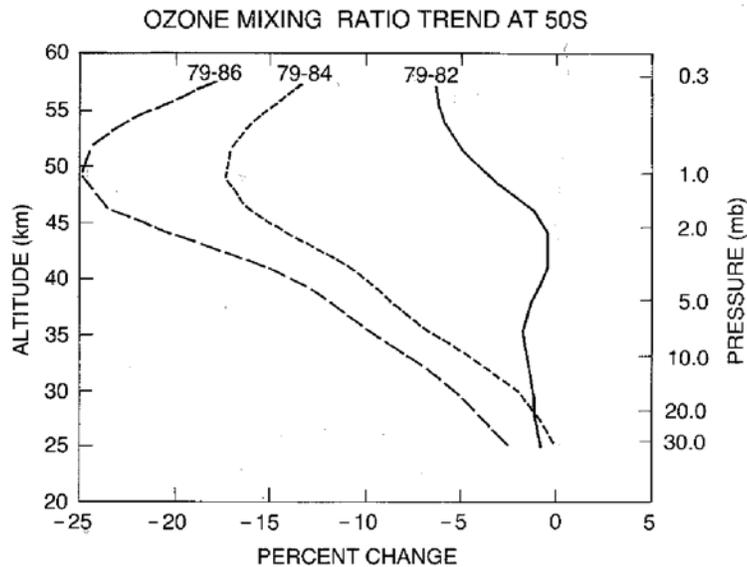


Figure 11. The trend in changes of SBUV ozone mixing ratio as a function of height for three periods: January 1979 to March 1982 (pre-EI Chichon period), January 1979 to December 1984 and January 1979 to October 1986. (Chandra, 1987). The altitude of maximum ozone reduction is 50 kilometers; atmospheric models predict the altitude of maximum ozone reduction by CFCs should be about 40 kilometers.

Johnston: Bob Watson called together a group of experts for this second ozone hole, including me. At the first meeting of our committee in December 1986, Bob sang the same song as he did for the Antarctic ozone hole. He said in effect: Here's a surprise. Here's something totally unpredicted by all the models, and is it real? Could it be instrumental inaccuracy? Do we have any other observations that confirm or deny it? We don't know what caused it; we've got to try to understand it.

After our first meeting Bob Watson called me up and said he wanted me to be chairman of this committee. I said, "I don't know a thing about satellites." He said, "That's all right, you can learn it fast enough." It appeared to me that there might have been some personal conflict if one of two or three of logical choices was put in charge of our committee. So I read up on satellite measurements. Watson took the high-altitude ozone hole as seriously as the he did the Antarctic ozone hole.

Watson appointed a sizable committee to analyze the data, and compare it with other measurements. To explain what we did I brought along this table:

Ozone Measuring Systems and Periods of Available Data

Type	Acronym	Full name	Time Period
Satellite	SBUV	Solar Backscatter Ultraviolet Instrument	10/78 to 2/87
Satellite	SAGE-I	Stratospheric Aerosol and Gas Experiment	2/79 to 11/81
Satellite	SAGE-II	Stratospheric Aerosol and Gas Experiment II	Since 11/84
Satellite	SBUV-II	Solar Backscatter Ultraviolet II	Since 12/84
Ground-based	Umkehr	Stations using Dobson meter in Umkehr mode	Since 1950
Satellite	SME	Solar and Mesosphere Explorer	1/82 to 5/86
Satellite	SMM	Solar Maximum Mission	1985
Satellite	LIMS	Limb Infrared Monitor of the Stratosphere	10/78 to 5/79
Rocket	ROCOZ-A	Rocket ozonesonde from Natal, Brazil	1985

The SBUV satellite made the measurements that showed the second ozone hole. The SAGE satellite flew a different orbit than that of SBUV and used a different method of measuring ozone.

Hughes: Had these satellites been designed specifically to measure ozone levels?

Johnston: They were designed to measure ozone and other things. They were designed to fly along special paths, and there were several sophisticated measuring systems on each of these two satellites.

Ozone depletion theories predicted that chlorine from CFCs would reduce ozone first in the altitude range, thirty-five to forty-five kilometers. The SBUV measurements indicated a big ozone decrease centered at fifty kilometers. The observed decrease was much larger than theory predicted, and it occurred at higher altitude.

Our chapter consisted of sixty pages in the two-volume *Report of the International Trends Panel 1988*. When we compared average data from SBUV and SAGE satellites with each other, it looked as if the hole was real. But then the group leader of SAGE said, "Now, wait a minute. You can't just compare these averages. These satellite fly in different kinds of orbit. What you've got to do is go through all the data and find where they overlapped." There followed an enormous reinterpretation of data.

Hughes: Who did that?

Johnston: The people on our committee. They were real experts. We had on the committee the top man in the SBUV satellite and the top man in the SAGE satellite, and each had a skilled crew. We agreed not going to talk about our project until we had a chance to redo all the data. So their crews did the work, wrote new programs, checked the programs, and reinterpreted all the data obtained by two satellites over a period of almost ten years. They went through and averaged over all intersections, situations where the two satellites were close to each other. It took at over a year to do this calculation. At the end of these comparisons, we found that the SAGE instrument did not see an ozone hole in the upper stratosphere.

Meanwhile, we were comparing the satellite data against every other thing in the table posted here. The Solar and Mesosphere Explorer [SME] measured ozone at and above fifty kilometers, and saw no ozone decrease at fifty kilometers, but it was a highly specialized instrument that had a problem with its long-term reliability, and its results were not definitive. The committee reviewed everything, went back to the beginning of each measuring device, and reviewed its capabilities, its calibration, and its data. The SBUV satellite that went around the poles measured the ratio of back-scattered ultraviolet sunlight at five different wavelengths, but it used only three of these wavelengths in its evaluating its findings. For day-by-day calibration, it had a little slot that stuck out an aluminum reflector plate to measure the absolute intensity of sunlight. The aluminum plate went out just a few minutes a day, but our team discovered that the efficiency of this plate had gone down with time. Well, the answer to this problem was that the surface of this calibrating plate was damaged by solar radiation, during the one or two minutes a day it was sticking out, and it was giving the wrong answer. We finally made a strong case that the second ozone hole wasn't real; it was the degradation of an optical instrument

I think there's at least one moral to that. When their toes are being stepped on by scientific discoveries, industry people tend to say that scientists are publicity-seekers and grant-grabbers, and that's the reason they're saying these things. By grant-grabber, they mean you get your NSF grant the next year if you come out with something spectacular this year. But here was a case where two ozone holes appeared at about the

same time. Both of them disagreed with the theory. Nobody understood either one. There was substantial personnel overlap in the Antarctic ozone expeditions of '86 and '87 and our committee, and so the same group of people found one hole was real and the other was not real. So if the Antarctic hole group was prejudiced against freons, the group disproving the reality of the other ozone hole must be regarded prejudiced in favor of freons, but the two groups were largely the same people. When scientific studies happen to have negative impact on the interests of industries or governmental agencies, their public relations offices react like adversarial lawyers, both against the scientists and the scientific findings.

INTERVIEW 8: SEPTEMBER 10, 1999

Tape 16, side A

Johnston: I want to modify one thing that I said in a previous discussion. I believe I said after the 1970s, I didn't do any more really creative work. The way I should put that: I didn't do any more creative work in pure chemistry, in advancing the chemistry frontiers. Atmospheric sciences are applied science, and I did some creative work there.

Hughes: You became more political at that point?

Johnston: That's not necessarily the same thing. I got pulled into politics, all right. For the years until about 1966, I made an effort to keep up with all the latest things in physical chemistry and kinetics and contribute at that level. But after four years out as dean, the field got far ahead of me, and atmospheric problems came up. Research for the next twenty years was more or less the forefront of atmospheric chemistry.

Hughes: The gross distinction there is between a basic science and an applied science?

Johnston: Correct.

Hughes: Because you were unable to keep up with all fronts of the basic science, do you think that it shaped the way you went about atmospheric chemistry?

Johnston: Maybe it provided me with an escape hatch, to start over again in an almost unexplored field.

Now, you asked me about advisory committees?

Hughes: Yes, advisory committees.

Johnston: I'm not going to list off all of them. I want to mention only some of the most interesting ones. Between 1971 to 1975, I was on the National Academy of Sciences Committee on Motor Vehicle Emissions. That was shortly after EPA [Environmental Protection Agency] was set up. The committee discussed the various pollutants that the automobiles emitted, with emphasis on oxides of nitrogen, organic materials, and smoke, reduction of which was needed to improve the quality of the air. What was scientifically and technically feasible. The committee had testimony from representatives of almost all the automobile engine manufacturers, including European and Japanese manufacturers. They came through one by one and discussed how hard it would be to do what others were saying needed to be done. We went over a large amount of material and published a big report in 1975.

In July 1974 I was an invited participant in the National Academy of Sciences summer study at Woods Hole, Massachusetts, sponsored by the Climatic Impact Committee on Ozone and Stratospheric Aviation. In 1975, when the Department of Transportation's Climatic Impact Assessment report came out indicating that there was strong evidence that a large fleet of supersonic transports would cause fairly large ozone reductions, most people lost interest in supersonic aircraft. At least public interest. Presumably the aircraft companies maintained a small staff thinking about it all the time.

From 1976 to 1982 the Federal Aviation Administration, FAA, had the High Altitude Pollution Program, abbreviated HAPP, that continued to study possible environmental effect of subsonic and supersonic aircraft. It reviewed the things previously done and brought them up to date and assimilated the effects of the chlorine chemistry, which was pouring in new results over that period. I was a member of the advisory committee for HAPP. At the end of my service on that committee in 1982, the Federal Aviation Administration gave me a certificate of commendation for service to aviation. I was amused that they gave me the commendation, since the Department of Transportation and FAA had for years treated me as their enemy.

Hughes: How did that come about?

Johnston: [laughs] Why did I receive that commendation when I was said to be anti-SST? They gave that citation to everyone on the committee.

DEPARTMENT OF TRANSPORTATION

FEDERAL AVIATION ADMINISTRATION



CERTIFICATE OF COMMENDATION

TO

Harold S. Johnston

IN RECOGNITION OF HIS SPECIAL CONTRIBUTIONS AS A MEMBER OF THE FEDERAL AVIATION ADMINISTRATION'S HIGH ALTITUDE POLLUTION PROGRAM SCIENTIFIC ADVISORY COMMITTEE. HE HELPED FOSTER A BETTER UNDERSTANDING OF THE EFFECTS OF AIRCRAFT EXHAUST EMISSIONS ON THE UPPER ATMOSPHERE, RESULTING IN SUBSTANTIAL SAVINGS TO THE FEDERAL GOVERNMENT AND THE AVIATION INDUSTRY. HIS EFFORTS SIGNIFICANTLY CONTRIBUTED TO THE NATIONAL AVIATION SYSTEM AND WARRANT THE APPRECIATION OF ALL WHO FLY.

WASHINGTON, D.C.

William J. Bolger
ADMINISTRATOR

Dec. 1982

Figure 12. Certificate of Commendation

Hughes: Who made the appointments to that committee? Did the FAA have to approve your appointment?

Johnston: Yes. I was still to a fairly high degree an expert chemist on these matters. Some people in the Department of Transportation saw that what I was doing was designed to be science and not politics. It was only the interest groups that interpret everything in terms of adversarial poles who thought I was their enemy. I was respected by some of the Department of Transportation people. FAA very much admired my 1974 article with Ed Quitevis where we showed that subsonic aircraft would increase atmospheric ozone, not decrease it, which many others were saying. This was the article that Robert Cannon prevented me from discussing at Woods Hole in the summer of 1974. He wanted to force manufacturers of subsonic aircraft engines to develop expensive low-nitrogen-oxides engines with the assertion that subsonic aircraft also reduced atmospheric ozone. FAA after 1976 was happy not to have to force manufacturers to produce expensive low- NO_x engines.

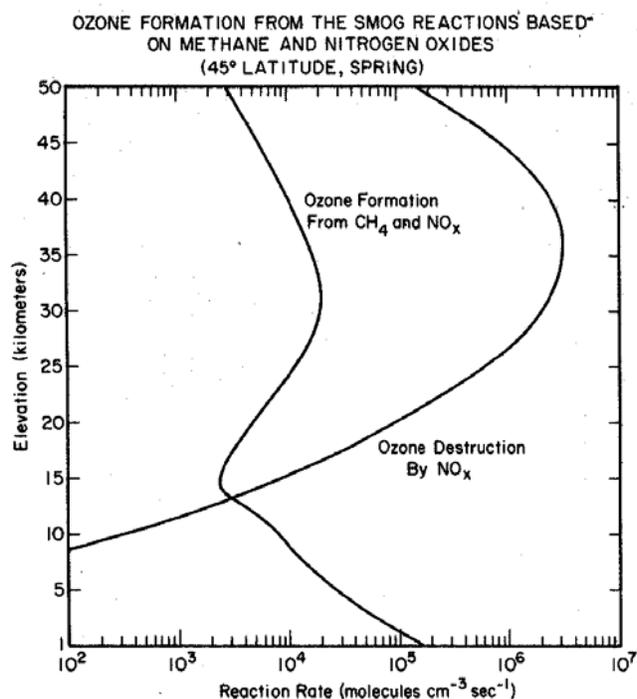


Figure 13. Vertical profiles of the rate of formation of ozone from the methane- NO_x -smog reactions and of rate of ozone destruction by the nitrogen oxides catalytic cycle. For a set of 36 reactions and observed vertical profiles of methane, ozone, and water vapor, there is a crossover at about 13 km altitude between ozone destruction and ozone formation so far as added NO_x is concerned. The 1971 SST cruising at 20 kilometer altitude is in the region where added NO_x destroys ozone; subsonic aircraft cruising at 12 kilometer altitude is in the region where NO_x produces ozone by way of methane- NO_x reactions.

Hughes: By then, you were such an obvious expert in atmospheric chemistry that it would have been a notable oversight to not appoint you?

Johnston: Perhaps, unless they wanted to run a controlled show, which they apparently didn't want at that time.

In his State of the Union Address in 1986, President Ronald Reagan said:

“...we're going forward with research on a new Orient Express that could, by the end of next decade, take off from Dulles Airport, accelerate up to 25 times the speed of sound, attaining low earth orbit or flying to Tokyo within two hours.”

This speed would require at least Mach 10, that is, ten times the speed of sound.

A national program was started studying the possibilities. An aircraft with Mach number greater than five is called hypersonic aircraft. It has to fly at much higher altitudes than the supersonic transport, and for fuel it has to use liquid hydrogen or liquid methane. It's a totally different system.

Boeing had kept some calculations going throughout the years. In 1989 they studied supersonic transports with Mach numbers from 1.2 to 25. Using what had been learned in the intervening fifteen years since 1974 about aircraft structures and strength of materials and so forth, Boeing concluded that a supersonic aircraft with Mach numbers between 2.4 and 3.2, not the hypersonic aircraft, would be technically feasible and economically profitable at this time. They recognized some hurdles to be overcome: economic, technical, airport noise, sonic boom, ozone reduction by nitrogen oxides, and other environmental problems.¹

Hughes: Who made those statements?

Johnston: It was a joint statement by a special group in NASA and the aircraft industry, especially Boeing. The aircraft industry provided big input. They said that making a new SST, renamed High Speed Civil Transport [HSCT], was a sensible thing to do if certain problems could be solved.

The aircraft engines as used in the early 1970s were inefficient, certainly compared to the ones being used in the 1990s. There have been big changes in the design of the engine for more efficiency. Remember, they used to have four engines on a big plane; now the recent ones have two. The new ones that have two engines are faster and more efficient. But as a byproduct of this increase in efficiency, they increased the oxides of nitrogen by a substantial amount, a multiple of three or four, maybe five.

Doug Kinnison, Don Wuebbles and I calculated the magnitude of ozone reduction by nitrogen oxides, as understood in 1989, given by Table 1. The fuel consumption and nitrogen oxide emissions correspond to 500 U.S. Mach 2.7 supersonic aircraft that were

1. Boeing, "High-Speed Civil Transport Study," NASA Contractor Report 4233, Prepared Contract NAS1-18377, NASA, Office of Management, Scientific and Technical Information Division, 115 pages., 1989.

studied in the early 1970s. Calculations were made at various assigned altitudes. The principal conclusion to be drawn from this table is that the calculated ozone reduction is strongly dependent on altitude of nitrogen oxides injection. This article indicated that Mach 2.4 aircraft, which cruise at sixteen to nineteen kilometer altitude, would cause much less ozone reduction than Mach 3.2 aircraft cruising at twenty to twenty-three kilometers.

Table 1. Calculated (1989) global ozone change with Lawrence Livermore National Laboratory (LLNL) two-dimensional model: assumed fuel consumption of 77 billion metric tons per year and nitrogen oxides emission index of 23 g(NO_x as NO₂/kg fuel), that is, nitrogen oxides injection of 1.8 million metric tons per year at various assigned altitudes of injection; chlorine 2.8 ppbv. Only gas phase chemistry.

Injection altitude, km	Supersonic			Hypersonic			
	16.5	19.5	22.5	25.5	28.5	31.5	34.5
Calc. ozone change, %	-0.7	-7.6	-8.6	-9.6	-10.1	-9.8	-9.2

I was on the science advisory committee to NASA's Atmospheric Effects of Stratospheric Aircraft [AESAs] from late 1988 to 1994, and then my term expired. I then went to the National Academy of Sciences advisory Panel on Atmospheric Effects of Aviation [PAEAN] for three years (1995-1997).

Howard Wesoky was the director of a new program, Atmospheric Effects of Stratospheric Aircraft. Wesoky issued a research announcement on July 1989, soliciting proposals for basic research on *The Atmospheric Effects of Stratospheric Aircraft: Modeling and Measurements in Support of the High Speed Research Program*. Key points in the section of Emissions Scenarios included:

“The NO_x emission index (EI) ranges from 30 to 50 g(NO₂)/kg(fuel) for current combustor technology applied to advanced ... engines for supersonic aircraft. It appears that significant effort would be required to reduce the EI to a range 5 to 20 ... in a commercial aircraft engine, and innovative technology is needed for reduction below 5.”

A broad approach was called for:

“It is important to consider as wide a range as possible for the aircraft emissions scenarios, including emission indices and operational ranges ... The emission indices must be realistic, including values for today's engines [about 50] and those projected for future development [about 5].”

The wide range for nitrogen oxides emission index was agreed to be 5, 15, and 45. Airline experts selected flight routes that they expected to support significant supersonic passenger service, and they estimated the number of flights per year and fuel consumed per year. For subsonic and supersonic aircraft, they summed the estimated fuel consumption over latitude bands. They concluded that 59 percent of supersonic

traffic would be in the north temperate zone and 34 percent would be in the tropical half of the world, 30°N to 30°S. These considerations replaced the previously overused concept of the narrow flight corridor over the north temperate region, spoken of as “the corridor effect.”

Model calculations made by participants in terms of the new AESA program gave ozone reductions by nitrogen oxides from the high-speed civil transports that were comparable to those found in the mid 1970s.

As I mentioned in discussing Climatic Impact Assessment Program [CIAP, 1972-1975], I thought nitrogen pentoxide (N_2O_5) would react with water (H_2O) in atmospheric sulfuric acid aerosols to form nitric acid (HNO_3),

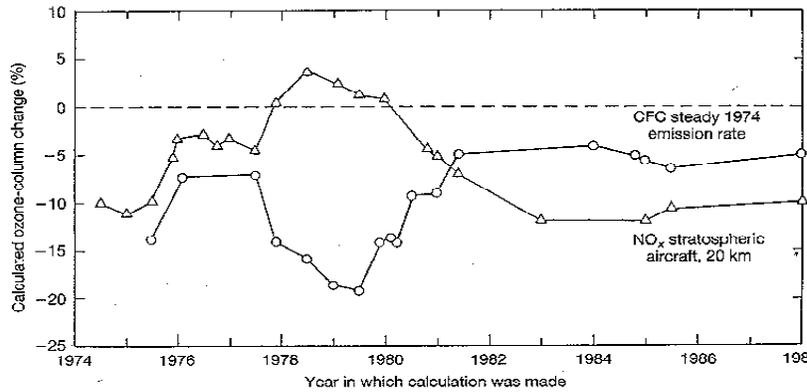


and I expressed this opinion in published articles, in written reports, and orally during the period 1971 and 1974. Although I never saw the report, a manager of CIAP told me in 1974 that SRI had found the reaction probability per collision to be less than one in a hundred thousand, and thus the reaction would have negligible effect on stratospheric chemistry. In 1988, Mozurkewich and Calvert found the reaction rate to be about one reaction per ten collisions between N_2O_5 and sulfuric acid aerosols, ten-thousand-fold faster than the quoted result by SRI in 1975.

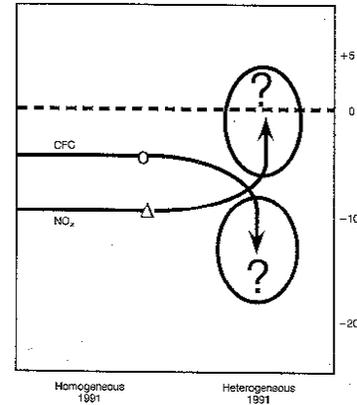
Hughes: What was the research background for this work?

Johnston: D.K. Weisenstein, M.K.W. Ko, J.M. Rodriguez, and N.-D. Sze [1991] were the first to include a heterogeneous reaction in a 2-D global model in a study concerning High Speed Civil Transports; this reaction was that of nitrogen pentoxide reacting with water in stratospheric aerosols. Weisenstein, Ko, Rodriguez, and Sze [1991] found this single heterogeneous reaction greatly diminished the calculated ozone reduction, in some cases reversing the sign of the net effect. I reviewed this article for the *Geophysical Research Letters*, recognized its enormous value, and strongly recommended that it be published, but I pointed out to the authors how they could improve their presentation in parts of their article. In anticipation of publication of their article, I prepared a figure to illustrate the effect of heterogeneous chemistry on calculated ozone changes by HSCT and by CFC (chlorofluorocarbons), and I presented this figure in all my subsequent lectures.

Calculated Global Ozone Change (%), 1974-88
Homogeneous Chemistry, LLNL Model
 (Δ) 500 US SST, 1971. (o) CFC @ 1974 Rate



Add Heterogeneous Chemistry. 1991



Year in which calculation was made

Figure 14. Effect of Heterogeneous Chemistry on Calculated Ozone Changes by HSCT (High Speed Civil Transport) and by CFC (Chlorofluorocarbons),

NASA and the aircraft industry resolved to design a new engine that reduced NO_x emission index to the value of 5 grams of NO_x per kilogram of fuel, about a factor of ten. NASA and the aircraft industry worked on it for ten years. Every year, the NASA manager would come out and say words to the effect: “We’re making great progress; I’m confident it can be done.” Low NO_x emission such as that sought for the HSCT had been demonstrated on laboratory bench tests using pre-vaporized fuel. But doing it in a laboratory is quite different from having an engine suitable to use on an airplane.

Hughes: Would you say the scientists at NASA are at the scientific level of their counterparts in academia?

Johnston: You’ve got to consider distribution in each case. I wouldn’t say the two curves superimpose exactly, but certainly the best people in the NASA group are quite comparable to the best people in academia. Many of them left the NASA group to accept professorships in universities and have done very well.

Hughes: Where do they come from largely?

Johnston: There’s a wide range of disciplines—engineering, atmospheric dynamics, physics, mathematics, computer science, and chemistry.

I was a member of the National Academy of Sciences Panel on Atmospheric Effects of Aviation from 1995 through 1997. The chair of the panel was Albert J. Kaehn, retired brigadier general of the U.S. Air force. Usually the National Research Council committees consist primarily of experts in the field under investigation, and additional experts may be hired as temporary consultants. The staff of PAEAN came up with and put into practice a bizarre idea: Experts in the field are not really needed on NRC committees; consider trial by jury where experts are avoided; if enough evidence is

there, a jury of citizens will come up with the right verdict. General Al Kaehn, who knew little about the stratosphere or ozone, was appointed chair of the panel. Apparently he was led to believe that the only task of PAEAN was to check up on AESA manager's strategic plan.

Chairman Albert Kaehn, Jr., invited me to write a statement for PAEAN giving my views of the history and achievements of the NASA program, Atmospheric Effects of Supersonic Aviation with respect to atmospheric chemistry, which I did in the summer of 1995. Jim Holton and I were co-chairs of the subpanel concerning the stratosphere and supersonic aircraft, during the first formulation of our report. We and two others made substantial contributions to the first draft of a report. But I believe that our NRC staff engaged in serious malpractice, and let themselves be lobbied by the person they were supposed to be investigating and advising.

Hughes: In what direction was the lobbying?

Johnston: NRC staff are supposed to help the committee in the mechanics of their job and are not supposed to try to determine the content of their reports, but, in the case of PAEAN, the staff aggressively did some jobs that committee members and chairs are supposed to do. Staff took the first draft of our report, rejected some of it, rewrote some sections introducing changes of meaning, sliced up some contributions and reassembled the pieces, and sent it back to the panel with numerous queries inserted in the text. In this process, many gross factual errors were introduced. After two iterations of this process the report became amorphous and unfit for publication by the NAS.

I have here some quotations of written material from the Chair and the staff to the panel. Let the staff be referred to as Staff(1) and Staff(2). [reading from a list]

General Kaehn's letter 5/96:

"I would like to remind you that this report must serve two primary purposes: to provide a scientific basis for driving the science to be conducted, and, equally important, to provide a level of understanding that assures resource allocators ... that they are making the right decision in continuing to fund the AEAP scientific initiatives and that the dollars will go to the right places within the project We do owe NASA some kind of report, recognizing that we've been in business over a year. With your concurrence, we told the customer that we would strive to produce an NRC report dealing with the stratospheric part of the program by summer."

From Staff(2) to Johnston:

"Staff(1) tells me that NASA HQ itself is now facing a 50% cut. It is imperative that our reports serve Howard well in 1) directing the expenditure of the money he has, 2) retaining the budget he needs to do the necessary science, and, in passing, 3) justifying his use of PAEAN as his advisory panel."

Staff(2)'s Assertion of Policy, 3/20/96:

“...we (meaning AI, Staff (1), and I) Obviously, our sponsor is audience no. 1.... Since Howard needs to defend and maintain his funding levels, I'd say the no. 3 audience is his agency bosses and their congressional defenders.... It seems to me that it should not include much in the way of math, or detailed explanations of the dynamics, chemistry, or any other areas. I think we should supply only enough scientific background and explanation to enable the reader to follow our arguments; we can include references if necessary.”

Staff(2)'s Assertion of Power, 7/30/97:

“There are a number of reasons why I don't give the sources of all the questions you see in text. What I note there may be a cross between two or more people's questions, may be the logical consequence of another change or question, may come from someone who could be dismissed as ignorant or having an ax to grind, may strike me as silly and potentially embarrassing, may be purely editorial, may be the politest way I can think of to present negative criticism (well-founded or not), or may be just a reminder — or any combination of the above. Certainly anywhere you feel a discussion among specialists is called for, I'll be happy to try to identify the ultimate source.”

To a considerable extent, these actions effectively cut off communication among the four or five stratospheric experts (the panel had sixteen members). From my previous experience on NAS committees, the staff is not entitled to set policy and micro-manage reports in this manner.

The title of the PAEAN report was “An Interim Review of AESA: Science and Progress.” In a discussion with our sub-panel concerning the report, I said that to carry out our task as given by the word “progress” in the title, we should give a brief account of the status of the SST environmental problems as they existed before AESA was set up, as the background for recounting the outstanding progress AESA had made, especially the observations in the stratosphere, in the chemical laboratory, and modeling the effects of heterogeneous chemistry. Staff(2) interrupted: “Oh no, we are only supposed to describe the progress of AESA since the last NRC report” [which was 1994]. “Howard doesn't want it.”

I pointed out the need for knowledge and model studies about the possible Mach 3.2 (or higher Mach) SST, which might arise at any time from domestic or foreign competitors of Boeing, and about higher emission indices if the NASA project should fail to meet its goal of designing an engine that would emit only five grams of NO_x per kilogram of fuel burned and be efficient, economical, and safe, or if another country builds SST with high NO_x emission index or flew at a higher altitude. Staff(2) opposed including such material, saying that, “Howard did not want PAEAN to do this.”

I reviewed the staff's revision of PAEAN draft report concerning atmospheric effects of stratospheric aircraft, and I wrote to the chair and staff:

Someone, I don't know who, inserted ghastly ignorant erroneous statements, for examples: Jan. 1997, Introduction, "In the course of burning the current fossil fuels, such aircraft would emit CO₂, H₂O, and O₃...." At thrust temperatures of jet engines, ozone is dissociated in microseconds; no significant ozone is emitted from jet engines. Also, NO_x was omitted from the list of exhaust gases. Calculated ozone reduction by NO_x was the main reason for setting up AESA in the first place. In the same version of the report, "the NO_x cycle is dominant between 16 and 20 km". The most important achievement of AESA was to discover in 1991 that NO_x is not dominant in this altitude region. It is frightening that anyone in a position to insert the first paragraph in the Introduction should be so ignorant of the HSCT history and problems to assert that ozone comes out of HSCT exhaust and to omit NO_x from the exhaust as an item worth mentioning.

I believe that the staff or chair or both cut down my material because they thought that I had an anti-HSCT axe to grind. If so, why didn't the chair or senior staff member privately challenge me? Who told them that I had an anti-HSCT axe to grind? Why did staff fight against my request for AESA broadening its scope? On scientific grounds we should explore the space around the region of interest to see if things change rapidly or slowly. I believe that Howard Wesoky lobbied the staff to suppress past history and to prevent revealing that higher Mach aircraft or engines with much larger NO_x emission index would have significantly higher calculated ozone reduction. I think the NASA managers wanted to give the impression that NO_x from supersonic transports never has and never will have an effect on ozone.

I reported these abuses to an officer of the National Academy of Sciences, and he replied that both Staff(1) and Staff(2) had already been scheduled to leave the National Research Council.

Hughes: You are convinced that they were aware of that history?

Johnston: Oh, absolutely. It had been published repeatedly in lots of places and discussed in our panel meetings.

Hughes: Well then, how could they, as scientists who presumably wanted to be received as credible individuals, limit the study in that way?

Johnston: I think industries and an agency like NASA mostly use science in order to achieve their goals. Rigorous science is required to achieve goals technical developments, such as synthetic chemistry, computer development, space flight, and aircraft design. When an agenda is threatened by considerations of consumer safety or environmental impact, rigorous science is required for long-term resolution, but I've collected in a file a substantial number of cases where industries or governmental agencies manipulate, twist, and tilt science to make it appear to come out in a way that serves their short-term interests. Also, they may launch character assassination campaign against individual scientists whose findings happen to come out in a way they don't like.

Hughes: What was your prime motive in serving on these various committees?

- Johnston: Well, they invited me to, and it's sort of a civic duty, being an expert in the field.
- Hughes: One reaction to an invitation to serve on such a committee could have been, "No, I've got better things to do with my time. I know that whatever report comes out is going to be manipulated by whatever agency is affected by it, and I don't want to be part of that."
- Johnston: Well, I learned a lot about manipulation by serving on these committees. If there's going to be any manipulation, there ought to be somebody in there watching them. [laughs]
- Hughes: Exactly what I was expecting you to say! [laughter]
- Johnston: Boeing in October 1998 suddenly withdrew from the High Speed Research Program, and the Atmospheric Effects Stratospheric Aircraft program was terminated in early 1999. The final report of the Atmospheric Effects of Stratospheric Aviation project, Kawa et al., 1999, consisted of well-written, informative 150 pages of text, twenty-six pages of references, and eight technical appendices. The text was top-quality scientific exposition within the subject-matter limits imposed by NASA management. The conclusions are well expressed by the following paragraph from on page x of the Executive Summary: [reading from a document]

"Based on a combination of model calculations and expert judgment, the estimated column ozone change in the Northern Hemisphere is -0.4% for a fleet of 500 HSCTs [High Speed Civil Transports] flying Mach 2.4 with an NO_x emission index EI(NO_x) of 5 g/kg, EI(SO₂) of 0.4 g/kg, and 10% of fuel sulfur converted to particles. Based on the same combination of model calculations and expert judgment for the uncertainty in component processes, the hemispheric ozone response will likely be in the range of -2.5 to +0.5%."²

From 1994 to 1999, the National Academy of Sciences/National Research Council supported the Panel on Atmospheric Effects of Aviation, which reviewed NASA's Atmospheric Effects Stratospheric Aircraft program. The PAEAN final report on stratospheric aircraft states on page 39:

"Future Stratospheric Aircraft. It must be stressed that the AESA assessment was restricted to studying the effects of only one type of aircraft (known as the Technology Concept Aircraft, TCA, Baughcum et al., 1998) that cruises at Mach 2.4 and has a NO_x EI between 5 and 15. This restriction seems reasonable given the fact that the TCA was the only type of stratospheric aircraft that has been seriously considered for commercial production recently. It is quite possible, however, that other types of stratospheric aircraft may be considered in the future (for instance "hypersonic" aircraft that cruise at higher speed and altitude). In such a case, it is imperative that the assessment calculations be redone to specifically test the effects of the appropriate mach numbers and emission indices. This is important because some very preliminary

2. S. Randolph Kawa, Assessment Chair, *Assessment of the Effects of High-Speed Aircraft in the Stratosphere: 1998*, eleven co-authors. NASA/TP-1999-209237, Goddard Space Flight Center, Greenbelt, Maryland 20771

studies have shown that hypersonic aircraft could have quite devastating effects on ozone (Oliver, 1994).”

Hughes: What do you know about Oliver?

Johnston: While sorting mail one morning in early 1994, I came across a plain brown envelope with no return address, and I tossed it in the pile of “probable junk.” When I opened the envelope, I found the following:

ATMOSPHERIC EFFECTS OF HYPERSONIC TRANSPORT AIRCRAFT:
A SUMMARY AND INTERPRETATION OF AVAILABLE INFORMATION

Robert C. Oliver, February 1994.

Prepared for National Aeronautics and Space Administration

INSTITUTE FOR DEFENSE ANALYSIS, IDA DOCUMENT D-1443

1801 N. Beauregard Street, Alexandria, Virginia 22311-1772

Contract MDA 903 89 C 0003, Task T-AG2-1136

Page v: This work was supported by the NASA High Speed Research
Program/Atmospheric Effects of Stratospheric Aircraft

under Contract IDA 903-89C-003

under IDA Task Order T-AG2- 1 136. Copy X of 40 copies

The meaning of the copy numbering is that only forty copies were made, it was sent to forty (or less) people each with a number between 1 and 40, so that if any copy showed up where NASA did not want it to be seen, the person who lost or donated it could be identified. In 1998 a committee of the National Academy of Sciences/National Research Council heard about it (I told them) and requested a copy of the HST report. A copy was entered into the record of that committee, and thus it is now in the public domain. So far as I know, the quotations I give here are the only public statement of the quantities in the Oliver Report. Some pertinent quotations from the booklet are:

Table . Comparison of supersonic and hypersonic aircraft as given by Oliver. The estimated global ozone changes include consideration of heterogeneous chemistry.

	Supersonic	Hypersonic			
Design Source	Boeing	Saenger	Douglas	Boeing	Boeing
Mach No.	2.4	4.5	5.0	6.0	10.0
Fuel	Jet A	liq. H ₂	liq. CH ₄	liq. H ₂	liq. H ₂
Mean emissions alt., km	18.3	25	25.5	27	34
NOx emission index	5*	300	120	100	200

	Supersonic	Hypersonic			
Fleet emissions NO _x , kg/yr ***	0.35 x 10 ⁹	15 x 10 ⁹	11	7	22
Global ozone change***	-0.4%	[-34%]	[-37%]	[-20%]	[-49%]

*NASA goal.

**Seat-miles per year equal to that of 500 Mach 2.4 aircraft.

*** “Notional” ozone change, in Oliver’s words, “Bracketed to emphasize the acknowledged lack of credibility.”

“Hypersonic (typically Mach 5+) commercial aircraft have long been discussed as futuristic transportation systems capable, e.g., of travel from New York to Tokyo in about two hours. Such vehicles, using either liquid hydrogen or liquid methane (the latter to about Mach 5), were explored over the Mach 4.5 to 10 speed range as part of the early NASA High Speed Civil Transport (HSCT) study program but were found to be unattractive economically relative to lower speed (Mach 2 to 3) supersonic aircraft However, some interest in hypersonic vehicles is still evident: The German Saenger program, e.g., is (or has been) exploring a hypersonic vehicle concept, to be hydrogen fueled and nominally capable of 10,000 km cruise at Mach 4.5; also Japanese interest has been reported.” (Page S-1).

“The 16-49% global depletion estimates shown for the hypersonic fleets are very large, and outside the range of available modeling studies; the perturbations to the stratosphere are massive.” (Page 39).

Hughes: Well, let’s go back to UC and talk about teaching. What importance did you place on teaching when there were so many other things that you were responsible for?

Johnston: The chemistry department here for a long time has had a strong policy, which I personally agree with, in taking undergraduate teaching seriously. When I got here, they still had the policy that every professor, but not organic chemistry professors, would conduct a freshman chemistry section. The students here are taught in a lecture hall holding 500 people, and the college had a policy of getting the best teachers in the department to teach the course.

The large lecture-hall format, of course, is impersonal, but the freshman students are broken up into laboratory sections of about twenty-five each. A faculty member would take a fairly considerable amount of time at the beginning of each laboratory section in going over the experiment and answering questions about the lectures. In my first years

here, I did a lot of that. Glenn Seaborg did that sort of teaching also. Right up to the last two or three years before he died in 1998, he would have one section of freshman chemistry students.

This was in addition to the teaching responsibility for graduate student courses and upper division courses. I typically taught the course in junior/senior physical chemistry and had one or two freshman laboratory sections. That was the most typical arrangement. I also taught some chemical kinetic courses and a special atmospheric chemistry course for graduate students.

In recent years, there has been some talk on the part of the faculty as to why should we teach so much more than everybody else on the campus? Recently, the teaching load has been reduced somewhat. Supervising and teaching the graduate student to carry out research is a very important role in teaching.

Hughes: How do you feel about that change in the policy?

Johnston: It's all right. If a professor was not in charge of one of the sections, a graduate student would be. I found the older I got, the more the students wanted to ignore me and learn from the graduate students, who are close to their age. And that's fine. They don't want to be told by their grandfather what to do. The teaching assistants are required to go to the lectures, and the professors who give the lab sections are supposed to go to lectures too. We fill out a bio-bibliographical report each year telling what courses we taught, what new courses taught, how many units we taught during the year, and so forth. Then also, the students write evaluations.

Hughes: Do you like teaching?

Johnston: Yes. I say that with a slightly restrained tone of voice.

Hughes: What is your restraint?

Johnston: Well, it's a lot of work. I and a lot of the professors at the beginning of a course throw away all the notes we've previously taken. We prepare lectures again, and try to make it clear and up to date.

Hughes: Is some of your restraint perhaps because if you had your strictly personal wishes to pay attention to, you would have been doing research?

Johnston: Well, when the load gets heavy, then I'd like to shift a little of the load. Of course, as a professor gets older, the responsibility to support past postdocs and graduate students adds to the workload. Every time they move, they need another letter of recommendation. Refereeing of papers takes a lot of work. There is a heavy workload in this profession.

I think in the department here we have not squeezed teaching to a place where it's really detrimental. We have some members of the department who are excellent speakers, very good on their feet, very good in their delivery. Many of them rotate teaching freshman chemistry.

Hughes: Does the College of Chemistry have a reputation for strength in teaching?

Johnston: Yes. I think that's been a plus with the administration for a long time.

Hughes: In your book, *Gas Phase Reaction Rate Theory*, you said that in your chemical kinetics class at Berkeley you offered each student an A regardless of exam grades if he or she wrote a publishable term paper.

Johnston: Yes. Well, the course I taught most often was physical chemistry. If students were interested in doing so, undergraduates could come into the my laboratory. Especially in the summer, or sometimes even while they were carrying a full course load, they'd come in the laboratory and contribute to a publishable paper. I didn't expect them to have the original idea and carry it all out themselves and write all the paper. But if they contributed significantly to a publishable paper, sure, they'd get an A.

The apparatus required in physical chemistry in recent decades has become so complicated, so elaborate, that undergraduates, even graduate students, take a long time to learn how to work the instruments and learn what they do. Some of the students who had what I regarded as a publishable paper but the research was never published would get the A anyhow.

Hughes: You were dean of the College of Chemistry.

Johnston: Yes, 1966 to 1970.

Hughes: How did you come to be dean?

Johnston: Well, there had been a very outstanding succession of deans. G. N. Lewis, Wendell Latimer, Ken Pitzer, and Robert Connick were deans. When Connick decided to finish being dean, there were several stellar professors who might have been chosen. Joel Hildebrand suggested it ought to be somebody who was a member of the National Academy of Sciences. That did limit the field somewhat. While Connick was dean, I was faculty representative to the architectural committee that designed Hildebrand Hall. I contributed input supporting the professors' needs for research, and teaching. The architects contributed the artistic point of view, and the university engineers insisted on the safety standards, including earthquakes. I spent a lot of time on that committee, and I guess Connick, who was dean, thought I did a good job. They had a search committee, not a wide search, because they wanted somebody local. Anyhow, I was invited by the chancellor to do it, and then I did it.

Hughes: Did you have any reluctance?

Johnston: Yes. [laughs] I knew it would mean giving up a large amount of time. But I was getting reassured, "You can have at least half time for research."

Hughes: Did it turn out that way

Johnston: It didn't turn out that way. [laughs] The load is very heavy.

At that time, we were having what we came to suspect—and I'm not going to say it happened—as being financial impropriety inside the business part of the department. I asked them to send me reports, and the reports came in, and I couldn't understand the legalese and accounting language. Anyhow, when I first started an investigation, somebody high in the group that I was investigating quit and took a job somewhere else. So we couldn't follow through. We didn't want to, because we didn't have the evidence. There were irregularities in the handling of grants to be suspicious about.

I did accomplish one thing. G.N. Lewis thought that every professor should do his own experimental and theoretical research. Some physical chemists were opposed to our appointing professors who did only theory. In other universities there was exciting work being done by theoretical chemists. Bruce Mahan was the chair of the chemistry department, and he agreed with me that we should bring in strong young theorists as assistant professors. Over the objections of some of our great experimental/theoretical physical chemists, we brought in young theorists, and now Berkeley has great success and strength in this field.

Hughes: Were there other notable events of those four years?

Johnston: Yes, how about the Free Speech Movement. I was there from 1966 through 1970. Do you like that one?

Hughes: Yes, that's a good one. Say something about how that affected your deanship.

Johnston: I was really pulled in different directions by influential and conservative old graduates, fund-givers, and the students. The students were always a little bit ahead of me in terms of what to expect. That certainly added to the work and added to anxiety.

Hughes: How active were the chemistry students in the Free Speech Movement?

Johnston: Really on the low side.

Hughes: How do you explain that?

Johnston: They had a good deal. [laughs] Especially the graduate students. They had total support, if they were on grants and contracts. The undergraduates did not have a better deal than everybody else in the university.

Hughes: You're talking financially?

Johnston: Financially and educationally. Students get an education that counts, if they do well. In general, chemists tend to be conservative.

Hughes: So what as dean did you have to handle?

Johnston: When a group would break into a classroom and want a teach-in, we had to have restrictions on that, control of that.

Hughes: Did that happen quite a bit?

- Johnston: Yes. We brought it under control. But when there are great big military helicopters flying overhead spewing tear gas on the campus, that's a difficult environment to live under. So I was very glad to get out of that.
- Hughes: Is four years a normal stint as dean?
- Johnston: It's usually longer than that.
- Hughes: How did you escape?
- Johnston: I wrote the chancellor and said, "I've had enough." [laughs] Well, five years I guess is a normal stint, and then a dean gets an appraisal, and maybe another five years.
- Hughes: How do you judge yourself as an administrator?
- Johnston: Very poor. [laughter]
- Hughes: I gather that you don't particularly like it.
- Johnston: I didn't.
- Hughes: What did happen to your research?
- Johnston: The forefront of my field of research was moving along so fast in those days that being out of it for four years, I never did catch up. And the atmospheric work came along, and I had a lot of, shall I say, vigor left over to apply to that once I got into it. For a long time, I was on the leading edge of atmospheric chemistry research. Now, there's so much good work going on that I can't even keep up with that any more.
- Hughes: Had you realized when you accepted the deanship that it would close the basic science part of your career?
- Johnston: No. I wasn't exactly promised, but I was assured I would have half time to keep up with research. I could maintain graduate students. But the dean job was eighteen hours a day. Toward the end, there was probably one thing in my mind, that I was slipping very far behind. Things were moving along so fast, kept accelerating, that I never really caught up. I think during recent years, I've done some good chemical research, but it was nearly always, not always, in support of atmospheric problems. We've studied the pure chemistry of substances which are important in the atmosphere. That's the way we often word contracts and applications.
- Hughes: Do you want to say a little more about your experiences at Caltech after the end of the war?
- Johnston: I think I mentioned the Athenaeum at Caltech, the big fancy building where graduate students intermingled with faculty and postdocs. I would go there fairly frequently, especially when I had a salary from the war research. In 1946, Gardiner Swain, who had just received his Ph.D. from Harvard, came out for a year's sabbatical to work with Pauling, and he brought his wife, Marguerite Stay Swain, along, and I liked them both quite well. We would have dinner together on fairly frequent occasions during the year.

Then in the summer after Gardiner returned to Boston to be a professor at MIT, Marguerite stayed behind to complete some work she was doing at Caltech. Marguerite said that her two sisters and her mother were coming out on vacation; they'd be here two weeks. Would I help entertain them?

Well, I did, and I eventually married one of them, Mary Ella Stay. [laughs] We don't need to go through all the steps in between.

From 1947 to 1956 I was instructor, assistant professor, and associate professor at Stanford University. When we were at Stanford [1948-1956], we built a nice house in what turned out to be a posh real estate development. It was on the top of a hill where we had a beautiful view across the bay to Mount Diablo. Of course, we had to sell that house when I left Stanford. We made some money on selling our house there. When we got to Berkeley, we found that anything comparable was far beyond our financial reach. We bought a quite satisfactory house in Kensington with a broad view of the bay. A fellow professor at Berkeley, Isodore Perlman, and I went in together and bought a 360-acre hunk of hill land in Sonoma County, sixty-five miles north of Berkeley. The Johnstons and the Perlman divided the land, sold some of it to a wealthy neighbor by the river, and we now have a house and 155 acres of land (half of it is wooded) and 400 feet of frontage on the Russian River. We rent the pasture to cattle grazing and named the property "h-bar." We designed and had made an official branding iron designed to print out h-bar in proper scientific form, but we never used it on cattle. While the children were growing up, they and Mary Ella spent the summers on the property, and I came up for weekends. During the school year, the family spent every other weekend there, until the children grew up and moved away.

Shirley, our first daughter, had very fond recollections of the Sonoma County property, and she lived there alone for ten years, during which she wrote a book. The book had some brilliant politics and beautiful language, but it didn't get published. It was too sophisticated for her targeted audience, science fiction readers. She married Brent Anderson, who is a high-ranking comic-book artist. They have one child, a boy, Bryce. They bought a house in Windsor, California, which is fifteen minutes away from h-bar. Brent has been the artist for a series of Superman-type books, and he's well known in his profession.

Linda Marie Johnston, our second child, got her bachelor's degree at Davis, California, and went to medical school at Emory University.

Tape 17, side B

Johnston: She did her residency at Indiana Medical School.

Hughes: What is her specialty?

Johnston: Pediatrics. She went to medical school there, and came to like a fellow student, Warren Bannister, who was working to be a pathologist, so they're married. For a long time, there were two doctors' incomes in the family. They bought 160 acres of prime land in Shenandoah Valley, Virginia. It is beautiful land, gently rolling, and mountains to be seen on both sides. They raise llamas, a few cattle, and rent out some of the land for the cattle. They bought an ancient house and ancient barn. The house and barn were not

burned down in the Civil War. The Civil War was active in the Shenandoah Valley. The armies surged back and forth over the valley. The Bannisters have four children (Sara, Laura, Joseph, and Aaron), so Linda has taken a leave of absence from being a doctor.

Our third child, David Finley Johnston, our only son, got his bachelor's degree in physics at Berkeley, and went to MIT and got a Ph.D. in physics. He developed a large number of good friends in the area. He was active in folk-dancing clubs, and he became a member of a skilled dance group, Mandela. David bought a small house within walking distance of Central Square. He and Dana Sussman married and moved to Arlington, Massachusetts. They have one child, Miranda Johnston.

Our youngest daughter, Barbara Dial Schubert, born 1969, got her bachelor's degree at the University of California at Davis with a major in philosophy. She went into the graduate program in philosophy at the University of California at Riverside and obtained a master's degree. She and Louis (Lou) Schubert married. After they were married, Barbara hasn't tried to work in philosophy, but has worked on painting, publishing one small book of paintings and has sold several of her paintings. They have two children, Liberty Noel [and added in proof, Manuelle Rose Schubert]. The family lives in Berkeley, California. Lou got a Ph.D. in political science from the University of Southern California, and teaches political science at the College of San Francisco.

Now we have four children and eight grandchildren. We still go about once or twice a month up to our place in the country. We built a house up there in 1966. It's no mansion, but it's a fairly good house, utilitarian and comfortable. We have a gorgeous view of Mount St. Helena framed by trees.

Hughes: Do you care to say something about your wife?

Johnston: Yes. She got her bachelor's degree at Mount Holyoke College. They didn't have a major in biochemistry in those days; she had to take courses in biology and courses in chemistry. She had a research position at Rochester University and was considering going to graduate school. We did a lot of correspondence with each other. I went back there once before we got married. She would be very happy, she said, to drop getting an M.S. in favor of getting an MRS. Between working at h-bar and taking care of four children, she's had a full-time job. I think the children are better off for it. She followed my mother and started reading to the children at six or eight weeks. She is a very vivacious and attractive. Her hair goes down to her knees, and she puts up in a braid that goes around her head. She gets along with people very well. Because of her hairdo and her personality, she's remembered by lots of people.

Hughes: Because of her background in biochemistry, has she been able to understand what you're doing in a way that other people might not?

Johnston: She's been understanding and helpful. When I was dean, she had to take over the social functions of the College of Chemistry. We had to plan a big dinner for all the faculty once a year, and the wives had regular coffees once a month. She got along with the deanship much better than I did. Her work was appreciated, and she worked very hard. Now she's a docent at the Oakland Museum. I could say a lot more about her.

- Hughes: Oh, I know you could, but unfortunately we're about out of time, and I want to ask you two questions. Chemistry is a potentially more applied science than some. It seems to me that your career has been a combination of both basic and a later phase that was more applied. Do you value one aspect of your career more than the other?
- Johnston: Well, one phase supports the other. My research in basic chemistry was the foundation for the applied work I did in atmospheric chemistry. Chemistry is more applied than some other sciences, but it has its own boundaries and its own pure research. Chemists trained at Berkeley are in high demand for a variety of industry and academic positions. If somebody had applied to this department for a professorship in atmospheric chemistry in 1971, I don't think he or she would have gotten in, because the department emphasized basic science.
- Hughes: That tradition goes back to G. N. Lewis, doesn't it?
- Johnston: Yes.
- Hughes: Is chemistry at Berkeley looked upon as being on the more basic side than on the applied?
- Johnston: I think those who know Berkeley well would have that attitude, but many professors have high achievements in both basic and applied work.
- Hughes: I was just trying to place Berkeley in the spectrum of basic science versus applied science.
- Johnston: Well, applied chemistry is chemical engineering. Atmospheric chemistry has aroused interest in recent years. I had trouble getting graduate students in atmospheric chemistry at one stage. They wanted to do pure science. But now the department has made one and a half faculty appointments at the assistant professor level in atmospheric chemistry. The half position is a split appointment with geophysics.
- Hughes: They are the first to be appointed in atmospheric chemistry at Berkeley?
- Johnston: Yes.
- Hughes: Is that a statement about the status of atmospheric chemistry, or could it also be a statement about Berkeley being more accepting of applied aspects of chemistry?
- Johnston: Well, atmospheric chemistry has improved its chemistry enormously over the past twenty, twenty-five years. It's completely different now. Its methods are the same as the best physical chemistry. Their focused interest makes it applied. Some enormously good work has come out, and with the observed ozone reduction, it's gotten a lot of notice. The quality of the science in atmospheric chemistry has gone up so much in the last generation that it's a different situation with assistant professors now than it would have been then.
- Hughes: So Berkeley couldn't afford to overlook it?
- Johnston: Right.

- Hughes: It's the quality of the science that made the difference, not the fact that it was in the news or applied?
- Johnston: Yes.
- Hughes: It's good science, so Berkeley wants it.
- Johnston: Yes.
- Hughes: Yes, I can imagine. It leads me to ask, because the latter part of your career was spent to a great extent in the public arena and, as we've said, on issues that had a decided political tinge, was that ever a sore subject around the department?
- Johnston: I don't think so. One purpose of tenure is for a professor is to go out on a limb or to be different. I've had very good personal relationships in the department. It has strongly supported me.
- Hughes: Would the department also say that it was an eventual aim to have the basic science applied in society and, if need be, by the very individual who has created the basic science?
- Johnston: Well, I'm not sure that the department ever formulated a policy along this line. It is the practice that each professor is expected to do outstanding work spread among four categories: Teaching, research, university service, and public service. For a professor the mix of work among these four categories may vary over his or her career. It is certainly understood that a professor does not conduct a business using university space or facilities.
- Hughes: So you were not an anomaly in the College of Chemistry.
- Johnston: I think I was not an anomaly in these respects.
- Hughes: I have one last question: what do you consider to be your greatest contribution?
- Johnston: It would be setting in motion the big research projects that have learned so much about stratospheric chemistry. I mentioned earlier that what I wrote in 1971 and what Claire Sterling, a newspaper reporter, said about my August 1971 article caused the Congress to set up the Climatic Impact Assessment Program. CIAP discovered many new things. It shut down on schedule in 1975. The Congress assigned NASA the task of carrying on the atmospheric research of CIAP. NASA established an Upper Atmosphere Research Program [UARP], which was pure research, and they have done spectacular things. I know that people in the Department of Transportation proposed a research program early in 1971, but it was "turned down at higher levels." Crutzen's 1970 and 1971 papers certainly would not have set the big program in motion. Maybe I shouldn't say that. I don't want to compare us. Crutzen is a great scientist. I'm just saying that his work did not have the attention given to it by others that mine did. It was the combination of the my article, and the publicity others gave to it, and Claire Sterling's editorial, that were instrumental in causing these big research programs. Rowland and Molina wouldn't have known about nitrous oxide or much of anything about the stratosphere if it weren't for the Climatic Impact Assessment Program. I told you

before, Rowland heard my lecture three times before his 1974 paper was written. He was a good student! Without CIAP, I believe that the Antarctic ozone hole would have been a total mystery when it happened, if anybody noticed it happening. People certainly wouldn't have blamed it on chlorofluorocarbons. Furthermore, if Rowland hadn't held his hard-hitting press conference in 1974, the public would have ignored his 1974 article.

You asked me for my frank opinion. I don't go around boasting about it, but I think my work was an essential link in initiating the sequence: Climatic Impact Assessment Program, Molina and Rowland's chlorofluorocarbon model, and NASA's Upper Atmosphere Research Program. There must be some places besides with my wife where I can say that to people! [laughter]

Hughes: Well, good. I thank you.

Johnston: You're sure welcome. And I thank you.

[End of session]

Biographical Notes of Harold Johnston[†]

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Born	Woodstock, GA, October 11, 1920
Education	Emory University, Atlanta, GA, 1937–1941, A.B. degree in Chemistry and English Literature California Institute of Technology, 1941–42 and 1945–47, Ph.D. degree in Chemistry and Physics
Employment	Civilian employee of National Defense Research Council at Caltech, 1942–43 Head of Meteorology Department, supporting field work with Chemical Warfare Service, Bushnell, FL, 1944–45 Instructor to Associate Professor of Chemistry, Stanford University (1947–56) Associate Professor, California Institute of Technology (1956–57) Professor of Chemistry at the University of California, Berkeley (1957–1991), Dean of the College Chemistry (1966–1970) Professor Emeritus of Chemistry since 1991
	Experimental research interests have been in the field of gas-phase chemical kinetics and photochemistry, involving oxides of nitrogen, ozone, fluorine, chlorine oxides, HO and HOO free radicals, etc., and in the fields of urban air pollution (1950–70) and stratospheric ozone (1971–). Theoretical research interests are in unimolecular reactions, transition state theory of bimolecular reactions, and kinetic isotope effects.
Memberships	National Academy of Sciences American Academy of Arts and Sciences American Chemical Society American Physical Society American Geophysical Union American Association for the Advancement of Science
Awards	1993 National Academy of Science Award for Chemistry in Service to Society 1985 American Chemical Society Award in the Chemistry of Contemporary Technological Problems 1983 Tyler Prize for Environmental Achievement 1974 Pollution Control Award of the American Chemical Society 1961 Guggenheim Fellowship; Brussels, Belgium 1956 Gold Medal Award of the California Section of the American Chemical Society
Honors	1998 Honorary D.Sc., Northwestern University, Evanston, Illinois 1998 Roger Revelle Medal of the American Geophysical Union 1997 National Medal of Science 1991 Berkeley Citation, University of California 1985 Distinguished Alumni Award, California Institute of Technology 1982 Certificate of Commendation, Federal Aviation Administration 1965 Honorary D.Sc., Emory University, Atlanta, GA
Lectureships	1990 Robert A. Welch Foundation Lectureship 1989 U. C. Berkeley Academic Senate Faculty Research Lecturer 1975 G. N. Lewis Lecture, University of California, Berkeley 1974 Sigma Xi National Lecturer 1973 George B. Kistiakowsky Lecture, Harvard
Scientific Advisory Committees	1961 Bourke Lecturer of the Faraday Society 1995–97 NAS Panel on Atmospheric Effects of Aviation 1988–94 NASA, Science Advisor to High-Speed Civil Transport Studies 1989–92 NAS Committee on Atmospheric Chemistry 1978–82 Federal Aviation Administration's High Altitude Pollution Program 1972–75 NAS, Committee on Ozone and Stratospheric Aviation 1971–75 NAS Committee on Motor Vehicle Emissions 1969–73 California Statewide Air Pollution Research Center 1965–67 NAS Panel to National Bureau of Standards 1963–67 Panel Member of President's Science Advisory Board on Atmospheric Sciences
Consulting	SRI, 1951; M. W. Kellogg company, 1952–53 National Bureau of Standards, summers of 1968 and 1969 Free consulting to small California businesses 1950 to 1996

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

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

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

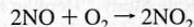
2.1. Fast Reactions Measured in the Laboratory Primarily by Absorption of Ultraviolet and Visible Light. 2.1.1. The "Fast" Reaction of Nitrogen Dioxide and Ozone. This study was based on my Ph.D. thesis at Caltech (1947). The method involved fast flow, fast mixing, and sudden cut off of the cell entrance 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.



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.

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

[‡] Grouped by subject matter and with comments.

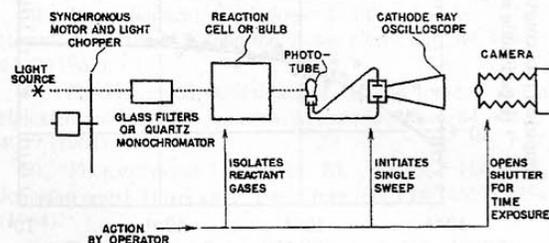


Figure 1. Schematic diagram of optical system for recording rate of fast reaction. Reproduced from ref 1 with permission from American Institute of Physics. Copyright 1949.

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).

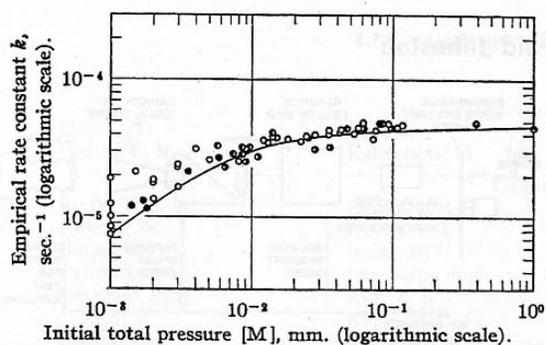


Fig. 6.—Comparison of experimental with computed rate constants; decomposition of pure N_2O_5 , 27° , curve given by Equation 21: \circ , Hodges and Linhorst; \bullet , Linhorst and Hodges; \ominus , Ramsperger and Tolman; \odot , Schumacher and Sprenger; \oplus , Daniels and Johnston; \ominus , Mills and Johnston.

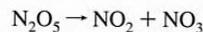
Figure 2. Solution to the problem of the 1930s, in which theory and observations appeared to be highly discordant. Reproduced from ref 3.

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.

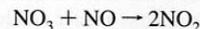
2.3.1. Unimolecular Reaction Rates of N_2O_5 . Using the 1949 fast reaction method at high pressures and two other systems suitable for intermediate and low pressures, Bob Mills and I followed the unimolecular decomposition of N_2O_5 from its first-order high-pressure limit down to its second-order low-pressure 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



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



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 $\text{N}_2\text{O}_5/\text{NO}_3$ 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 Hecklen and Harold S. Johnston, *J. Am. Chem. Soc.*, **84**, 4394–4402 (1962).

48. "Photochemical Oxidations. II. Methyl Iodide." Julian Hecklen and Harold S. Johnston, *J. Am. Chem. Soc.*, **84**, 4030–4039 (1962).

59. "Photochemical Oxidations. III. Acetone." Harold S. Johnston and J. Hecklen, *J. Am. Chem. Soc.*, **86**, 4249–4254 (1964).

60. "Photochemical Oxidations. IV. Acetaldehyde." Harold S. Johnston and J. Hecklen, *J. Am. Chem. Soc.*, **86**, 4254–4258 (1964).

51. "The Photo-oxidation of the Simple Alkyl Iodides." J. Hecklen, 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."

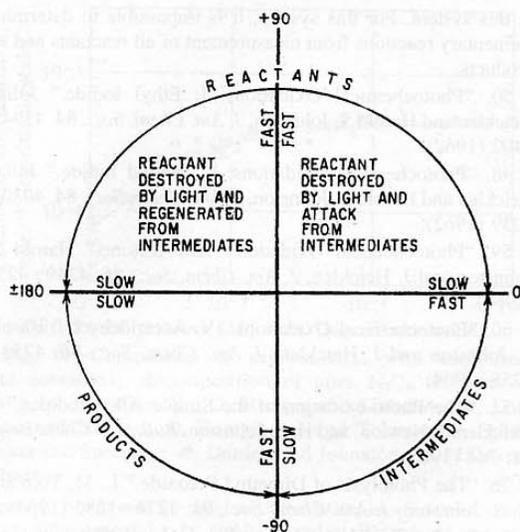


Figure 3. Phase relations between photolysis light, reactants, intermediates, and products in complex photochemical reactions. Courtesy of Harold Johnston.

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 ($2\text{NO}_2 + \text{O}_3 \rightarrow \text{N}_2\text{O}_5 + \text{O}_2$) 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 develop-

ment 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 Nitroxy." 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 $\text{O}_2(^1\Delta_g)$ 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 $k = Ae^{-B/RT}$. 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,

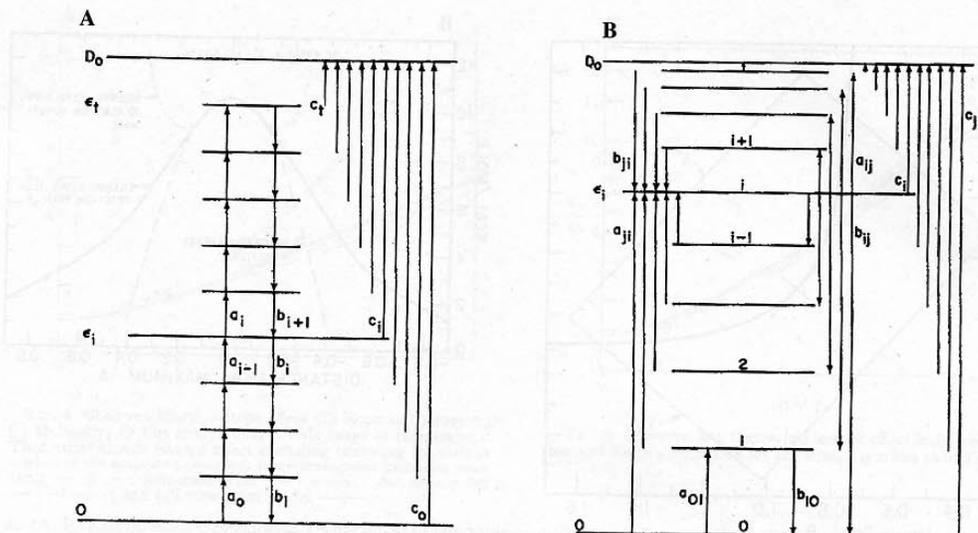


Figure 4. (A) Truncated harmonic oscillator: Only nearest neighbor transitions are considered for energy transfer. All states dissociate to continuum. (B) Morse function. All vibrational transfers allowed. All states dissociate to continuum. Reproduced from ref 86.

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: $E = -R[d \ln k/d(1/T)]$. 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

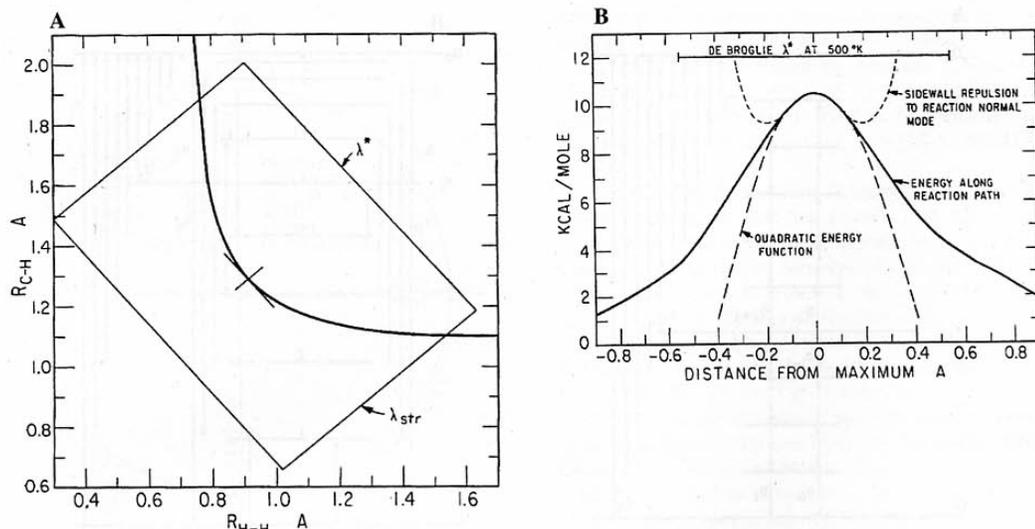
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Figure 5. (A) Different way to look at quantum effects in hydrogen atom transfer reactions, which implies large degrees of two-dimensional quantum mechanical "tunneling". Reaction path for the reaction $\text{H}_3\text{C} + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$. 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 $\text{H}_3\text{C} + \text{H}_2$. 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).

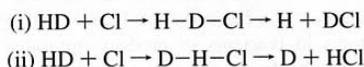
3.4. Quantum Mechanical Calculations. We used computer programs developed by Professors H. F. Schaefer III and W. A. Lester, Jr. to calculate potential energy surfaces for Ne–H–H and the nitrate free radical.

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 : ${}^2\text{A}_2'$, ${}^2\text{E}''$ -(${}^2\text{A}_2$, ${}^2\text{B}_1$), and ${}^2\text{E}'$ 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:



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).

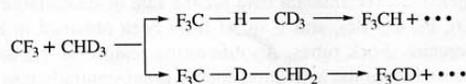
3.5.2. Tunneling Effects. Other Articles Concerning Kinetic Isotopic Effect.

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



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

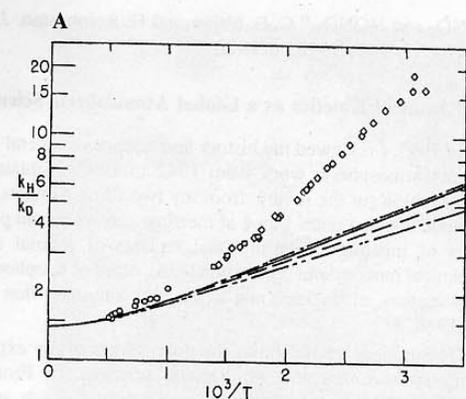


Fig. 4. Observed kinetic isotope effect (O Roux and Johnston; \square McNesby; \diamond this study) over a wide range of temperature. Theoretical kinetic isotope effect excluding tunneling for various models of the activated complex: three-mass-point including reactants —; four-mass-point —; five-mass-point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

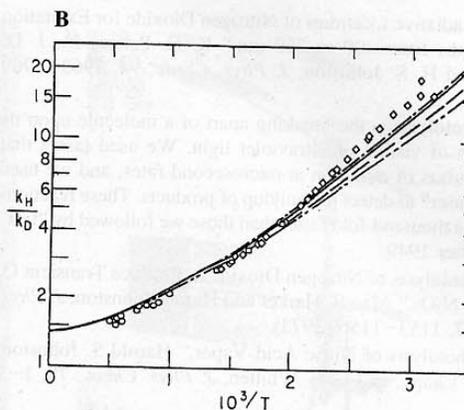


Fig. 6. Observed and theoretical isotope effect including Johnston and Rapp's correction for tunneling (symbols as in Fig. 4).

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).

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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 (1990).

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, NO₃, and N₂O₅." 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 NO₃ and the Kinetics of the N₂O₅-O₃ System." Richard A. Graham and Harold S. Johnston, *J. Phys. Chem.*, **82**, 254–268 (1978).

121. "Photodissociation Quantum Yields for the NO₃ Free Radical." Frank Magnotta and Harold Johnston, *Geophys. Res. Lett.*, **7**, 769–772 (1980).

124. "Kinetics of the Reaction of Cl with ClNO and ClNO₂ and the Photochemistry of ClNO₂." H. H. Nelson and H. S. Johnston, *J. Phys. Chem.*, **85**, 3891–3896 (1981).

132. "NO₃ Quantum Yields from N₂O₅ Photolysis." Diane Swanson, Brian Kan, and Harold S. Johnston, *J. Phys. Chem.*, **88**, 3115–3118 (1984).

155. "Dissociation Energy and Photochemistry of NO₃." H. F. Davis, B. Kim, H. S. Johnston, and Y. T. Lee, *J. Phys. Chem.*, **97**, 2172 (1993).

162. "NO₃ 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 N₂O₅ Photolysis." D. Oh, W. Sisk, A. Young, and H. Johnston, *J. Chem. Phys.*, **85**, 7146–58 (1986).

149. "NO₃ 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 N₂O₄." 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

ClNO₂ and HONO₂." 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.

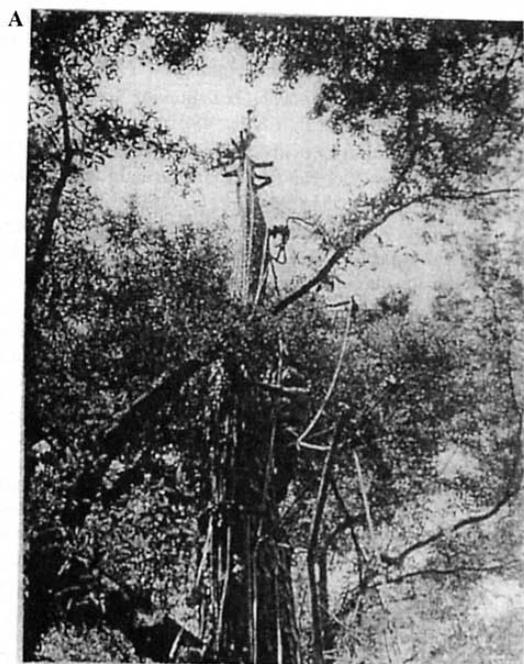
This review article shows the three stages of my experience with meteorology and atmospheric sciences. (i) From 1942 through 1945, I did laboratory research at Caltech and field research with the Dugway Proving Ground Mobile Field Unit of the U.S. Chemical Warfare Service, which involved micrometeorology 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 years 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.



No. 15
Looking up Tree from East Direction

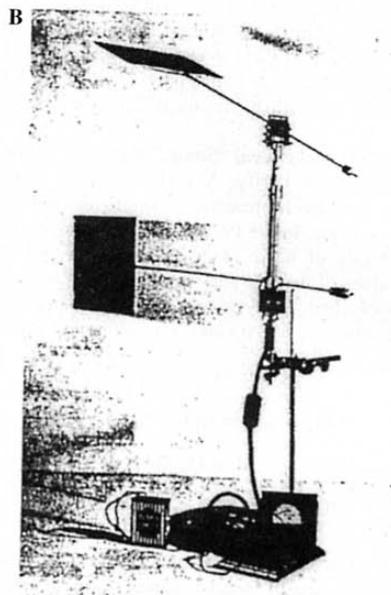


Figure 8
Photograph of Assembled
Vertical Gustiness Meter

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.

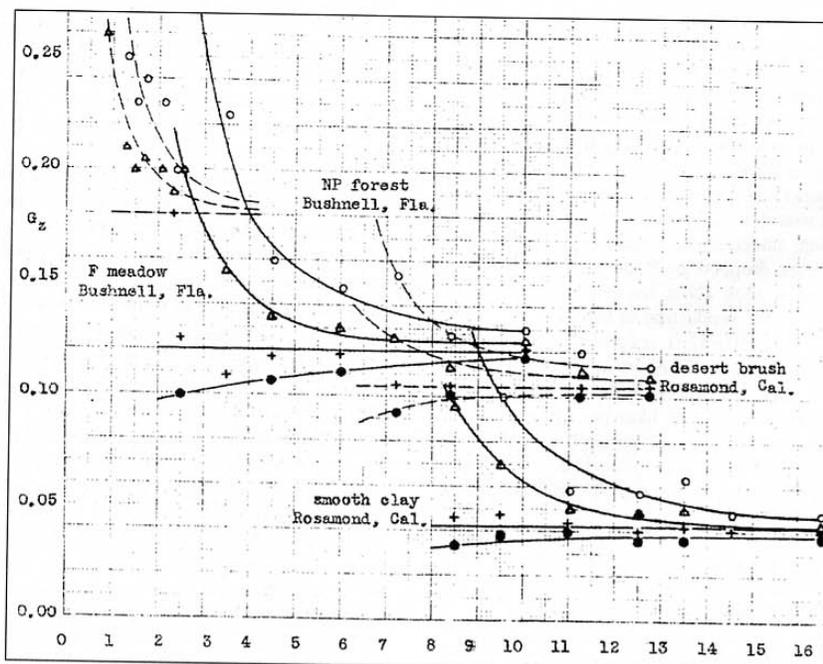


Figure 8. Vertical gustiness (which gives vertical component of turbulent velocity) plotted against wind speed (miles per hour) at 2.0 m above the ground. For each terrain, the temperature K at 2.0 m minus the temperature at 0.3 m was: Filled circle, +0.5; symbol +, 0.0; triangles, -1.0; open circles,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

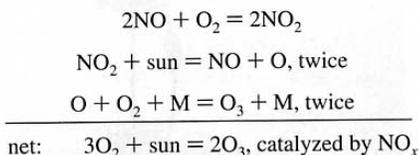
Johnston assisted by Arthur Pardee, Second Lieutenant Alan Englander, Second Lieutenant William Ironside, 1944.

Report #2. "A study of turbulent diffusion of gas clouds over

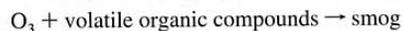
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several terrains," Report OSRD No. 6185, 84 pages, by Harold Johnston, Robert Merrill, and Robert Mills. 1945. (part I) An Empirical Approach to the Effect of Turbulent Diffusion on Gas Clouds over Several Terrains, pp 1-23; (part II) A Critical Examination 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 NO₂, abbreviated NO_x.

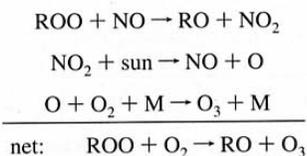


Ozone itself is a toxic lung irritant, it damages materials, especially rubber, and it spoils a number of vegetable crops. Ozone reacts with hydrocarbons and other volatile organic compounds, which come from automobile exhaust, oil refineries, and other industries, to make particles that reduce visibility,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



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 peroxy radicals and thus probably photochemical combustion would do likewise. I proposed that ozone is formed by the reaction of peroxy radicals with oxygen: ROO + O₂ → RO + O₃. Many years later others found that this reaction occurs, not as an elementary reaction but as a three-step sequence:



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).

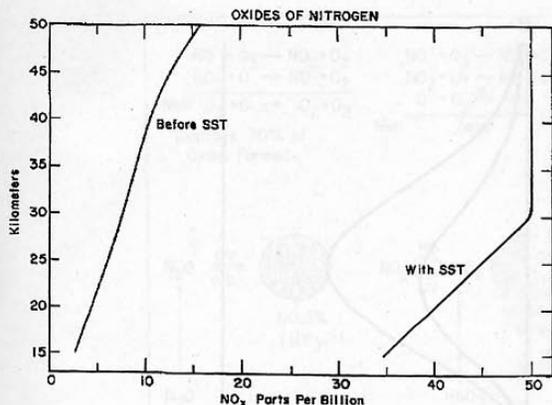


Figure 9. Park and London's assigned vertical distributions of nitrogen oxides in the atmosphere before and after there are 500 SST (U.S. 1971 design) cruising at 20 km altitude. Reproduced from ref 94 with permission from John Wiley & Sons, Inc. Copyright 1974.

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, $2\text{NO} + \text{O}_2 = 2\text{NO}_2$, 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

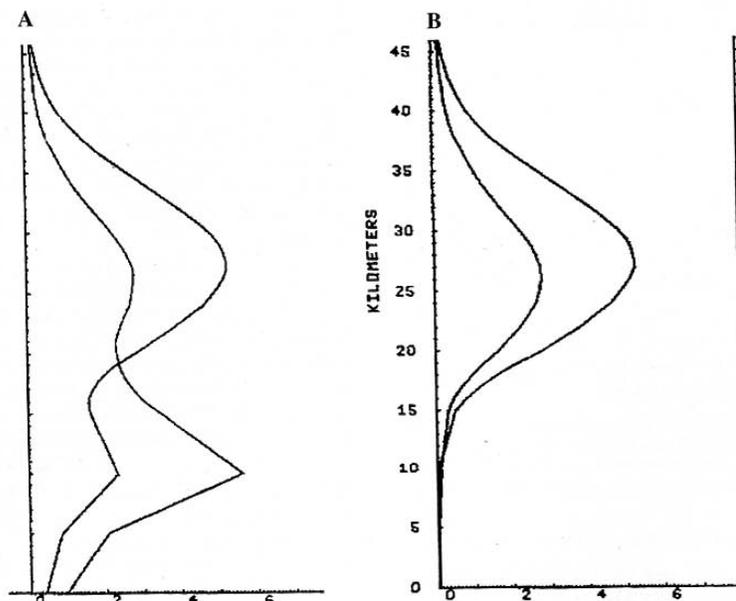


Figure 10. (A) Calculated vertical profiles of ozone based on Park and London's two NO_x profiles including their incorrect value for the rate of the reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$. The calculated ozone reduction was 1.8%. (B) Calculated vertical profiles of ozone based on Park and London's two NO_x profiles including the correct value for the rate of the reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$. The calculated ozone reduction was 40%. Reproduced from ref 94 with permission from John Wiley & Sons, Inc. Copyright 1974.

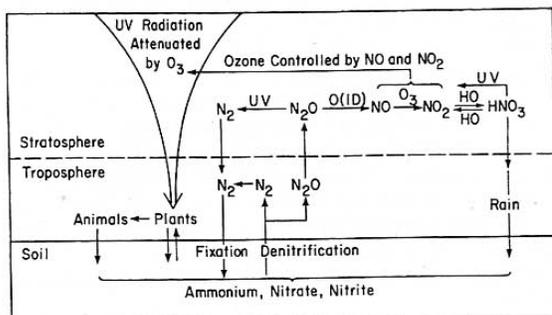


Figure 11. Nitrogen cycle and the newly recognized secondary cycle involving stratospheric NO_x and ozone. Figure 3 of ref 83, courtesy of Harold Johnston.

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, $P_{\text{SEQ}}(\text{O}_3)$, (ii) gross ozone loss, $L_{\text{SEQ}}(\text{O}_3)$, and (iii) net ozone change, $D_{\text{SEQ}}(\text{O}_3)$ 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,

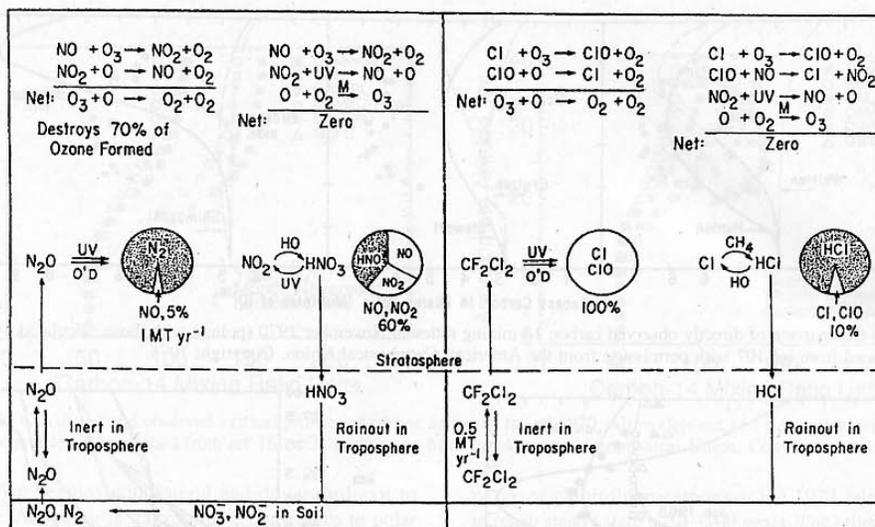


Figure 12. Parallels between the natural nitrogen oxides and the artificial chlorofluorocarbons with respect to stratospheric ozone. Both N₂O and compounds such as CF₂Cl₂ are inert in the troposphere and are broken down to active radicals in the stratosphere; the active radicals engage in catalytic cycles 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).

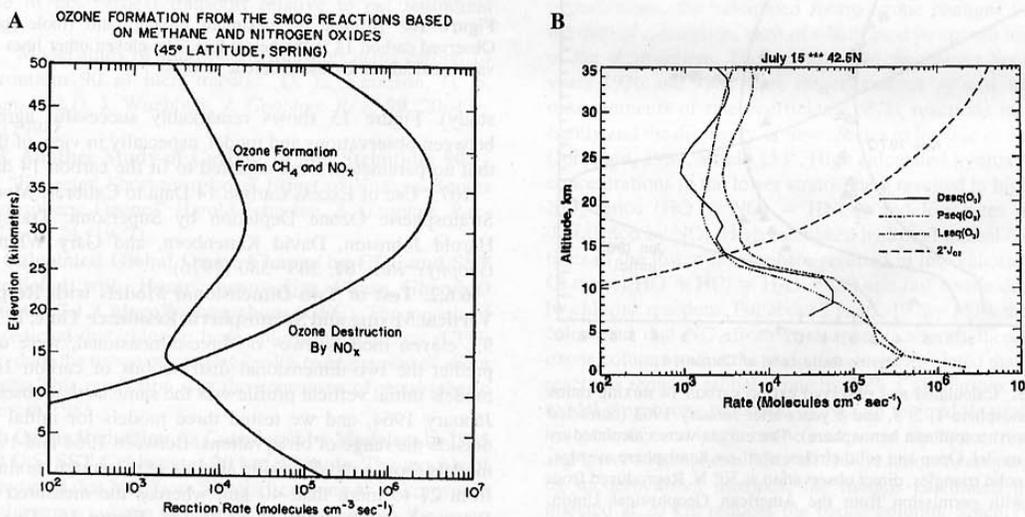


Figure 13. (A) Vertical profiles of the rate of formation of ozone from the methane/NO_x/smog reaction and of rate of ozone destruction from the NO catalytic cycle. Reproduced from ref 105 with permission from Academic Press. Copyright 1975. (B) Calculated vertical profiles by the sequence SEQ method. 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 14 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,

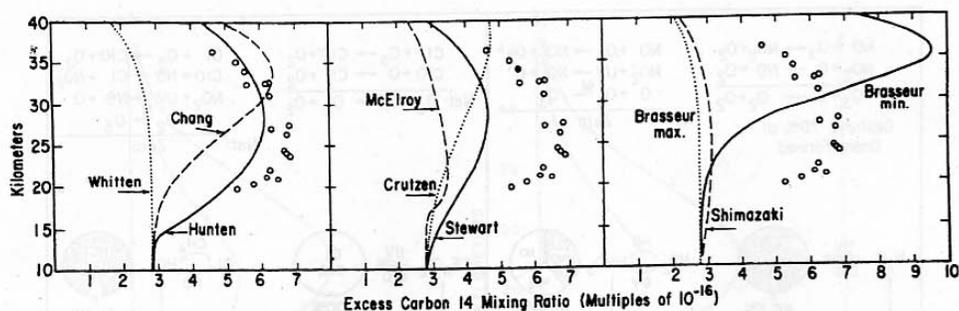


Figure 14. (A–C) Comparison of directly observed carbon 14 mixing ratios in November 1970 (points) with those calculated by nine models of K_z (lines). Reproduced from ref 107 with permission from the American Geophysical Union. Copyright 1976.

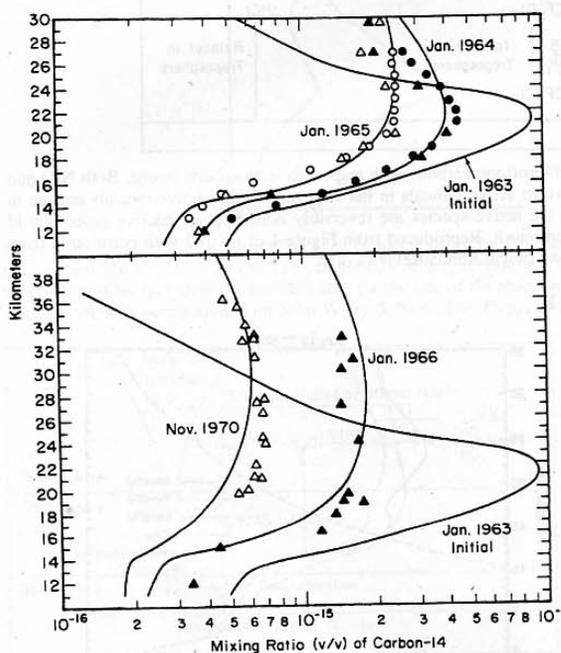


Figure 15. Calculated and observed excess carbon 14 mixing ratios in the stratosphere 1, 2, 3, and 8 years after January 1963 (corrected for transport to southern hemisphere). The curves were calculated by Hunten's model. Open and solid circles, northern hemisphere average; open and solid triangles, 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

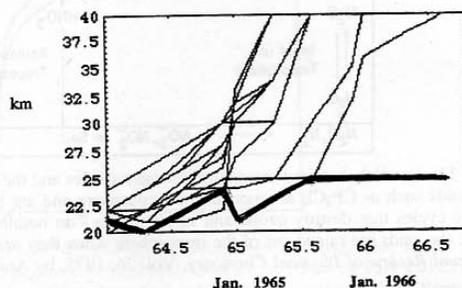


Figure 16. Altitude of maximum mixing ratio (mole fraction). Observed carbon 14 is the heavy line. The eleven other lines are the values calculated by the different models.

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.

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-

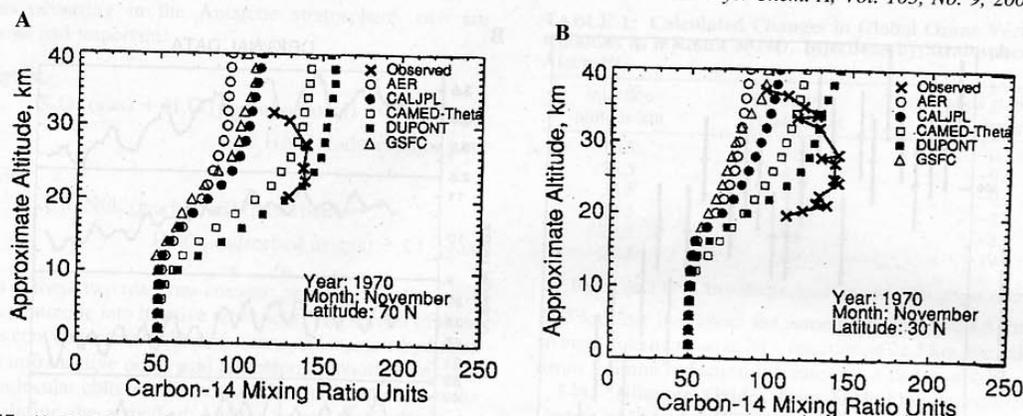


Figure 17. (A, B) Calculated and observed vertical profiles of carbon 14 in the fall of 1970. All models out of 11 disagreed with the shape of the measured vertical profiles. Reproduced from ref 161 with permission from the American Geophysical Union. Copyright 1994.

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 $\text{cm}^{-3} \text{s}^{-1}$ 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^{14} 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 ($\text{HO} + \text{NO}_2 = \text{HNO}_3$) 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 ($\text{HO} + \text{HCl} = \text{H}_2\text{O} + \text{Cl}$) 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

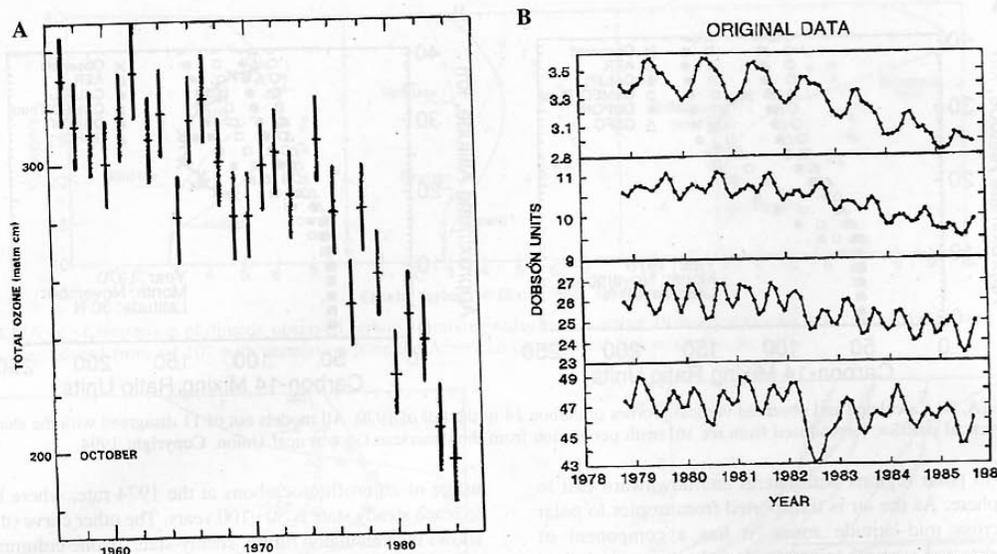


Figure 18. (A) Observed south polar ozone columns during October from 1957 to 1984 from ground based Dobson station. "Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction." Farman, J. C., B. G. Gardiner and J. D. Shanklin, *Nature*, **315**, 201 (1985). Reproduced with permission 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."

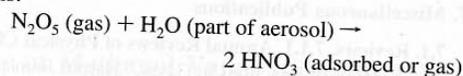
141. "Trends in Ozone Profile Measurements," Chapter 5 of *Report of the International Ozone Trends Panel-1988, Vol. 1* (World Meteorological Organization Global Ozone Research and Monitoring Project, Report No. 18), pp 383-442.

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 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.

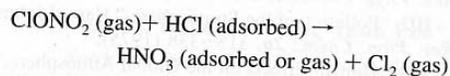
The 1987 expedition, new laboratory results, continued satellite measurements, and model calculations proved that heterogeneous Cl/ClO chemistry, in an unusual environment produced by atmospheric winds and low temperatures, caused the large reductions of Antarctic ozone. The Antarctic clouds consist 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:

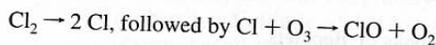
Hydrolysis:



Catalysis:



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,



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 against 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

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.

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.

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 NO₂⁺, HNO₃, and NO₃⁻ 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, N₂O₅(gas) + H₂O (on Aerosol Particles) → 2HNO₃. 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 N₂O₅, 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 N₂O₅ 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 N₂O₅ reactions on sulfuric acid surfaces. I have saved relevant correspondence in which I recommended to CIAP that they should study the heterogeneous reaction of N₂O₅ plus H₂O to form 2HNO₃. 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.

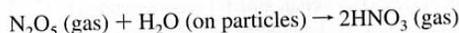
When laboratory chemists restudied this problem almost 15 years later, they found the reaction of N_2O_5 with sulfuric acid aerosols would occur at a rate 10 000 times faster than that reported by the hurried study in 1974. At this fast rate the reaction plays an extremely important role in the global 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:



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 $\text{E}(\text{NO}_2)$ 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 1991, 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. 1, 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. 1 (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 $\text{NO}_3\text{-CH}_2\text{O}$ 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 $\text{N}_2\text{O}_5 = \text{NO}_3 + \text{NO}_2$," 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 $\text{CH}_2(^3\text{B}_1)$ 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).

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