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# RESEARCH IN RETROSPECT: Some Biogracffiti of a Journeyman Chemist

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## ABSTRACT

Small effusive leaks in vacuum systems, as in Knudsen cells and classical molecular beam machines, are responsible for many contributions to science in the twentieth century. Beginning in the 1950s, big convective leaks have turned out to be even more powerful and versatile investigative tools. Forming supersonic free jets, they have greatly expanded molecular beam methods, become the cornerstone of cluster science and technology, rewritten the book on molecular spectroscopy, and are adding new dimension to mass spectrometry. This account is the story of one man's experiences as a bystander and participant in these developments.

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## *School—From Grade Through Graduate*

Two degrees in chemistry and over half a century of membership in the American Chemical Society would seem to classify me as a chemist. However, my first faculty appointment in 1959 at Princeton, after two decades in industry and administration, was in mechanical engineering. The next, in 1967 at Yale, was in engineering and applied science, nominally as a chemical engineer. Not until 1993, when I came to Virginia Commonwealth University after being retired from Yale, could I call a Chemistry Department home. To tell the whole truth, I must admit to a joint appointment in the Chemistry Department while I was at Yale. That courtesy was welcome, but I'm afraid, did little to change my image or to enhance tunneling through the barrier to interaction posed by half a mile of real estate. (Indeed, I have found that the distance between adjacent floors in the same building can inhibit interaction.) In light of this background,

it is probably not surprising that most of my chemist friends seem to consider me an engineer, while my engineering colleagues regard me as a chemist. Nor has such ambiguity in identity been without its benefits. Soon after my return to the groves of academe, after a dozen years in industry, I began to realize that muttering about Mach numbers to chemists and molecular orbitals to engineers lent me an aura of expertise in both camps, as undeserved as it was gratifying. The Good Book says, "A prophet is not without honor, save in his own country!" I say "Amen!" Labels aside, when I look at my résumé I am persuaded that its structure is more the result of a random walk along the paths of opportunity than of any purposeful pursuit of prowess in a particular profession. I hasten to add that whatever may have guided my meandering, the rewards have been as many as the regrets few. Here and now, in Rabbi Ben Ezra's "last of life for which the first was made," I fan the embers of fading memories in an attempt to understand how and why such meandering has been so fruitful.

One ember still glowing in the ashes of those memories is the day in ninth-grade algebra when my first-semester exam paper came back with this message in red ink: "Don't ever try to be a scientist or engineer!" Although I have ignored that well-meant advice, it actually was right on target. My lack of fluency in mathematical language has been a lifelong impediment. That literally red-letter day was in 1929, a year after we moved to Berea, KY from Hackensack, NJ, where we had been living since I was born, "we" being my father, mother, and brother, Norman, who was my junior by what then seemed much more than the three and a half years that separated our birth dates! Dad, with a degree in electrical engineering from Rutgers, had been superintendent of the Metacloth Company, a small enterprise in Lodi, NJ whose main product was cotton duck treated by immersion first in a concentrated ammoniacal solution of copper hydroxide and then in acid. The so-called cuprammonium solution dissolved some of the cellulose that reprecipitated in the acid bath to fill the pores of the cloth. Residual copper provided a characteristic blue-green color along with a high resistance to attack by microorganisms and white ants. Consequently, "Metacloth" was in fairly steady demand for tents and tarpaulins in tropical latitudes.

The Metacloth Company was sold in 1926, and Dad was unceremoniously dumped by the new owners. Meanwhile, approaching 50 and finding equivalent jobs scarce, he was paying the bills by working as a temporary draftsman at the Fokker Aircraft company in Teterboro, NJ. The value of having a trade as back-up for a profession was an enduring object lesson for a youngster on the eve of the Great Depression, but a then more exciting fall-out of the Fokker

connection was his chance to sit in the cockpit and pretend to fly the Spirit of St. Louis when it was parked for a time in a hangar at Teterboro after Lindbergh flew it to Paris! Meanwhile the family fortune seemed to continue downhill, much further than my brother and I were aware. Just before Dad lost his job, he and Mother had invested their life savings in a new (for us) house that everyone insisted was worth “every nickel” of the \$15,000 that it cost, but in the post-1929 depression, all their nickels were lost.

My mother firmly believed that a door never closed but what another one opened. The door that opened for the Fenns was at Berea, KY, a small community of 3500 permanent residents in the foothills of the Cumberland Mountains at the edge of bluegrass country, roughly halfway between Cincinnati, OH and Knoxville, TN. The town was home for a remarkable institution known by the same name but officially entitled Berea College and Allied Schools. It comprised a student body of about 1700, divided among four schools: (a) The Foundation-Junior High school, with an ungraded program through which students with as little as two years of formal schooling could progress at their own rate up through the equivalent of eighth grade, finishing with a standard and accredited ninth grade curriculum; (b) The Academy, which provided an accredited curriculum for grades ten through twelve; (c) the Normal School, with a two-year program leading to a Teaching Certificate; and (d) The College, which offered accredited programs leading to bachelor of arts degrees in the liberal arts and sciences as well as bachelor of science degrees in Home Economics and Agriculture. Dad’s new position was teaching Auto Mechanics and Practical Electricity in the Industrial Arts Department of the Foundation School and Academy. We moved to Kentucky in time for me to enter the eighth grade in the “Training School” of Berea’s Normal School in the fall of 1928. The next fall I entered ninth grade in the Foundation School, where I had the sobering encounter with algebra that started this story.

In later years Dad and Mother both said time and again that losing his good job in New Jersey was the greatest blessing that we could have received. To this day my brother and I share those sentiments and count ourselves especially privileged to have been reared in what was a truly remarkable community. Its soul was its President, William J. Hutchins, father of Robert Maynard Hutchins, the “boy wonder” of the American education scene who became Secretary of Yale at the age of 24, Dean of its Law School at 26, and President of the University of Chicago at 30. “William J”, as the father was fondly known at his own institution, was truly one of nature’s noblemen. A striking man of vision and patrician to the core, his Berea was a singular stage on which the play was always provocative and the message meaningful. Name an outstanding man or

woman of letters, the arts, science, or religion of those days and the odds were high that he or she came to Berea and talked at one of the thrice weekly united chapels for students from all schools. Attendance was required of all, and resented by most, but at my fiftieth reunion, there was a remarkable consensus among my surviving classmates that the community experience of those united chapel services was by far the most memorable and valuable component of their education. Alas, that tradition has long since disappeared, one more victim of “students’ rights” and television.

I redeemed myself somewhat in ninth-grade algebra with a final grade of B in the second semester. Furthermore, I managed to make straight A’s in the Academy math courses that followed: Plane Geometry, Advanced Algebra, and finally Solid Geometry and Trigonometry. Chemistry was the only formal science course that I took in the Academy, and its most memorable lesson had more to do with probabilities than chemistry. I learned the hard way that it doesn’t pay to guess on a true-false test that is scored by subtracting the number of wrong answers from the number of right ones. The first major exam included fifty true-false questions on which my score was seven as I remember, even though I thought I was well prepared. What I hadn’t appreciated was the teacher’s reasonable argument that a wrong answer was a guess and that the odds were that there were as many right guesses as wrong ones. Therefore the true measure of one’s knowledge was the difference between the two! In many years of teaching thermodynamics I have used well-worded true-false statements as a very revealing probe of a student’s understanding of the subject, but I always explain the dangers of guessing.

When I entered College with the class of 1938, I had decided to major in Chemistry, but I’m not sure why. Certainly, none of my class work had tilted me in that direction. Nor did a “Chemcraft” chemistry set for my tenth Christmas promote much of a reaction on my part because none of the experiments seemed very interesting. Perhaps the main reason for that choice was my respect and affection for Julian Capps, Professor of Chemistry. He and his charming wife Hilda, along with our next door neighbors, George and Elinor Bent, were my parents’ closest friends. I got to know Julian very well. He was a great raconteur (as well as a great trencherman), who could recite Milton and Shakespeare. He had a rare sense of humor and an amazing storehouse of knowledge of all kinds, from natural history to soap-making. Any doubts I might have had were swept away in his freshman chemistry course. He was a magnificent teacher, who made his subject live, in part because he had worked in industry and could relate the classroom to the real world of both commerce and everyday life much more convincingly than did any textbook. I really looked forward to going to class, a sentiment that is rare among today’s first-year chemistry students.

As now taught in too many universities, introductory chemistry courses are crucibles in which interest in the subject is cremated rather than ignited. Later, when growing appreciation of life in academe made me think seriously about becoming a teacher, Julian Capps was my role model.

Not all my experiences in chemistry were unqualified delights. Quantitative Analysis in my second year gave me fits. I had to do gravimetric phosphate determinations on three samples of each of eleven unknowns before I managed to obtain one set of acceptable results. However, I had done well enough in first-year chemistry to qualify as a teaching assistant, a highly desirable student labor post that commanded top pay—18 cents per hour! A seeming pittance, except that meals were 11 cents each and to live in a dormitory cost 65 cents per week!

During my sophomore year, an experiment in another kind of chemistry turned out to have a big effect on my chemical education. I fell in love with a girl in the junior class. Determined to catch up with her and graduate at the same time, I went to summer school in 1936 at the University of Iowa because it had a 10-week session that allowed me to earn 12 semester hours of credit in organic chemistry under “Uncle Charlie” Raiford and in inorganic chemistry under Professors Jacob Cornog and Perry Bond. All in all it was a grueling “vacation.” The romance that had blossomed in the spring and sent me off to summer school, withered the following fall. However, because I would be within two courses of finishing my degree requirements by the end of that year, my third in college, I managed to get classified as a Senior and became a provisional member of the Class of 1937 at the June commencement, the objective inspired by a young man’s fancy of the previous spring. Because job prospects were dim for fresh college graduates, I was beginning to think seriously about graduate study in chemistry.

My courses in chemistry thus far had required only some facility in simple algebra. Straight A’s in all of Prof. Peck’s courses in the Academy had excused me from freshman math, all that was then required for a chemistry major. Fortunately for my future, our next door neighbor, George Bent, was visited by his brother Henry, then on the chemistry faculty at Harvard. From there he went to the University of Missouri, where he ended up as Dean of the Graduate School. His son, Henry Jr. wrote a well-known book entitled *Entropy*. When Henry Sr. discovered that I was thinking about graduate school in chemistry and had no college math, he was aghast and spent a couple of hours impressing me with the importance of mathematics in chemistry. As a result I spent much of my third and last year of college immersed in that subject. Fortune had tossed me another favor in the form of Berea’s new curriculum, based on four 9-week quarters instead of two 18-week semesters. Thus, a standard “three-

hour” course met six hours a week for 9 weeks instead of three hours a week for 18, an arrangement that I heartily endorse, in part because a student takes only three courses at any one time instead of five. The particular advantage for me was that both Course B and its prerequisite Course A could be completed in two 9-week quarters instead of two 18-week semesters. Thus, in my senior year I was able to take Analytic Geometry, Differential Calculus, Integral Calculus, and Complex Variables, all in that same year! It was pretty heavy going, but it enabled me to survive in graduate school with the help of one more remedial undergraduate course in Advanced Calculus. The record seems to say that I have also survived after graduate school, but a lack of mathematical skills has been a substantial handicap throughout my career. The implications of both the remarks in red ink on my algebra exam and the advice of Henry Bent were both right on target.

During that hectic last year, I applied to several schools for graduate study in chemistry. Yale and Northwestern responded with teaching assistantships that would meet most of my expenses. I first leaned toward Northwestern but for reasons I don't have space to enlarge on, I finally chose Yale, a decision that delayed by 45 years my meeting Malcolm Dole, then a young professor of Chemistry at Northwestern whose later experiments on electrospray ionization changed the course of my scientific life. Meanwhile, I still had to complete my degree requirements by spending the summer at Purdue University, where I took physical chemistry with lectures by Roy Newton and laboratory under Hershel Hunt, as well as a course in chemical microscopy under Ed F. Degering. Those courses broadened my chemical horizons, but in some ways the following few weeks were more educational. A donor had given a new arc welding machine to the auto mechanics shop at Berea. Included was a four-week course in welding at the Lincoln Electric Company in Cleveland. Nobody else wanted the course, so I went, spurred on by the stories of jobs for welders on pipeline projects at \$18 an hour and the memories of how my Dad had kept us alive by his abilities as a draftsman. After six hours of welding daily for four weeks, I was certificated as a master welder and could deposit a pretty good bead, even on vertical and overhead welds. I was on the afternoon shift, so I attended an evening course on Welding Engineering, very well taught by the company's chief engineer and very educational.

### *After College*

At Yale I found myself in a new and different world. I had done time in two much larger universities and one much smaller college, but I was completely unprepared for, and awed by, the splendor of Yale's buildings. Their architecture had been disdainfully dubbed “Fifth Avenue Gothic” by the self-styled experts who sneered at such expensive imitation of the old world. But a wide-eyed small

town youth from Kentucky found it all fascinating and loved to wander around and through all the gardens, gargoyles, and gates. I had a room in the Hall of Graduate Studies from which I could look out on the forest of chimneys, slate roofs, and Gothic towers that looked like a Hollywood version of a medieval city. I ate in an elegant dining hall, complete with menus and waiters, twenty one meals per week for a now incredible eight dollars. Even so, to save money I took advantage of an option in the board contract and religiously fasted for three consecutive meals every week to save \$1.15! My assistantship paid a total of \$850 for nine months, of which \$350 went for tuition and fees. By such frugalities as the weekly "fast," I was able to make that \$500 cover all my out of pocket expenses in New Haven.

On the appointed day in September, the six new graduate students in physical chemistry met in Sterling Chemistry Laboratory with Professor Herbert Harned, the local patriarch in that subject, whose faculty included Lars Onsager, Benton B. Owen, Rodney Smith, George Murphy, John Vance, and Gosta "Gus" Ak-erlof. With little or no ceremony, no introductions, and no opportunity to ask questions or indicate preferences, we were assigned to our advisors. I recall "Herbie" as he was known but not addressed, saying to me, "Fenn, you might as well go with Gus." Thus, began what blossomed into a close friendship that lasted until the day Gus died, many years later, in Princeton.

The Yale curriculum for chemistry graduate students in those days was pretty much cut and dried. During the first year we took four courses, spent 12 to 14 hours per week as assistants in undergraduate labs, and the rest of the time got our feet wet in the laboratory on what would become our dissertation research. At the end of that first year, the faculty, on the basis of course grades and day-to-day observations, decided whether or not each student was PhD material. Those for whom the thumbs were down were given a Master's degree and dismissed. The others continued, almost always receiving a PhD after two more years. The second year was much like the first except that we took only a couple of courses and spent much more time on our research projects. At the beginning of the third year, we had to take a two-day written comprehensive exam. While I was a student, all who took that exam passed it, so I don't know what the consequences of failing would have been. One very big difference in the third year was that we could no longer be teaching assistants but were expected to spend full time on our research project. Thus, unless we were lucky enough to win one of the two fellowships available to third-year students, we were on our own financially.

My solution to the finance problem was to get married, not to my sophomore flame but to Margaret Wilson, who became supervisor of my student labor at Berea while I was working in the Registrar's Office. She was a beautiful



woman by whom I (then in the tenth grade!) was smitten the first day she started work as Assistant Registrar. Always ten years older than I, she seemed to be so far beyond my reach that I never dreamed she could ever be more than the close friend and confidante that she had become. We had gone out together occasionally while I was in college and, when I was home, after I graduated. Romance bloomed while I was at Yale and she finally agreed to become my bride at end of my second year. She was my “fellowship” during that third year at Yale, supporting us both with the 50 cents per hour she earned at various odd jobs. To this day I marvel that the daughter of a very conservative minister had the courage to face the inevitable elevation of eyebrows by everybody everywhere at our flagrant departure from the social norm. One of my closest friends told us decades later that he had been sure our marriage would not last more than a year or so. In fact it was not until 1992 that I lost my bride of 53 years in a New Zealand car crash. She was then 85 but looked and acted ten years younger than the husband she had “snatched from the cradle.” The plain truth is that in matters of matrimony this society’s norms are genetically out of joint. Women on average live about ten years longer than men and yet become the wives of husbands who are several years older. That is why widows greatly outnumber widowers. In choosing a mate men should follow the advice of Ben Franklin in his letter to a young man on choosing a mistress. The message: Be sure she is older than you are.

It was only in choosing a graduate school that I had exercised any influence on the research I would do for my thesis. That influence was unwitting because I had no idea about the faculty research interests at either Yale or Northwestern. Indeed I had only the vaguest idea of what graduate study was all about. Thus, I felt neither joy nor apprehension when I was summarily assigned to Gus Akerlof’s group. Most of the research by Harned and his colleagues was on the properties of electrolyte solutions, the more dilute the better. So narrow was this focus that I left Yale, halfway believing that “Physical Chemistry was the study of slightly contaminated water.” Gus was a bit of a maverick because he had an interest in concentrated solutions. In essence what I had to do was measure the potential difference between electrodes of silver-silver chloride and platinum-hydrogen in solutions of HCl with molalities from 0.01 to 10.0 in solvents comprising methanol in water at intervals of 10% from 0 to 90, at temperatures from 0 to 50°C. I think the total number of emf measurements was around 3000, taking into account that each measurement was made in triplicate, i.e. for each of three separate cells containing the same solution. My routine for most of two years was to prepare six cells, two sets of three, each set with the same solution, and let them equilibrate over night with hydrogen bubbling over the Pt electrodes. If the emfs in each set of three cells agreed

within some forgotten number of tenths of millivolts, then I would haul 50 pounds or so of ice from the basement to my thermostated bath to bring the temperature down to near  $0^{\circ}\text{C}$ . The rest of the day would be spent recording emf values for all six cells at every ten degrees as the thermostat was heated to  $40$  or  $50^{\circ}\text{C}$ , depending on the vapor pressure of the cell solution. All the results were fitted by least squares to a quadratic curve for the dependence of emf on concentration. The least-square calculations were all carried out by a hand-cranked Monroe Calculator, except when I was lucky enough to grab the one electrically driven machine in the calculating room.

Obviously, I was something less than inspired by this introduction to "original research." The experiments were a boring, pointless chore, with few redeeming features. The results contained no surprises and nothing of much interest to anyone, least of all me. It was some years later before any of them found their way into the literature and then only as part of a table in a review article that Gus had been asked to write. My dissertation attested to the sterility of that project, consisting as it did of 45 pages of tables with only three pages of text! Although this first experience in research shattered some illusions, my sojourn at Yale was a rewarding experience. I made many long-lasting friendships with both fellow students and faculty. The physical chemists were a very congenial group, and Herbie Harned was really a very interesting man. He and his wife were very kind and warm-hearted people. They held an open house every Friday night, which both students and faculty felt obliged to attend more or less regularly. More often than not we ended up around the piano in a group sing-along with Roger Bates, a Sterling Fellow and accomplished musician, at the keyboard.

I learned a lot about life and lore outside of chemistry: to play bridge, to drink beer, and to smoke a pipe during the dull seminars every Tuesday night. I had many interactions with many interesting people. The weekly university calendar was filled with provocative events ranging from seminars to sermons and concerts to contests. My perspectives were stretched by memorable if abstruse encounters with great minds, including lectures on resonance by Linus Pauling and two required courses in statistical mechanics under Lars Onsager (known to the students as Norwegian I and II). Gus and his wife Rosalie, who was the sister of Joe Hirschfelder, looked after his students with great care and affection, making their house our home away from home. Rosalie took my new bride under her wing, showering us newlyweds with almost too much attention. I was extremely fond of Gus and most grateful for his always calm demeanor and seeming imperturbability. He strongly disapproved of marriage for graduate students, but when I told him I wanted to take a wife, he protested not at all and simply said, "OK, we take it from here." He and she became extremely fond of each other, and he told me many times that marrying her was

the smartest thing I ever did, an opinion shared by everyone that has known us both. All in all, my time at Yale was happy and rewarding, but I left with a much diminished interest in scientific research, and no desire to return, even for a visit. The exciting prospect for the future was a job in the research department of the Phosphate Division of Monsanto Chemical Company in Anniston, AL. The starting salary was \$2700 per year, the going rate at the time for new PhDs in industry and a mind-boggling jump from the \$500 or so a year we had been living on. I couldn't understand why my mother laughed when I once remarked that I didn't know how we could spend so much money!

### *Interim in Industry*

Monsanto had recently acquired the Anniston Plant when it bought out a small chemical company started by a legendary character named Theodore Swann, who had pioneered the production of phosphoric acid from elemental phosphorous. It came by tank car from a plant in Columbia, TN where it was produced by smelting "phos rock" in an electric furnace. At Anniston it was burned in air to produce its pentoxide, which could be hydrated to form acid of any desired concentration. Major customers for the acid per se included the soft drink industry, especially the Coca-Cola Company in nearby Atlanta. According to the local folklore, the first tank car of food grade acid to be delivered was filtered through laboratory büchner funnels because the filtration plant was not ready in time to meet the deadline on the sales contract! Much of the phosphoric acid left the plant in the form of sodium and potassium phosphates that among other applications were widely used as soap builders and water conditioners and in food products such as baking powders.

The other main product line, which some said was the main reason Monsanto bought Swann Chemical Company, comprised biphenyl and its chlorinated derivatives known as Arochlors, the now notorious PCBs. Biphenyl was produced by bubbling benzene vapor through large baths of molten lead at a temperature of around 800°C. Liquid metal as a heat exchanger provided rapid heating and close control of the temperature, thus minimizing formation of by-products that comprised mostly ortho, meta, and para diphenyl benzenes. The various Arochlors were characterized by their chlorine content, which ranged from 10 to 60% by weight. One of their main uses was as transformer oils because they had very good heat transfer characteristics, would not burn, and were very inert. Indeed, they were so inert and sticky that the chemists insisted that if Arochlor ever got into a laboratory some of it would remain forever! Because it was so inert, we practically bathed in the stuff, never dreaming that it might be toxic. I dare say that even today, 50 years later, the PCB content of my fatty tissue would horrify the EPA!

Of the various projects I worked on at Monsanto, the three most interesting were (a) the determination of heat capacities of various phosphate salts and their hydrates; (b) the design of a distillation column for the separation of the ortho, meta, and para diphenyl benzenes in high boiler by-product of the biphenyl process; and (c) the development of a process to recover chlorine from the byproduct HCl of Arochlor production. The last of these was the most important. In the production of Arochlors, half of the chlorine consumed ended up as HCl, whose disposal was a problem. Thus, the possibility of using the old Deacon process for oxidizing that HCl with air to recover some of that waste chlorine was attractive. At realistic temperatures for this reversible reaction, catalyzed by  $\text{CuCl}_2$  on alumina, the equilibrium distribution of chlorine atoms was two thirds in HCl, only one third in  $\text{Cl}_2$ . The new idea was that biphenyl vapor added to the process stream would react with chlorine irreversibly to form chlorinated biphenyl and HCl, which would then be reoxidized. In bench scale tests we found operating conditions that would convert most of the HCl to triply chlorinated biphenyl. The next step was the design and construction of a pilot plant to test the process on a more realistic scale. That plant design was not completed before I left.

While waiting for that plant to be built, I was assigned to a group investigating the reovery of fatty acids from tall oil, an abundant by-product of pulp production from pine trees. In that group was James W. Mullen, II, a young PhD organic chemist from Princeton. He and I became good friends, sharing a growing dissatisfaction with the way things were being run at work. Jim insisted that sooner or later he was going to start a research company and that when he did he wanted me to join him. Talking about what we might do was fun, but it all seemed like pipe dreaming to me. Having become increasingly disenchanted with the work situation, we both resigned and left Anniston on the same day. Jim went back to Richmond for a while and then to Bell Labs in New Jersey. I took my family, which now included an 18-month-old daughter, Marianne, to Wyandotte, MI, where I had found a job in the research department of Sharples Chemicals.

Immediately upon arrival I was pressed into service on a pilot plant that was adding hydrogen sulfide to tri-isobutylene (TIB) to form tertiary dodecyl mercaptan. In preliminary tests this "3B mercaptan" had been found one of the most promising substitutes for lauryl mercaptan as a "modifier" for the polymerization of butadiene in the manufacture of synthetic rubber. War in the Pacific had put coconut oil, and therefore lauryl compounds, in very short supply, so our 3B pilot plant was considered an essential component of the wartime Rubber Program. We were under pressure to produce a dozen drums of the stuff for a full-scale test run at a big GRS (government rubber synthetic) plant

in Louisville, KY. When the pilot plant was running well, we could make about 10 or 15 gallons in an eight-hour shift. To make the needed 660 gallons would thus require from ten days to two weeks of continuous operation, with a plant that rarely performed well for more than a day or two at a time. The process, developed at Sharples, was based on what Jack Olin, Director of Research, referred to as a “milk bottle” reaction because it was so simple. When a trace of boron trifluoride was added to a mixture of liquid  $\text{H}_2\text{S}$  and TIB, which were miscible in all proportions, addition of  $\text{H}_2\text{S}$  to the double bond proceeded to equilibrium with ionic rapidity. The reaction was mildly exothermic and completely reversible, so the conversion of TIB to mercaptan was favored by low temperatures and with a two or three fold excess of  $\text{H}_2\text{S}$  was essentially complete at around  $-50^\circ\text{C}$ . To prevent back reaction when the product warms up, one must quench the catalyst activity at the low temperature. The process to meet these requirements consisted essentially in using  $\text{H}_2\text{S}$  as the refrigerant in a nearly closed cycle refrigerator. A stream of TIB joined the liquid  $\text{H}_2\text{S}$  from the condenser into a reactor tube along with a trace flow of  $\text{BF}_3$  catalyst. At the end of the reactor tube, the liquid flashed through a needle valve, confluent with a small jet of steam to quench the catalyst, into a gas-liquid separation chamber from which the cold gaseous  $\text{H}_2\text{S}$  flowed out the top into the cold side of the exchanger, counter current to the incoming reaction mixture, thereby cooling it so as to maintain the low temperature needed for high conversion. From there the gas entered the compressor and went back through the circuit. Liquid mercaptan product along with steam condensate was drawn off the bottom of the separation chamber into a decanter to separate the product from the water. The plant was jury-rigged and prone to leaks in the valves and packing, but the big operating problem was the compressor, an old reciprocating steam booster that leaked several pounds an hour of  $\text{H}_2\text{S}$ , a gas much more toxic than carbon monoxide. It was in a shed outside the small room housing the reactor. The windows and door were kept wide open to keep the air as fresh as possible.

$\text{H}_2\text{S}$  is also highly malodorous, but unfortunately for safety purposes, the olfactory nerve fatigued rapidly, so we could not smell the gas. Our reliable signal to get out into fresh air was the appearance of strong halos around lights. That signal saved our lives but also meant that we could soon expect extreme photophobia and strong irritation of the mucous membranes around the eyes, altogether an excruciating experience that lasted from 12 to 24 hours. All this was taking place in January and February when on the evening and midnight shifts the wind-chill factor would frequently reduce the effective temperature to well below zero. Because of the  $\text{H}_2\text{S}$ , the windows and doors were always open so the inside temperature was about the same as the outside. We were cold, cold, cold. Another hallmark of the 3B project was the odor of the mercaptan.

The pure product was not too bad, but on wool or leather the result was very objectionable to some people but reminded others of roast beef! We got used to it, but I can remember many times going into a bar or cafe for a beer or a cup of coffee at the end of a shift and within a few minutes seeing everybody else leave!

In spite of all the discomfort, the morale was high in the 3B team of about eight people. Perhaps it was the shared misery together with the feeling that our work was important that resulted in a remarkable esprit de corps. We had a big party when we finally shipped the dozen drums of product to Louisville, but we suffered a tremendous blow when the news came back that the plant had somehow lost track of our modifier and was unable to identify the rubber that was made with it! However, because there was no bad rubber produced and because additional lab tests indicated that 3B mercaptan really was a good modifier the decision was made to build a plant for its production. The 3B gang cooperated with the engineers in designing the new plant, tested a lot of the components, and helped in the shake down runs when it finally went on stream. In comparison with the plumber's nightmare with which we had proved the principle, the new plant looked and ran like a Rolls Royce. To see it turning out nice clean product in a steady stream in a warm, bright, odorless building gave us all a deep sense of pride and accomplishment.

For the next six months or so I was involved in a variety of forgettable small projects. Then I was asked to become a liaison between the research department and the company patent attorney, Maurice Crews, who lived and worked in Philadelphia and, like my graduate school mentor, was also known as Gus. Not a chemist, he had done most of his work for the Sharples Centrifuge Company, a leading manufacturer of industrial centrifuges whose owners had backed the creation of Sharples Chemicals. In the next ten months I made a lot of trips to Philadelphia and learned a lot about patents that has been very useful over the years. One day in June of 1945 a letter came from Jim Mullen saying that he had finally started his company and wanted me to join him. I took a train down to Richmond to find out more. At Bell Labs he had become involved in Project Bumblebee, a large-scale effort by the Navy to develop a ramjet-powered anti-aircraft missile for the fleet. The ramjet depends upon ram pressure from high-speed flight to compress air enough so that its expansion after heating by combustion could perform propulsive work. It was clear that supersonic flight velocities would be required to achieve substantial thrust, but nobody knew whether thrust could exceed drag. The name, Bumblebee, derived from a bit of aeronautical badinage to the effect that by the laws of modern aerodynamics it is impossible for a bumblebee to fly but the bumblebee, not knowing any aerodynamics, goes ahead and flies anyway! The project was being directed and coordinated by the Applied Physics Laboratory of Johns

Hopkins University, which had just completed the wartime development of a Proximity Fuse for anti-aircraft shells. Jim had wangled a subcontract to carry out research on combustion problems in high-speed flows and was building a small lab on some land he had bought on the James River, right next to Du Pont's big rayon plant. His enthusiasm was infectious, and I found the prospects very intriguing.

All excited, I persuaded Magee, my wife's nickname from Anniston on, that we should go to Richmond. By then Marianne had a sister Barbara, born in Wyandotte and we were expecting our third child in October. I took them all to Berea, where my mother had volunteered to put them up, welcoming the prospect of some company, I think, because my father had died just a few months earlier. Back at Wyandotte, I sold the house, feeling fortunate to get what we had paid for it because the looming end of the defense business had the Detroit area very apprehensive about the possibility of a postwar depression. I also arranged to store our furniture until we had a place to live in Richmond. I took my leave from Sharples and drove back to Berea. After a few days there I drove to Richmond to start my new job and to look for a place to live, finally finding something I liked and could afford. My family, now including John Jr, born in Berea, arrived by train just before Christmas.

Experiment, Inc., the name Jim gave his company, prospered over the next seven years. It was an exciting experience to watch and participate in its growth from a total of three employees when I arrived to perhaps 50 or so when I left. Most of its business was based on R&D contracts with government agencies, for which the central theme was combustion and propulsion. There were some important dividends from my investment of time at Experiment. One was some familiarity with dynamics and thermodynamics of compressible flow, a newly popular area of research spawned by the advent of jet propulsion and sometimes referred to as aerothermodynamics, or aerothermochemistry if changes in chemical composition were involved. Another was the opportunity to do some research in combustion, both applied and fundamental. Jim was a strong believer in publishing results. Thus it happened that 1949 saw the first publication of my life, a paper with him and a junior colleague, Moe Irby, on ignition in high-speed flow, almost a decade after I left graduate school. After several more papers, visits to other labs, and attendance at various meetings, I began to get a little recognition in the combustion community. Moreover, in an about face from my feelings at Yale, I found that I enjoyed doing research and communicating with others about my findings and theirs. As mentioned earlier, I had once thought that someday I would like to be on a college faculty. That feeling had faded somewhat at Yale but was revived a bit at Experiment, Inc. when I found myself enjoying the research I was doing as well as the

interaction with new employees fresh from the university and with students who sometimes worked there during the summer.

For these and other reasons I was extremely intrigued when Princeton offered me a position as director of Project SQUID, a program of pure and applied research “in those fields of science and engineering relating to Jet Propulsion.” Financed by the Navy and administered by Princeton University, it was named after the jet-propelled decapod of the sea. (That name had additional but unpremeditated relevance in that both the animal and its namesake secreted ink, the former in clouds that confused predators, the latter in print that confused readers!) The organizational structure comprised a prime contract between the Office of Naval Research (ONR) and Princeton University, with subcontracts at any one time from Princeton to from 12 to 20 or so university and industrial laboratories. The overall purpose was to cultivate interest and support research in such fields as combustion, fluid flow, and heat transfer destined to play important roles in the then dawning age of jet propulsion. One of the “other reasons” for my interest in going to Princeton was that my Yale mentor, Gus Akerlof had set up a laboratory in its newly established James Forrestal Center to develop, with Navy (but not SQUID) support, an electrical discharge process for the production of hydrazine, an attractive rocket propellant. Gus had once visited me at Experiment, Inc. and had put my name in the pot when he found out that the previous director of SQUID was leaving.

### *Once Again Academe*

At Princeton I would report directly to Hugh Taylor, longtime Chairman of Princeton’s Chemistry Department, then Dean of the Graduate School and Chairman of the University Research Board. The position was “with rank of Professor” and the Dean assured me that I would be welcomed as an active member of the academic community. And so, after much soul searching, Magee and I decided we would leave the “Cradle of the Confederacy” for what was often called “the northernmost southern town in the country” because over the years so many of Princeton’s students had come from below the Mason Dixon line. The job turned out to be very interesting and highly educational. I had to travel a lot but was able to visit many laboratories and meet well-known scientists in many fields all over the country. I got to know the people in the ONR pretty well, and my circle of acquaintances included people in the Army Research Office and Air Force Office of Scientific Research, which for a while provided some support for Project SQUID and had representation on its Steering Committee.

ONR had a branch in London (ONRL) that maintained a rotating corps of 12 to 15 Scientific Liaison Officers whose job was to promote interaction between scientists and engineers in Europe and America by visiting laboratories and



attending scientific meetings. They would get to know the investigators, learn about what they were doing, help them establish contacts with their counterparts in America, arrange visits, find items of equipment, assist with travel arrangements, and the like. Research laboratories in Europe were beginning to recover from the trauma of World War II and welcomed the communications links and the help with their needs that ONRL could provide. After I had been at Princeton for about three years, I received a surprise letter from Sam Aspinall, Scientific Director of ONRL. Sam had been a third-year graduate student in organic chemistry when I arrived at Yale but I'd had no contact with him since. His letter invited me to serve for a year at ONRL as a Liaison Officer in Combustion and Propulsion. ONR Washington approved and I persuaded John Scott, who had just finished his PhD in Aeronautical Engineering at Princeton, to mind the store at SQUID for a year. So Magee and I, along with the children, then 9, 11 and 13, went to London for the calendar year of 1955. And what a wonderful year it was! The children still insist that London was the high point in the Fenn family saga, which has been downhill ever since!

I share some of those sentiments because that year in London was also a marvelous experience for the parents. The kids were in school, so Magee was free to roam London. I visited many laboratories in many countries, made many many friends, and learned about "more things than had been dreamt of in my philosophy." Among these "things" was my stumbling on to something that was to set the stage for the rest of my scientific life. Up to that time flames and their behavior were the focal point of practically all attempts to elucidate the kinetics and mechanisms of the important reactions in high-temperature combustion. I had become convinced that with their extremely high gradients of temperature and composition, flames were much too complicated to be useful as stages for the study of those reactions. I often recalled a comment by Philip Rudnick, a professor of Physics at Vanderbilt who was active in the Propulsion Panel of Project Bumblebee. He said that the more he learned about flames the more he was convinced that they were organisms whose study properly belonged in the province of biology! I'm sure that view strikes a responsive note in many investigators who have been exasperated by the vagaries of flame behavior that seem to give them a life of their own. Indeed, the analogy can be extended. Flames, like organisms, are born, need oxygen and food (fuel) for nourishment, grow and multiply to the extent that those necessities are accessible, and are poisoned unto death when immersed in their own waste products!

For some time I had been musing about using molecular beam experiments instead of flames to study combustion reactions. A little of the beam mystique had rubbed off on me from I (for Izzy) Amdur at MIT during visits with Fred

Keyes, whose work on transport properties was supported by SQUID. Izzy was using small-angle scattering of high-energy beams (formed by charge-exchange neutralization of accelerated ions) to probe intermolecular potentials. The idea of bringing about reactive collisions by colliding a beam of reactant molecules with a surface or with other gaseous molecules had been contemplated since the late 1920s. In spite of several attempts, no really convincing results had been obtained when we left for London at the end of 1954. The age of reactive scattering dawned just after we returned in 1956 when Datz and Taylor reported that intersecting beams of K atoms and HBr molecules produced detectable amounts of KBr. These results gave some substance to my musings, but there was a fundamental problem with the idea of applying the same elegant methodology to combustion reactions. Activation energies for the most interesting of those reactions are from 0.5 to 2.0 or more eV, 10 to 100 times higher than for the reaction studied by Datz and Taylor. Amdur's charge exchange beams could easily produce beams with much higher energies but because of space charge effects could not provide useful intensities at energies as low as a few electron volts. His high-energy—small-angle scattering approach was not applicable to reactive collisions. To produce beam molecules from classical effusive sources with energies of 0.5 eV would require source temperatures of 3000 K. Neither materials of construction for the source nor reactant molecules other than atoms could stand so much heat.

One day in London I was calculating exhaust velocities for various rocket propellants and suddenly realized that many reactant molecules at the velocities attainable with some propellants would have translational energies as high as 2 or more eV. I began to fantasize about using micro-rockets in vacuum as molecular beam sources, anticipating by 30 years an experiment we later performed for another purpose! I then remembered that rocket visionaries had often touted hydrogen as an ideal propellant fluid for nuclear powered rockets because its low molecular weight meant it could achieve very high flow velocities upon expanding through a high-pressure ratio. If hydrogen were seeded with a low concentration of heavier reactant molecules such as oxygen and then expanded through a nozzle into vacuum, maybe those oxygen molecules would be carried along like dust particles in a wind storm and reach translational energies of a few electron volts. I began to get excited, even though in sober moments the whole idea seemed preposterous.

A few days later I was leafing through an issue of the *Zeitschrift für Naturforschung*, to which ONRL subscribed. I ran across the now famous paper by EW Becker and K Bier in 1954, reporting the production of intense beams of hydrogen molecules by expansion of the gas from high pressure through a small converging diverging nozzle into vacuum. Unknown to me, that idea had

been proposed in 1951 by Kantrowitz and Grey in an also-now-famous paper in the *Review of Scientific Instruments*. The next paper in the same issue of that journal had recounted a not very successful attempt by Kistiakowsky and Schlichter to reduce the Kantrowitz-Grey idea to practice. Both of those papers were referred to in the Becker paper and also happened to be in the ONRL library. Then I really began to get excited. I later learned that 25 years earlier, TH Johnson, a Sterling Fellow at Yale, had produced intense beams of mercury atoms by expanding the vapor from a “boiler” at several hundred torr into vacuum, but his truly pioneering results had been ignored (1a,b). Later in his career at the Franklin Institute he found diffraction in the scattering of hydrogen from an LiF crystal, confirming the wave nature of particles much heavier than the electrons of Davisson and Germer (2a,b). Unfortunately, some eight weeks earlier, Estermann, Frisch, and Stern had found the same result, so Johnson’s work again went unnoticed while Stern got the Nobel Prize. An able investigator who was 25 years too early with one brilliant experiment and 8 weeks too late with another, Johnson had every right to feel frustrated by the fickleness of fate.

The message of the results obtained first by Johnson and much later by Becker was that convective flow of gas into vacuum from high pressure could produce beams with much higher intensities than could effusion of gas from a traditional source at low pressure. Moreover, these convective beams turned out to have much narrower velocity distributions than their effusive counterparts. Consequently, the achievable intensity within a narrow velocity interval, a highly desirable feature, could be very much higher with convective beams. Back at Princeton, I found that John Scott was going to the University of Virginia as an assistant professor of Aeronautical Engineering. He was wondering what research he ought to work on, and I told him about the beam possibilities that I had been thinking about. I also told him that if he would submit a proposal on such work to Project SQUID, I would try my best to get support for it. He arrived at Virginia to find a group using beam scattering experiments to characterize the exchange of energy and momentum between molecules and surfaces. Their goal was to understand and predict surface heat transfer and drag for aerodynamic bodies at very high altitudes where flow was molecular rather than continuum. The high intensities achievable with supersonic free jets, or nozzle beams, as they would come to be known, would be most useful in these surface-scattering experiments. The seeded beams I was dreaming about would allow them to study drag and heat transfer in molecular flows of  $N_2$  and  $O_2$  at velocities much closer to those expected in high-altitude flight. As a result of their enthusiasm and mine, the first successful nozzle beam system in America was built in Charlottesville, VA. I should really say, the first one since Johnson built his at Yale.

Meanwhile, I was getting more and more eager to become more directly involved in this new field of research. I had by this time learned that I could not become an active participant in academic research unless I had some direct association with a department. SQUID had been supporting research on two-phase flow by Shao Lee (Charlie) Soo, a young assistant professor of Mechanical Engineering. In a visit to his lab one day I met Robert Drake, the new chairman hired to refurbish the department's image by expanding its research. I described my wild ideas on free jet beams and said, "If I write a proposal and get some support, will your department provide a home for the project?" Bob had done his doctoral research in rarefied gas dynamics at UC Berkeley, so he knew what molecules were and immediately said yes. I prepared a proposal on which I was listed as a Consultant because I was not on the faculty. The co-PI's were Bob Drake and Michel Boudart, my next door neighbor and close friend on the faculty of Chemical Engineering.

The proposal was submitted to NSF, who sent it for review to Immanuel Estermann, a coauthor with Stern and Frisch of the landmark paper on diffractive scattering of hydrogen from LiF, one of two papers cited when Stern won the Nobel prize. Estermann had become Director of ONR's Material Sciences Division whose Power Branch was responsible for Project SQUID! He took reviewing seriously and spent a day in Princeton discussing the proposal. The fact that his daughter lived there was no doubt something of an inducement for him to make the trip. He had visited Becker's laboratory in Marburg, Germany and was aware of the difficulties involved in fabricating the tiny converging-diverging nozzles prescribed by Kantrowitz and Grey. As he took his leave he said, "John, I'm afraid this research may be too difficult to pursue with graduate students, but I think it is important so I'm going to recommend support." He apparently was as good as his word because NSF gave us all the money that we had sought and we began work in the fall of 1959. Michel Boudart was hosting Jacques Deckers, a young PhD who had done his doctoral research on ions in flames with Van Tiggelen at the University of Louvain. Jacques was very excited about our beam project, and Michel turned him over to my tender love and care (or me to his, I'm not sure which). With Bob Drake looking over our shoulders, we began design of the system.

One of the lessons from the experiments of the Kistiakowsky and Becker groups was the need for lots of pumping speed. When the salesman from NRC showed us the performance characteristics of its 32-inch oil diffusion pumps, Jacques' enthusiasm overcame my reticence (or timidity?), so the main chamber of our system became a long horizontal tank evacuated by two of those big pumps. In retrospect I think that in choosing those big pumps as the heart of our system we were either much wiser or more fortunate than we

knew. Those who work with vacuum systems learn early that there is no such thing as too much pumping speed. Sooner or later they always wish they had more. It's nice not to have to worry about the vapor pressure of finger prints, even nicer to be able to sustain disasters. We arrived one Monday morning to find the system completely filled with some 700 gallons of water from a failed cooling coil! We drained and decanted, easily separating the silicone pump oil from the water. After wiping out the interior surfaces of the pumps, pipes, and chamber, we took a color photo because all those surfaces, which were mild steel, now sported a beautiful beige coat of rust! We closed up the system and ran the forepumps for a couple of days, passing a small flow of air through the system to help dry things out. With fingers crossed we started the diffusion pumps—and got the best vacuum we had ever achieved!

Meanwhile Dame Fortune had smiled at me in another way. Not long after the beam project started, Charlie Soo, who had been teaching thermodynamics to the mechanical engineers, suddenly announced he would leave at the end of the first semester. Bob Drake, not knowing I had barely passed the only course I had taken in that subject, asked me if I would accept a temporary appointment to teach the sophomore course in the second semester. After a deep breath and a small prayer I said yes. Things must have gone pretty well because at the end of the term he asked if I would consider a permanent position on the faculty. All of a sudden I had the chance to realize a long-cherished ambition to become a first-class citizen in the academic community. Moreover, because my appointment as SQUID's director was "with rank of professor" I automatically became an instant full professor of Mechanical Engineering, a transmutation that would be much more difficult in today's world of fair employment practices. I continued to run SQUID until 1962 when by mutual agreement of all parties its headquarters moved to the University of Virginia and John Scott became director.

After the apparatus started working well (3), its first application was the measurement by Bob Koros, one of Michel Boudart's students, of the sticking coefficient of water molecules on ice at liquid nitrogen temperatures. The simplicity and success of the experimental design were strong, almost tangible, evidence of both the achievability and utility of high beam intensities from free jet sources. Bob simply suspended a small target from a calibrated helical spring of glass and measured the time-dependent extension of the spring with a cathetometer outside the vacuum system. Nearby baffles, filled with liquid nitrogen, maintained the target at low temperature. The beam flux of water molecules from a source at a few tens of torr of water vapor, measured with a simple snorkel gauge to be described later, was sufficiently intense to deposit in a few hours enough ice to extend the calibrated spring by measurable

amounts. In an analogous experiment, Jim Anderson, another Boudart student, found that oxygen molecules incident on a heated germanium wafer reacted to form a volatile  $\text{GeO}$  molecule. Above a threshold temperature that I've forgotten, the reaction probability was 0.04, as I remember, and was independent of temperature and incident intensity.

Because there was a lot of competition for time on the beam machine and because bona fide beam experiments were time-consuming, many of my students carried out nonbeam experiments. Using sampling probes in free jets, Vic Reis, my first graduate student, investigated the separation of heavy and light species during free jet expansion of mixed gases (4), originally discovered by the Becker group and confirmed by several other investigators. The consensus was that these separations were due to radial pressure diffusion of species from the jet axis, with the lighter species moving faster than the heavy. Vic showed that in fact the separation occurred during stagnation of the supersonic flow on the front face of the sampling probe. Nobody really accepted his unequivocal experimental result until a few years later when Rick Sherman at Berkeley in a theoretical paper showed that diffusion effects were negligible at the Reynolds numbers of all the experiments! George Maise showed that the same stagnation separation resulted in adiabatic thermal recovery factors much above those in uniform gases. John Chang was able to correlate the species separation with the anomalous recovery factors and also characterized the viscous enhancement of measured stagnation pressure on small probes in free jets. Ron Kostoff developed a torsion balance that could measure thermal accommodation coefficients at high temperature. Uri Navon studied the decrease in the evaporation rate of water achieved by compressed surface monomolecular films of cetyl alcohol and stearic acid. He showed that almost half of the effect is due to their action as a rigid surface boundary that causes viscous damping of the natural convection (Benard cells) induced by evaporative cooling at the surface.

Meanwhile, of course, studies in the beam machine were going on apace. I could fill a book with stories of our early adventures in the new and still strange land of supersonic free jets, i.e. big leaks in vacuum systems, but can only hit some high spots in this account. Estermann's fears about the difficulty of making tiny converging-diverging nozzles proved to be groundless. Because of entropy generation by viscous effects at the walls of the diverging action, simple converging nozzles work much better. Indeed, as we learned, almost any old hole or tube would serve as a nozzle as long as it did not have a diverging section downstream of the plane of minimum area. In the early days of our studies the major diagnostic tool was a so called "snorkel" for measuring beam intensity. It comprised an ionization gauge to measure total pressure in a glass envelope into which the only access was a small tube whose open end intercepted a fraction

of the beam flux. The difference between the steady state pressure inside and outside the envelope was a measure of the inlet flux. With this simple device to measure beam intensity, we were able to optimize dimensions and locations of the nozzle and skimmer, and their dependence upon operating conditions such as source pressure in the nozzle and background pressure in the separately pumped nozzle exhaust chamber.

A much more powerful diagnostic tool than the simple measurement of beam intensity was and is velocity analysis of the beam molecules, first applied to free jet beams by the Becker group. The approach is to determine the distribution of flight times over a known distance for molecules in beam segments produced by chopping the continuous beam with a rotating shutter. By developing this time-of-flight (TOF) technique for our lab when he became a postdoc, Jim Anderson was able to determine the terminal translational temperatures in free jet expansions, i.e. the gas temperature at the end of the collision dominated continuum flow regime, after which all collision-dependent processes stopped. He also formulated a model for the expansion that could predict the terminal temperature of the jet molecules in terms of the diameter of the nozzle along with the pressure, temperature, and composition of the source gas (5). Terminal temperatures below 1 K could be readily reached. Indeed, by going to very high source pressures, Ron Gentry at Minnesota has recently achieved terminal temperatures in the millikelvin range and below. With TOF velocity analysis, Jim Anderson and Nesim Abuaf were finally able to show that heavy seed molecules could indeed be accelerated by a light carrier gas to translational energies approximately equal to the product of the thermal enthalpy of the source gas molecules and the ratio of the molecular weight of the seed species to that of the carrier gas. Thus, for example, with source temperatures of only 900 K, we could accelerate argon molecules with hydrogen to energies of almost 3 eV (6).

Because of the extremely low temperatures reached during the free jet expansion, the resulting beams have very narrow velocity distributions indeed. Effusive sources cannot readily operate much below 200 K with most gases, so their velocity distributions are much broader. Thus, not only do free jets produce beams with much higher total intensities than can effusive sources, but essentially all of their beam molecules have nearly the same translational energy, a most desirable feature in most beam experiments. To obtain translationally monoenergetic beams by effusion, one must resort to velocity selectors, complicated and expensive devices that at best can provide only 1 or 2% of the incoming flux in a velocity interval as narrow as is routinely obtained in beams from free jets. Moreover, as we learned, free jet beams can have very narrow distributions of rotational energy, virtually impossible to achieve in effusive beams because there are no rotation selectors. This important feature was

revealed by exploiting the adiabatic nature of the expansion. Clearly, from the magnitudes and distribution of terminal velocities of the beam molecules, we could determine their translational energy. Because the expansion was adiabatic, measured source temperature specified their terminal total energy. Thus, an energy (more properly enthalpy) balance indicated how much energy remained in rotation and vibration at the end of the expansion. It turned out from many perspectives that for most simple molecules there was very little relaxation of vibrational energy in the molecules of jets from our small nozzles. The assumption of a Boltzmann distribution provided a reasonable value for terminal rotational temperature. Such enthalpy balances allowed Ron Andres and his student Dave Miller to measure the rotational relaxation rate in nitrogen. They withdrew their beam samples at various stages in the expansion by locating the skimmer at various axial positions in the jet. In this way they determined the axial profiles of both translational and rotational temperatures as well as density. From such data, they could extract the rotational relaxation rate. Skimmer interference effects limited this approach to large nozzles and low densities, both of which were experimentally demanding. A few years later my student Bob Gallagher was able to overcome these difficulties by measuring only the terminal rotational temperature. He then obtained method-of-characteristics (MOC) solutions for free jet expansion to determine temperature and density histories. With rotation-translation (R-T) relaxation rate as a parameter, he could match observed and calculated values of terminal rotational energy to identify the correct rate.

The widespread acceptance of free jets as beam sources began in earnest after a Gordon Conference that John Scott and I organized in the summer of 1965. The 90 some attendees included a substantial fraction of all the investigators in the world who were using beams in scattering experiments. Almost all of their beams were from classical effusive sources and were to be found in departments of science. The relatively few practitioners of free jet technology were in departments and institutes of engineering. More often than not their papers appeared in the proceedings of the biennial International Symposia on Rarefied Gas Dynamics, not everyday reading for chemists and physicists. At the Gordon Conference we who had seen the light preached a few sermons on salvation through free jets and many of those who "came to scoff remained to pray." I still remember Dick Bernstein's appearing at the Thursday night banquet wearing a big badge saying "I believe!" Things changed rapidly after that Conference. Within three or four years free jets had become the beam sources of choice in many laboratories. Today they seem to reign supreme, having even played substantial roles in some of the work that led to the 1986 Nobel Prize in Chemistry for Dudley Herschbach, Yuan Lee, and John Polanyi.



Another virtue of the low temperatures achievable in free jets had emerged in 1961 when Bentley in the United Kingdom and Henkes in Germany quite independently reported mass spectrometric observations on dimers and other small oligomers of the gas molecules in free jet expansions. These were the first harbingers of what has become a rapidly expanding new field of research. At sufficiently high source pressures the very low temperatures reached during free jet expansions result in supersaturation of the jet gas while it is still in continuum flow, thereby triggering the onset of nucleation-condensation processes. For nozzle diameters sufficiently small, the axial decrease in density can be so rapid that the collisionless flow regime is reached soon enough to stop all collision-driven processes that started earlier in the expansion. Such interruption of nucleation-condensation gives rise to the production of clusters whose size distributions, ranging from dimers to tiny droplets, can be prescribed for a particular species by appropriate choice of source conditions including temperature, pressure, and nozzle size. Because of the ultra low temperatures that can be achieved, pure and mixed clusters and so-called van der Waals complexes can be formed from such unlikely partners as potassium and helium, for example. It is the ability to achieve these unique combinations of conditions that has made free jet expansions a cornerstone of the rapidly expanding arena of "cluster science" concerned with the properties and behavior of small aggregates of molecules, intermediates between gaseous and condensed phases and sometimes referred to as a fourth state of matter.

Although we had quantitatively characterized the low temperatures reached in free jets by early 1964, our ignorance of molecular spectroscopy kept us from harvesting what turned out to be a bumper crop of new information from free jets. Ten more years passed before Smalley, Wharton, and Levy at Chicago ushered in a new era of spectroscopy with their landmark demonstration in 1974 of how the elimination of rotational bands by free jet cooling could "clean up" the vibrational spectra of polyatomic molecules. Since then, the field of jet spectroscopy has exploded, not only for the study of internally cold individual molecules but also for the study of the uncommon species like clusters and van der Waals molecules for which tunable lasers are often the most powerful means of interrogation. I think there are now many more jets used in creating and/or conditioning species for spectroscopic examination than are used to produce molecular beams for scattering experiments.

For the first attempt at reactive scattering with the high translational energies achievable by seeding, Jim Anderson began with what we thought was the most attractive candidate, the reaction  $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ , which ever since Bodenstein had been considered truly bimolecular. That is to say, two molecules of HI are formed by a single sufficiently energetic encounter between a molecule of

$\text{H}_2$  and one of  $\text{I}_2$ . (It has more recently been suggested that the reaction may usually involve a reactive intermediate and thus more than one step.) In the forward direction, the large mass difference between  $\text{H}_2$  and  $\text{I}_2$  would require unattainable collision velocities to deposit the needed activation energy in the center of mass. Therefore, we chose the reverse reaction,  $\text{HI} + \text{DI} \rightarrow \text{HD} + \text{I}_2$ , as better suited to the seeding technique. The use of DI in place of one HI was to simplify the detection problem because there would be a large background of nonproduct  $\text{H}_2$  due to its use as the accelerating gas. The experiment consisted in firing an accelerated beam of HI molecules into a cell filled with DI and monitoring the effluent from the cell for HD product molecules (with a small quadrupole mass analyzer). To make a long story short, Jim found no detectable amounts of HD even though he put as much as two to three times the energy requirement for the reaction into the collision center of mass. Michel Boudart later called this negative result "the Michelson-Morley experiment of chemical kinetics!" It seemed to show that translational kinetic energy is not very effective in overcoming at least some kinds of activation energy barriers.

In hindsight we should not have been surprised. Clearly in this reaction one needs to get energy into the HI bond, and it has long been recognized that collision translation energy is generally inefficient in exciting strong covalent bonds. Since our experiment, the advent of tunable lasers has convincingly demonstrated many times that vibrational excitation is what makes molecules reactive. Nevertheless we were terribly disappointed at the time. We had finally achieved the long sought dream of many, a flexible and convenient method for producing molecules with suprathermal translational energies, only to find that those energies didn't seem to be very useful, at least for the promotion of chemical reactions, the goal that motivated our whole program.

About then I was beginning to feel a bit frustrated with the situation at Princeton. The Departments of Mechanical and Aeronautical Engineering had merged to form a Department of Aerospace and Mechanical Sciences led by Court Perkins, who had been chairman of Aeronautical Engineering and was also assistant dean. Up to that time the university had not provided any financial support of any kind to the Beam Lab, as it was known. I had hired John Bittner as a technician in my group. He was a Hungarian refugee and a wonderfully clever man who also was one of the best machinists on the campus. I was uneasy at having John entirely dependent for his livelihood upon my ability to raise grant money. I wanted assurance from the university of some job security for him if my grant funds dried up. In addition we needed a few thousand dollars worth of minor modifications to the building that would greatly improve the usability and availability of space for what had become a substantial group of a dozen or so people. Court flatly rejected both requests. There were also

problems due to what Jim and I regarded as unfair differences in the treatment accorded him and Ron Andres by the Department of Chemical Engineering, of which Dick Wilhelm was chairman.

Meanwhile, Yale had approached me about joining the faculty of the successor to its School of Engineering, the Department of Engineering and Applied Science in the Faculty of Arts and Sciences. A search committee proposed my name as someone who could rebuild the group responsible for the areas related to classical Chemical Engineering, once a strong Yale tradition. I found myself in sympathy with the educational philosophy underlying the new department. Consequently, in view of Princeton's indifference to the Beam Team's needs and after a curious and sometimes comical sequence of misunderstandings, I finally agreed to accept Yale's invitation, which included offers to all of my colleagues in the Beam Lab. As our departure date approached, Dick Wilhelm, who had refused to extend Jim's three-year appointment, suddenly offered him immediate tenure and me a professorship in Chemical Engineering! In addition, John Bittner was given reasonable assurance of job security. By that time, however, I felt obliged to honor my commitment to Yale, having heard by the grapevine how much they counted on my coming. Ron decided to stay in Princeton as did John, whose wife didn't want to give up the new home they had just bought. Jim, turned off by Princeton's behavior, chose to come with me to New Haven. Also joining us were Dave Marsden a British postdoc in the group and Uri Navon, the Israeli student whose thesis was on the inhibition of water evaporation by compressed monomolecular films. He had accepted Yale's offer of an assistant professorship.

When I decided to leave Princeton, I agreed to leave my lab intact for a year so that the several students using the apparatus could finish up their thesis research. At the time the grant had almost \$100,000 in uncommitted funds. It seemed to me that logic and fair play should let me use at least some of those funds to purchase new gear for use at Yale so that I could get started. In return I would agree to leave the installed and operating system permanently at Princeton. Court Perkins went to NSF in Washington and apparently learned that our molecular beam lab, whose activities he had previously ignored, had achieved some appreciable recognition. Without conferring with me, he arranged for Princeton to buy new equipment with those unspent funds, leaving Yale and me with the substantial expense and headaches of transplanting the old gear to New Haven. That meant that I could do little or nothing for a year while Ron Andres, on the faculty of Chemical Engineering and heir apparent to my lab, ordered new gear and had it all ready to install when the old system was uprooted. Moreover, Court earmarked \$500,000 of funds available to the department, mostly from the aerospace industry, to construct a gold-plated copy of our apparatus and a

new building to house it out at the Forrestal campus where most of the aerospace section of the merged department was located. That new beam lab would be for Arnold Kelly, a young Assistant Professor who had a student working on a project of his in my lab. I told Court that building, supporting, and operating such a large beam facility was too big a burden for a young faculty member bucking for tenure. I urged him and Dick Wilhelm to make Ron and Arnold join forces in a cooperative effort. My suggestion fell on deaf ears, and they went ahead with the bifurcated arrangement. In the next eight years there were no publications from Arnold's new lab. He was let go and his apparatus was dismantled. Ron published four papers of which only one was experimental. I still feel that Princeton's behavior in this affair was pretty shabby.

After a year of waiting on my part, the major effort of moving the old gear to Yale began in earnest. Jim Anderson and Dave Marsden shouldered much of the burden of packing and moving. Unfortunately, Dave never had a chance to use the system he helped rebuild. A few months after the move he lost his life in a tragic accident when a northbound police car in pursuit of a fugitive, jumped the divider on I-95 in Westchester and collided head-on with Dave's car heading south. His loss was a blow to the lab but devastating to his wife Isabel and their three young children. They moved to Ottawa where Dave's brother was teaching at Carleton University. Isabel's parents were not too far away in Montreal, so she had family support at hand.

Having by then learned how to get by with less pumping speed, we had cut the big chamber in half to form two smaller systems, each with one of the big diffusion pumps. One remained coupled to the nozzle chamber with its 16-inch booster pump; the other stood on its own. In the first few years at Yale, we pursued a variety of projects, some of which will be described briefly. A major effort by Bob Gallagher, who was called to military service from Princeton and returned as a graduate student, made an extensive study of relaxation of internal energy in jet molecules by the enthalpy-balance method described earlier in the account of our work at Princeton. His data on a wide variety of species provided values of the characteristic rates for the exchange of internal and translational energy, mostly R-T but some vibration-translation (V-T). An important result, useful in later studies, was the discovery that in CO<sub>2</sub> and several other species there was little or no relaxation of at least some vibrational modes. A provocative finding in H<sub>2</sub> was an apparent resonance in R-V exchange between the  $J = 8$  and  $v = 1$  levels.

In some offbeat TOF experiments without free jets, we used velocity analysis to show, for the first time unequivocally, that species evaporating from solid surfaces had Maxwellian velocity distributions corresponding to the surface temperature. In an extension of those experiments we investigated the vaporization

of ammonium salts and showed among other things that the vaporization of crystalline ammonium perchlorate occurs by the separate desorption of intact  $\text{NH}_3$  and  $\text{HClO}_4$  molecules. This observation answered a long-standing question in the mechanism of solid propellant combustion. A related and much argued question in which I had long been interested was whether the evaporation coefficients were near unity for polyatomic molecules leaving a liquid surface, as had been amply demonstrated for monatomic species such as metals. Most experiments with liquids of polyatomic molecules indicated much smaller values, e.g.  $\approx 0.04$  in the much studied case of glycerol. We developed a method for measuring the evaporation coefficients of relatively large polyatomic molecules with which Sandra Lednovich showed unequivocally for the first time that several such species, including glycerol and oleic acid, had evaporation coefficients very close to unity. The key need was to provide a liquid surface in vacuo that was clean. To do this we developed a continuous version of Langmuir's wiping technique. Postdoc Mahadeva Sinha subsequently obtained some provocative results in preliminary scattering experiments with these clean liquid surfaces, but we finally gave up when his successor could not reproduce them. In the last few years Gil Nathanson at Wisconsin has done really elegant and revealing experiments on liquid surface scattering of molecular beams. I proudly and shamelessly claim a tiny role in that landmark work because his surfaces are produced by our variation on Langmuir's theme.

We also pursued a few studies on clusters, which had by then become a booming application of free jet expansions. Our most significant finding was Jim Searcy's discovery of a singular stability for a cluster comprising a proton with 21 water molecules in a free jet expansion of moist argon when there was a corona discharge in the source gas (7). To my knowledge that result was the first hard evidence for what have come to be known as "magic numbers" in cluster size distributions.

About two years after the Yale lab became operational, Jim Anderson started a collaboration with Chuck Kolb and his colleagues at Aerodyne Research Corporation, which led to some of our most rewarding studies. Air Force observations had found IR radiation from  $\text{CO}_2$  molecules in the far field of exhaust plumes from rockets flying at very high altitudes. The best explanation seemed to be excitation of the asymmetric stretch mode of those  $\text{CO}_2$  molecules by collisions with molecules of the ambient atmosphere, e.g.  $\text{N}_2$ . The flight speeds were so high and the gas densities so low that the collision velocities were well above the excitation threshold (2.8 km/s for  $\text{N}_2$ ). The Air Force wanted to know the magnitude and the velocity dependence of the cross sections for such excitation. With that information, their computer codes could calculate the radiation distribution patterns from various types of rockets under various

flight conditions. That capability could be useful in identifying the source and mission of observed rockets. Calculations showed that by combining seeding and source heating we could reach collision velocities up to 6 km/s by opposing two free jets of light gas, one seeded with  $N_2$  the other with  $CO_2$ . If the nozzles were far enough apart, the jets would be sufficiently rarefied to achieve single collision conditions. The idea was to focus radiation from the collision zone on a sensitive InSb detector. With appropriate calibration and calculations, the excitation cross sections could be obtained from the intensity of the radiation. To make a very long story very short, we ultimately succeeded in determining T-V cross sections for  $N_2$ - $CO_2$  collisions at velocities from near the threshold up to about 6 km/s, but only after many many months of a grueling search for a tiny whisper of signal in a cacophony of noise. We often felt like blind men in a dark room looking for a black cat that wasn't there. Success finally came only because of the tireless efforts and limitless patience of Subbarao ("Batchie") Ryali, a loyal colleague for many years after Jim Anderson brought him into the group to work on this rocket plume radiation problem.

Jim himself had to leave not long after the work started because Yale reneged on its promise to him and to me that if he were qualified he would get tenure within three years. That promise persuaded him to come to Yale with me in spite of Princeton's last minute offer of tenure. There was no question about his qualifications. Along with four others he was highly recommended for promotion to tenure by our Department of Engineering and Applied Science. The excuse was that funds were limited so that only one slot would be available and the department would have to make the selection. That slot went to the only candidate of the four from the Applied Physics Group because they had by far the most votes, the Chemical Engineers the fewest. I was terribly distressed and tried to resign and make my slot available for Jim but the administration adamantly refused the exchange. As things turned out, Jim, who was a tremendous experimentalist, went to Penn State where he has thrived as a theorist, having learned to solve the Schrödinger Equation with unprecedented accuracy. Nor was losing Jim the only blow. When I was invited to Yale to rebuild Chemical Engineering there were 12 faculty members in that group, a number that I was assured would not be decreased. When a crunch came in the early 1970s, that number ended up at six, a 50% cut. None of the other groups in Engineering lost more than 20%! Moreover, in terms of numbers of students and publications as well as the amount of grant funding, the Chemical Engineering group, on a per capita basis, was substantially above all the other groups. It continued to lead for the next ten years, but the number of its faculty remained at six, the smallest in the department! That treatment fueled my ultimately successful fight to make Chemical Engineering an independent department, a

course later then followed by all the other groups. The Founding Societies and the Engineering Schools had been affronted by Yale's unconventional attempt to depart from their traditions. They responded by making both curriculum accreditation and graduate students almost impossible to obtain. When we went back to orthodoxy, accreditation came almost immediately, even though nothing had changed in the curriculum. It doesn't pay to be right if the rest of the world insists on being wrong!

After high translational energies failed to activate a chemical reaction, their success in determining T-V cross sections was particularly sweet as a vindication of our efforts in developing the seeded beam technique. Unlike some investigators I know, who eschew solving practical problems as a prostitution of science, I am always delighted when something I have a hand in turns out to be useful. Maybe that attitude proves that I am really an engineer! In any event, our success in measuring excitation cross sections paid some additional rewards. The "well done" of our sponsors was still ringing in our ears when they asked whether we would be able to obtain a resolved spectrum of the radiation we were measuring, i.e. to determine the distribution of rotational states in the excited molecules. At the time I had no expertise whatsoever in infrared spectrometry. All I knew was that my then colleague Gary Haller had long been trying to get funds for a Fourier Transform Infrared (FTIR) spectrometer because it was the most sensitive of available instruments. Thus, my half-joking response to the Air Force query was "Sure, if you will buy us an FTIR spectrometer." Knowing that such a machine would cost upwards of \$100,000, I thought that would be the end of that. Not at all. Said the Air Force, "Here is your money. Go to!" So off we went but, as it turned out, not very rapidly. It took two more years of frustration before we finally obtained a rotationally resolved emission spectrum of collisional excited CO<sub>2</sub> molecules, for us a tour de force.

In the determination of "total" T-V excitation cross sections, i.e. without spectral resolution of the radiation, we could locate the detector inside the vacuum system fairly close to the collision zone between the two jets. In the new assignment we had to "pipe" the radiation out of the vacuum system into the FTIR spectrometer. The photons had to travel a couple of meters, passing through a window, several lenses, and an interferometer before reaching the same InSb detector. Once again we had to undertake a tedious search-and-destroy mission for sources of noise and signal attenuation. After a year or more of no success we began to feel very uncomfortable at having nothing to show for either our efforts or the sponsor's money. We knew from the previous study that we could get very strong signals from the collision zone when the source of the jet containing CO<sub>2</sub> was heated because V-T relaxation did not occur during

the expansion. So we trained the spectrometer on a jet from a heated nozzle. Straight-away we began to obtain spectra that to us seemed beautiful after months of nothing but noise from collisionally excited molecules. Moreover, these spectra showed distributions of rotational energy states that were markedly non-Boltzmann. Similar results were obtained with CO and later with COS and N<sub>2</sub>O. We further found that the “non-Boltzmannality” increased as source temperature decreased. From such spectra we were ultimately able to gain insight on the relative roles of R-R and R-T transfers during free jet relaxation. Some of the most interesting of those later results have not yet been published, largely because we were diverted by two more smiles of Lady Luck.

The first one followed from an accidental discovery during the search for noise in the total cross-section studies. To achieve the highest collision energies required, the N<sub>2</sub>-seeded gas has to be hot. One day Batchie shut off the gas flow to both nozzles in order to measure the response of the detector radiation from the hot nozzle. Much to his surprise the signals were larger than when the both gases were flowing in an actual experiment! Upon investigation he found that the CO<sub>2</sub> flow had not been completely shut off; the large detector signal was due to radiation from molecules heated by a single collision with the front end of the hot nozzle, a disk only 3 mm in diameter. At that time the only direct observations on internal energy exchange during molecule-surface collisions had been by DJ Marsden in 1966 (not the David Marsden who had been our colleague). He had determined the distribution of rotational energy in nitrogen molecules before and after collision with a surface by spectrally analyzing the fluorescence induced by electron impact. We decided to follow up on Batchie's discovery by obtaining FTIR spectra of radiation from CO<sub>2</sub> incident on a hot surface from a rarefied cold jet. The very first experiments gave spectacular results, and in the next few months we obtained a lot of beautiful data on vibrational and rotational accommodation in molecules of CO, CO<sub>2</sub>, NO, and later COS during single collisions with a hot surface (8). To our knowledge those results constituted the first such data ever reported. A striking and unexpected finding was that in gas-surface collisions the efficiency of energy transfer for the three degrees of freedom of these polyatomic molecules is in the order  $V > R > T$ . In gas-gas collisions that order of efficiency is in general exactly reversed.

About that time at an AFOSR contractor's meeting Lennard Wharton reported that CO molecules incident on an oxygenated platinum surface departed as CO<sub>2</sub> molecules with translational energies much above those expected from thermal equilibrium with the surface. Some of the reaction energy apparently ended up as translation energy in the product CO<sub>2</sub> molecules. It occurred to me that some of that released energy might also find its way into vibration and rotation and that FTIR spectra might reveal its distribution. Dave Mantell, a physics graduate



student, was talking with Gary Haller about working on a surface problem of some sort. Gary, whose bag was heterogeneous catalysis, had helped us select and install the FTIR machine, knew about our surface accommodation work, and was eager to participate in it. Unfortunately, he didn't have funds to support another student, so I agreed to carry Dave on our Air Force grant. The two of them wanted to look at internal energy accommodation on truly clean surfaces. I persuaded them instead to look at the internal energy states of nascent  $\text{CO}_2$  molecules formed when CO molecules were incident on an oxygenated platinum surface as in the Wharton experiment. Once again we were lucky and hit the jackpot. Those newly formed species turned out to be much hotter internally than the surface on which they were formed. For the next couple of years we had a ball looking at the distribution of rotational and vibrational energies in those nascent  $\text{CO}_2$  molecules. For the first time ever we were able to put together a fairly complete picture of the distribution of reaction enthalpy among all the possible sinks—the surface as well as the rotational, vibrational, and translational degrees of freedom in the product molecules (9). What we learned provided some clues on details of the reaction mechanism. Contemporaneous with these studies, and also in our apparatus, Bret Halpern of Chemical Engineering and his student Moris Kori exposed a very thin layer of carbon on a platinum surface to a stream of oxygen atoms from a microwave discharge. FTIR spectra indicated excitation of as many as five or more vibration levels in the resulting CO molecules. The observed distributions were statistical except for a deficiency in the lowest level, which the investigators concluded was due to a more rapid flow of energy to the surface from that level than from the higher levels.

These surface interaction studies peaked in the early 1980s. By that time we were already (or only, depending on one's perspective) 30 years into the "modern" era of supersonic free jets in vacuum. These big leaks had proved to be immensely versatile and productive tools that had substantially extended the boundaries of old research arenas and opened up many new ones. Investigators all over the world were using free jets in many ways other than as sources of molecular beams for scattering experiments, the objective that drove their development. Indeed, the free jets now employed for that purpose are far outnumbered by those used to produce clusters and/or to condition molecules for spectroscopic studies. Even so, the now most widely practiced use of free jets is as a lock for transporting ions from sources at atmospheric pressure into vacuum for mass analysis! Once again I was lucky enough to get in on that new game near the beginning of its great growth.

In 1968, shortly after I arrived at Yale, Malcolm Dole and colleagues at Northwestern University and the Bendix Corporation published a paper in the

Journal of Chemical Physics that reported the production of gas phase ions of intact oligomers of polystyrene with molecular weights up to 500,000 (10). Their approach was to introduce a dilute solution of the polymer in a volatile solvent through a hypodermic needle into a chamber through which nitrogen flowed at atmospheric pressure. A potential difference of several kilovolts between the needle and the chamber walls would produce an intense field at the needle exit and disperse the emerging liquid into a fine spray of charged droplets that would drift down the field toward the end wall of the chamber. In the end wall would be a small orifice into a vacuum chamber housing a mass analyzer. As the droplets evaporated their surface charge density would increase until Coulomb repulsion overcame surface tension. At this stage, the so-called Rayleigh limit, the resulting instability would break up the droplet into a plurality of smaller droplets, each of which would repeat the evaporation-to-instability sequence. If the original solution were sufficiently dilute, this sequence would lead to ultimate droplets small enough to contain only one macromolecule, which would retain some of the droplet charge to become an ion as the last solvent evaporated. Some of the resulting mixture of macroions and bath gas would pass through the small orifice to emerge as a supersonic free jet in the vacuum chamber.

No conventional mass analyzer could weigh ions as massive as Dole hoped to produce, so he chose an unconventional approach. During the free jet expansion, the macroions would be accelerated to the readily calculable velocity of the bath gas (nitrogen) and then be directed through a set of retarding-potential grids to a Faraday cup from which the current to ground would be measured by a sensitive electrometer. Scanning the retarding potential on the grids would provide a current-voltage curve with a dip at each value of potential just high enough to prevent ions of the corresponding energy from reaching the Faraday cup. The potential at each such dip would be a measure of the kinetic energy of the ions that were being blocked. By assuming an ion velocity equal to the calculated velocity of the jet gas, one could obtain its mass from the value of its energy as measured by the potential required to prevent it from reaching the Faraday cup. The results reported in the paper seemed to confirm this scenario.

Not a systematic and conscientious reader of the literature, I was unaware of Dole's paper, but it had caught the eye of Professor Seymour "Sandy" Lipsky over in the Medical School. Sandy was a longtime student of mass spectrometry and chromatography with whom Csaba Horvath, a colleague of mine in Chemical Engineering, had had a long collaboration. Fortunately for me, Dole's paper had referenced some of our early work on the acceleration of heavy neutral molecules with  $H_2$  and He. When Sandy learned from Csaba that the John Fenn of Dole's references was at Yale, he got in touch with me and showed me

the paper. He was excited about the possibility that Dole's ionization technique might work for large biomolecules like proteins and make them accessible to mass spectrometric analysis. I too was excited at the prospect of a new application for free jets and persuaded a new graduate student, Mike Labowsky, to repeat Dole's experiments. Our vacuum system had more pumping speed than Dole's. Moreover, we understood free jet expansions a little better than he did and had the benefit of his experience. We made some changes and did get some results that seemed a bit cleaner than his, but we soon stopped further work. Earlier results of Friedman and Beuhler at Brookhaven had convinced both Dole and us that the large ions we hoped to produce would not give rise to secondary electrons from a dynode unless they were accelerated to several hundred kilovolts. Consequently, we had given up the megafold gains provided by ion multipliers and were using much less sensitive electrometers to measure ion currents that were painfully small. Moreover, the retarding potential method of mass analysis left much to be desired. Meanwhile Dole retired from Northwestern and moved to Baylor University, where he continued working with electrospray ionization but was using ion mobility to characterize the ions. He thus had much larger signal currents but much less information on the nature of the ions.

In 1981 Masamichi Yamashita joined our group for some postdoctoral studies. I had met "Gado" while on leave at the Institute of Space and Aeronautical Studies of the University of Tokyo in 1979. He had no particular research objectives, so I suggested that it might be interesting to revisit electrospray ionization, not with macromolecules but with solute species small enough to be weighed with an available quadrupole mass analyzer whose upper limit for mass was 400 Da. The effect of solute concentration on the mass of the solute cluster ions that Dole's charged-residue ion-forming mechanism should produce, might reveal something about the sequence of Coulomb explosions Dole had postulated. Gado liked the idea and built an apparatus by modifying an idle "minibeam" system we had assembled in Princeton. He was a marvelous experimentalist and within a few months was beginning to produce provocative spectra of solvated  $\text{Li}^+$  clusters when he electrosprayed dilute solutions of  $\text{LiCl}$  in 1:1 methanol-water, our workhorse solvent because of its good behavior. Many other solvents can be used, including nearly pure water, though its high surface tension makes spraying difficult and its high heat of vaporization slows the desolvation of both droplets and ions. The "nearly pure" that modifies water reflects the need for some conductivity in liquids to be sprayed.

One day Gado ran a "quaternary cocktail" of half a dozen tetraalkyl ammonium and phosphonium halides at concentrations of a few parts per million. The resulting spectrum showed a single clean peak for each cation species with no evidence of fragmentation even though none of those species could have

been vaporized without catastrophic decomposition. Thus encouraged, he ran a dilute solution of a vitamin B tablet and obtained a nice clean peak for each of its several species that had a molecular weight below 500, the upper limit of our quadrupole analyzer. Then he tried the amino acid arginine with similar success. Spreading his wings still further, he found he could obtain mass spectra for almost any organic compound as long as it had polar groups to which solution cations (or anions with the spray needle at a negative potential) could be bound, for example by ion-induced-dipole interaction. In addition to this versatility, electrospray mass spectrometry, or ESMS as the technique is now known (sometimes with an I for ionization before the M), is remarkably sensitive, producing peaks with very high signal-to-noise ratios for solutes at micromolar or less concentrations in sample solutions. We learned later that the Alexandrov group at St. Petersburg had also started to investigate ESI about this time. Their early emphasis seemed to be more on metal cations than on organic species.

Meanwhile, in 1976 Iribarne and Thomson had found that charged droplets produced by pneumatic atomization of ion-bearing liquid could produce free ions, a technique referred to here as aerospray (AS). Two years later Marvin Vestal and coworkers introduced thermospray (TS) in which analyte solution flows through a small bore tube hot enough to vaporize most of the solvent. The rapidly expanding superheated vapor atomizes the remaining liquid. Evaporation of the resulting droplets produces solute ions. Iribarne and Thomson proposed that the electric field on a charged droplet enables solute ions to evaporate from its surface, a mechanism that many believe best accounts for ion formation in all three spray techniques. ES is now the most widely used because its droplets have the highest charge/mass ratios and thus produce the most ions.

One day Sandy Lipsky, who had been keeping up with our adventures, brought to our lab his longtime friend Brian Green from VG Instruments, a well-known British manufacturer of mass spectrometers, now part of Fisons, Ltd. Almost immediately Brian asked if ESMS would work with large molecules. We couldn't say because our analyzer's mass range only went to 400 Da. Brian arranged to have VG lend us a used quadrupole mass spectrometer whose mass range went to 1500 with unit resolution (on a good day in the right phase of the moon). By the time it arrived Gado had gone back to Japan and Craig Whitehouse had joined the group as a graduate student, thanks to Sandy Lipsky for whom he had worked between college and graduate school. Also an extremely able experimentalist, Craig put together a new system to house the new mass analyzer. We then found we could get beautiful spectra with peptides having masses up to at least 1200 Da. Some of the ions were doubly charged, an intriguing result. After its initial enthusiasm for ES, VG lost interest because they decided that TS had more commercial promise.

*And Now Emeritus—Prestige Without Privilege*

In 1987 I was retired—by mandate—from my faculty position but was able to hang on to my lab for a while. About that time, we decided to pursue the intriguing observation of ions with more than one charge by using poly ethylene glycols (PEGs) as analytes. That choice stemmed from our belief, supported by intuition and some experiments, that the number of charges on an ES ion was determined by the size of its parent molecule. PEGs readily formed ES ions by attaching solute  $\text{Na}^+$  cations to their oxygen atoms. Moreover, samples were available with the same essential composition and structure over a wide range of molecular weights and at no cost, thanks to the generosity of the Union Carbide Corporation. Over the next year or so, Shek Fu Wong and Chin Kai Meng, postdoc and graduate student respectively, were able to show that ES ions of PEGs indeed exhibited charge multiplicity that increased with oligomer size. Unfortunately, at high molecular weights the superposition of broad charge distributions on a similarly broad distribution of oligomer sizes resulted in a multiplicity of peaks too close together to be resolved by our analyzer. The spectra comprised broad jagged bands that looked like very noisy sine waves. Indeed, a reviewer of our first paper asserted that what we were calling a spectrum was simply dirt in the system! We argued that the peak of the “sine wave” occurred at an  $m/z$  value of the most abundant oligomer with the most probable number of charges. On the basis of this reasonable and justifiable assumption, we concluded that oligomers with molecular weights around 8,000 and 20,000 formed ions with respectively up to 10 and 23 charges! Many subsequent measurements by other investigators have confirmed these conclusions.

Then we did what in view of our peptide results we should have done in the first place: tried protein molecules as solute species of uniform molecular weight. The result was another jackpot. The spectrum for each protein turned out to comprise a coherent sequence of peaks, the ions of each peak differing from those of adjacent peaks by a single adduct charge. The number of peaks (ion charge states) increased with the size of the parent molecule. Thus, the ES spectrum for bovine insulin, ( $M_r = 5,730$ ) showed three peaks corresponding to parent molecules with four, five, and six charges. For horse heart cytochrome c ( $M_r = 12,400$ ) there were 10 peaks for ions with from 12 to 21 charges, and for bacterial alpha amylase ( $M_r = 54,700$ ) there were 24 peaks for ions with from 35 to 58 charges. In each of these cases, and for most peptides and proteins in low pH solutions, the adduct charges were protons. This charge multiplicity of ES ions had the obvious advantage of greatly extending the mass range of any analyzer, very inexpensively. Our modest quadrupole had an upper mass limit of 1500 for the usual singly charged ions, but with it we had already “weighed”

ions with masses of 76 kDa! Even so, utter dismay was the initial response of every mass spectrometrists that saw one of these first spectra. They were all sure that with a multiplicity of peaks for each species, the spectra would be much too complicated to interpret. Moreover, such multiplicity meant that available charge was being divided among so many peaks that the signal-to-noise ratio, and thus analytical sensitivity, would be greatly decreased. Wrong on both counts, as it turned out, these mass spectrometrists had underestimated the power of the modern computer, as I myself am still wont to do.

When we began to get these results with proteins, Matthias Mann had joined the group as a graduate student. I had met him at the Max Planck Institut für Strömungsforschung in Göttingen while I was a guest sponsored by the von Humboldt Foundation, and he was working on his diplom research under Peter Tönnies. After staring at these new spectra for a few days, I said to Matthias one afternoon, "If you stop to think about it, each one of these peaks constitutes an independent measurement of the molecular weight of the parent molecule. There ought to be some way to average their information content to arrive at a more reliable value of that molecular weight." Two days later he walked in with a deconvolution algorithm by which a desktop computer could transform a measured spectrum with a multiplicity of peaks into a deconvoluted spectrum comprising a single peak that would have been obtained if all the parent ions had been singly charged. The  $m/z$  value of that single peak was the molecular weight of the parent species. Moreover, the algorithm could unravel the complex spectrum obtained with a mixture of several proteins, the deconvoluted spectra comprising a single peak for each species. In principle the number of species that can be resolved is limited only by the effective resolution of the mass analyzer.

These findings are summarized in an article in *Science* (11), but were first presented at the annual meeting of the American Society for Mass Spectrometry in San Francisco in 1988. Only 15 or 20 people were in the room but after that presentation what has been called the Electrospray Revolution spread rapidly. At that 1988 meeting there were altogether seven papers and posters on ESMS, two from our lab. The others, on small molecules, were from the labs of Henion at Cornell and Smith at the Pacific Northwest Laboratory, the first two groups to copy our methods. Six years later, at the Chicago meeting, there were over 300 communications involving ES ionization. A former colleague recently told me that in 1994 the term electrospray appeared in either the title or the abstract of 315 papers in the journals covered by the Science Citation Index! (By comparison, the corresponding score for fullerenes was 285.) All major manufacturers of mass spectrometers now provide ES sources for their new instruments, and many older machines are being equipped with them. I have no

firm figures on sales, but I think it safe to say that ESMS is now practiced in literally hundreds of laboratories throughout the world. If all the research activity in spectroscopy, cluster science, and molecular beam scattering experiments is added in, supersonic free jets must be counted a major tool in modern scientific research. Once a pox on many houses of laboratory research, big leaks in vacuum systems are now respected, admired, and even commercially exploited, a sure sign of intrinsic value in a culture that increasingly regards profitability as the summum bonum. Moreover, I suspect that ES applications are still in their infancy. Much of the present activity is purely analytical, concerned with detection and identification by molecular weight determination and sequencing of amino acids in proteins and base pairs in oligonucleotides. Brian Chait showed that the charge state distribution on ES protein ions reflects the conformation of the parent in solution. Now Fred McLafferty investigates the rate and extent of H-D exchange and their dependence on conformation and charge state of protein ions in the gas phase. Such possibilities were almost inconceivable a few years ago. Recently, Siuzdak et al (12) reported that viruses could undergo ESMS without losing their viability! In a very real sense, ESMS has opened windows on solution chemistry and biochemistry that promise exciting vistas I wouldn't have thought possible when I was a graduate student. Now I enjoy immersion in the electrolyte solutions that 55 years ago I had barely stuck my toe in but couldn't wait to get out of! It seems certain that much more excitement remains in store.

I am often asked, "Don't you get a lot of satisfaction out of seeing so many people now using the techniques and methods to which you introduced them?" The apparently obvious but simplistic answer to such questions is "Of course!" Among the greatest rewards for both parents and teachers are the joy and satisfaction of seeing their one time charges use and benefit from the lessons they, their mentors, taught them. On the other hand, those rewards can be soured a bit by resentment when the mentor's own interests become threatened by the success of his or her protégés. The explosive growth in ESMS has been accompanied by an exponential increase in the competition for limited research support. It was hard enough for me to get funding in the beginning when nobody else was working on it or believed in it. Indeed my first proposal to NIH was rejected on the grounds that "it is impossible for this investigator to obtain these spectra with his apparatus"! Of the fourteen proposals I have submitted to that agency, only three have been funded. One of the rejects was a supplemental proposal that the Study Section ranked in the top 5% of all candidates, but that year the Council decided to reject all supplemental proposals because funds were short. A revised, and I thought improved, version submitted as an independent proposal in the next competition was ranked in the bottom third

of all applications! So much for the reproducibility of peer review. All six of my proposals to DOE were rejected, even though the last one was highly recommended by the reviewers. Meanwhile that agency has spent millions on ESMS in its own labs, more in one year on just one group than my group has had since the beginning from all sources put together. I particularly object to competition by groups in DOE labs for grants from other agencies, especially when their proposals are based on techniques and concepts they have filched from others. In my view, funds from the likes of NIH and NSF should not be used to supplement the budget of an agency that has irresponsibly wasted so much of the taxpayers' money. My lab is now supported on its first grant from NSF on this subject, but with the competition for funding becoming more intense, my view of the future is dim. I often feel reminded of the old adage "No good deed deserves to go unpunished."

Actually, I am not quite as bitter about this record of rejection as I may sound. My ten years on Project SQUID gave me some experience on the dispensing side of research support. There are always more technically worthwhile proposals than can be financed with available funds, so decisions must be made on nontechnical grounds. In other words one must look for reasons to deny support to worthy investigators. Basing such decisions on age seems unethical and is illegal, but those charged with the responsibility for supporting science and technology must take the long view. Society dare not ignore the future by neglecting its youth and spending too large a fraction of its resources on its senior citizens. Nor should it turn its back on us old folks. That dilemma underlies the present consternation about Medicare and will precipitate the confrontation between youth and old age that seems inevitably bound to engulf the Social Security system. To insure the health of the scientific community and reap the rewards of research, society must nourish our successors during their development as we elders pass beyond our primes, vigorous though we may be (or think we are!). Even so, it is sometimes hard for me to accept the reality that hundreds of investigators get support for their proposals on ESMS research, not all of which is all that good, while its originator gets rejection slips. It is particularly galling when rejection is on the grounds that he hasn't proved that what he proposes will work, i.e. he hasn't already done what he seeks funds to try! In my view, such a comment is a judgment cop out.

The Patent System operates on the basis that the person who first conceives an invention (or makes a discovery) and reduces it to practice is entitled to a limited monopoly that gives him or her an exclusive right to practice that invention for a period of 17 years from the issue date of the patent. (That period was recently changed to 20 years from the application date.) In return for that limited monopoly the inventor is obliged to present a full disclosure



of the details of the invention or discovery. The underlying rationale for this arrangement is that society benefits more from free use of the disclosure after the patent expires than it would by denying the monopoly and risking the possibility that the details of the invention or discovery might remain a secret indefinitely. I often muse about the possibility of an equivalent arrangement for the research-support industry. An agency that sponsors research in a new area discovered by an "inventor" (originating investigator) should be required to provide support for that inventor in his own research. The extent of that support might be some modest percentage of the total amount of funding the agency supplies to other investigators in the new field, subject to appropriate limitations. I believe that such an arrangement would stimulate investigators to disclose new ideas promptly and would discourage some growing tendencies to keep ideas secret until their inventors are able themselves to explore and exploit them surreptitiously. My research support situation would probably be in better shape today if we had never disclosed, or even discovered, what we have learned about ES ionization!

The observant reader may have wondered why I have returned to Richmond, VA, where my career in reasonably basic research really began at Experiment, Inc. 50 years ago. After I was forced to retire, Yale became increasingly inhospitable toward my continuing research, even though the results which ignited the explosion of interest in electrospray came after my retirement. Not only was the university unwilling to give me space for a new mass spectrometer I had at last acquired, I was asked to give up two thirds of the space I was occupying. Yale's position: It is university policy that emeritus faculty are not entitled to lab space except under exceptional circumstances! I then applied for an open slot as an assistant professor in Chemical Engineering, precipitating a flap in administrative councils, so I heard by the grapevine. I finally received a letter from the Provost saying that because an assistant professorship was a ladder faculty position, expected to culminate in tenure at Yale or elsewhere, and because I had been tenured and under applicable law could be required to retire, the university felt justified in refusing to consider my application! (Both federal law and Yale policy require that age shall not be a consideration in filling an entry level position!)

Other universities had offered me lab space, but Magee had many ties to New Haven, was active in YUWO (Yale University Women's Organization) and wanted to stay in New Haven, so I muddled along there as best I could. After I lost her in New Zealand I began to think seriously about leaving Yale when Fate smiled once more. During a trip to Richmond to see old friends, I encountered Freda Mullen, widow of the Jim Mullen who first brought me to Richmond. One thing led to another and we are now happily married. Moreover,

I have a lab at VCU for as long as I can finance it. I realize I've already spent my fair share of research funding, but there remain many things I am eager to learn. I just hope I can find enough support to continue stumbling for a while along the road ahead, kicking over stones here and there, driven by curiosity to find out what may be hidden under the next one. Perhaps the Fate that has already flooded me with good fortune can fling me another favor or two.

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