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Evolution: Science and Scientist

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Science attracted me even in early years; a microscope, a gift from an aunt and uncle, was fascinating but too passive. When I received a long-wanted chemistry set at about age 8, I began the meandering course of a life of curiosity and bewilderment about the world. The chemistry set grew into a home laboratory, nothing of the scale described by Oliver Sacks, but nonetheless a source of many hours of delight and fascination. Visiting my grandparents in Fort Collins meant that my pal Alan and I could go to the trash bins behind the Chemistry Building of Colorado Aggies (now Colorado State University) to find beakers and flasks that we could clean and add to our labs. A great prize was the discovery of a battered copy of James B. Conant's *Organic Chemistry*, a book that opened a world beyond *Microbe Hunters*, *Magic in a Bottle*, and *Crucibles*. It was clear by the time I was 15 that physics, being about ladders leaning against walls and pulleys, was boring, and chemistry, dealing with the structure of the atom, was fascinating. And mathematics was always there, but the fascination of its beauty stayed hidden from me until I reached university. Fortunately, my tolerance for other sciences did expand with time.

The Westinghouse (now Intel) competition was a turning point. The outstanding physics teacher of East High School (Denver), not my teacher but someone I knew, casually suggested that I might want to enter, and offered the forms to me. The tasks were light, apart from carrying out a scientific project, so, I thought, "Why not?" I knew I'd enjoy doing a systematic project and I did (in retrospect, I saw that it was almost certainly nonsense) so I completed the requirements for entry, with no expectations at all. An early-morning phone call some weeks later informed me I'd won a trip to Washington! My photo appeared in a local paper, and I was, briefly, a bit of a celebrity. But the trip to Washington did change my direction. I met real scientists for the first time, and, even more important, a group of other teenagers setting out to become like those scientists. It was in Washington that I learned that one could get a fine education in science at Harvard, as well as one in liberal arts. And by that time, I had decided I wanted to learn about a lot more than science before I began a professional career. (In fact, I had only a very diffuse, unformed notion of what sort of career I might have, apart from something that would let me do science.) Consequently, I applied to Harvard, having already applied to MIT and Caltech, and accepted as soon as I was admitted.

Four years exploring everything possible, except biology: chemistry, physics, mathematics, history, literature (English and German), music, art, psychology, philosophy, they were all there. One only needed to go to the lectures and do the reading; it was not necessary to take more than the basic requirements for formal credit. Auditing provided a matchless opportunity to try everything. Even in graduate school, that habit continued a bit.

Graduate school—where? I decided to stay at Harvard for two reasons. One was that Harvard's senior physical chemists were away during my undergraduate years, so I had never met them. The other was a girl friend, later (and still) wife. I tried to do a Ph.D. thesis that combined experiment and theory, but the experiment I tried was simply too difficult and complex for a student with a research budget of about $300 per year. (It was done a decade later by Bob Freund at Bell Laboratories.) However, as soon as I completed the theoretical study of the π-electrons of butadiene, working with Bill Moffitt, I decided to do experiments. There was an excellent opportunity to do something simple, in a collaboration with Bill Klemperer and Stuart Rice. They were studying the infrared spectra of gaseous alkali halides and found a discrepancy between their results for lithium halides and some early results from ultraviolet spectra. I remeasured those ultraviolet spectra and reconciled the two sets of experiments. Then I noticed that spectra of NaI taken 30 years earlier showed a fine-line structure, unlike any of the other alkali halides. I reexamined these and convinced myself-that there had to be something very interesting that distinguished this molecule from all the others, especially KI, that one might expect to be very similar. This led me to my first original theoretical investigation, the way a quantitative difference between the two molecules could lead to qualitatively different spectra, because of the way one obeyed the Born−Oppenheimer approximation and the other did not.

Pseudorotation of PF_5 and other molecules was the next theoretical problem I studied. Somehow I'd learned that the NMR spectrum of PF_5 showed that all the fluorines appear equivalent, despite the trigonal bipyramidal structure of this molecule. It was probably my fellow student Andrew Liehr who told me; he'd found that result as an undergraduate at the University of Illinois, working with Herbert Gutowsky. Then another classmate, Felix Smith, described the pseudorotation model he and Bill Moffitt were exploring to try to explain the structure of CH_5^+. It turned out that the same model had been used by John Wheeler and Edward Teller in the 1930s to try to describe the ^{20}Ne nucleus as five alpha-particles. It also turned out that neither CH_5^+ nor the ^{20}Ne nucleus conformed to the trigonal bipyramid model, but PF_5 did! When I wrote my paper on PF_5, the pseudorotation was something I took pretty much for granted, even as rather obvious, and focused the main effort on showing how tunneling rates of a series of homologous compounds could be estimated from knowledge of one member of the series. It was a lesson in how one's own ideas of what is important do not always fit with those of other people. In any case, a couple of years later, George Whitesides did the experiments that showed that the pseudorotation picture is correct for 5-coordinated phosphorus.

At the same time I was working on pseudorotation and floppy molecules, I was laying out plans for an experimental program to take absorption spectra of free, gaseous halide ions in alkali halide vapors. Stuart Rice and Bill Klemperer had done thermodynamic calculations of the compositions of alkali halide vapors, calculations that suggested that if one could heat these vapors to temperatures of order 2000 K, one could produce enough free halide ions to provide clear absorption spectra. Giangualberto Volpi, then a postdoctoral associate with George Kistiakowsky and a lab partner of mine, asked, when I told him I'd like to study very hot alkali halide vapors, "Why not

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use a shock wave? I thought about this, looked into it and decided it was just the right approach. And then I went off to the University of Michigan, to set up a shock tube.

That was truly serendipitous. Otto Laporte was one of the senior bright lights of Michigan's Physics Department, and an expert in shock waves and shock tubes. He and his graduate students were enormously helpful, especially regarding the design of the apparatus. My first postdoctoral associate, Neil Spokes, came to me from the Gaydon group in London with many fine ideas and very considerable skill in the lab. Our first spectra were one-shot experiments, one fast flash timed to go off and provide the source for an ultraviolet absorption spectrum at a time just after the shock, usually the reflected shock, passed the windows in the shock tube. We did not know what the absorption cross sections would be, so we did not know how large a sample to use. Our first spectral plate, taken with NaI vapor, showed a black stripe over the length of the plate from the spectrum of the lamp alone, and a black stripe going only halfway across the plate from the spectrum. Its sharp edge was the mark of the onset of the continuous absorption of I^-, from the threshold for its photodetachment. In our first shot, we'd determined the electron affinity of the iodine atom to almost two significant figures than it had ever been known previously.

Neil Spokes had come from a group where the technique of flash photolysis was a lively new method. Neil wanted us to try flash photolysis. I was all for it, but insisted that we first find a truly interesting system to study. My colleague Martin Stiles, in physical organic chemistry, provided such a system. Martin was pursuing a direction related to one initiated in Germany by Liselotte Pohmer (better known at Chicago as Lielo Closs) and, somewhat reluctantly, her director Georg Wittig: the study of benzyne, *ortho*-C_6H_4, benzene with a triple bond. Martin invented a new precursor for benzyne, *ortho*-benzene diazonium carboxylate, benzene with one hydrogen substituted by an N_2^+ group, and the adjacent hydrogen, substituted by a CO_2^- group. Martin reasoned, correctly, that such a molecule would release N_2 and CO_2 very readily. It does. The first time he made it, the material blew a Büchner funnel to powder, fortunately behind a protective shield. But the chemical products showed that benzene diazonium carboxylate is indeed a benzyne precursor. That would clearly be the object of our flash photolysis study! We built the apparatus during our last months in Ann Arbor, as we prepared to go to Yale; days, I would pack things, and nights, we'd run experiments. The very first photolysis showed that the products contained the dimer and trimer of benzyne, and very soon, we had spectra of benzyne itself. When I settled at Yale, these experiments (as well as the shock tube studies) continued, augmented by a new time-of-flight mass spectrometer that allowed us to make unambiguous assignments of at least the masses of the species whose spectra we'd been taking. An undergraduate, John Clardy, extended this work by synthesizing the extremely sensitive, explosive meta and para isomers of the original benzene diazonium carboxylate. Of course we studied the optical and mass spectra of these.

As Stuart Rice's biography says, we moved to Chicago when I joined The University in 1964. In fact, I accepted my position late in the Spring of 1963, but it was obvious that the natural time to move would be at the end of the following Spring Term. That had one unfortunate consequence for me; I never met James Franck. Each time I started to investigate a new problem, particularly a theoretical problem, it seemed that the first person to think about that problem, whatever it was, was James Franck. Franck died during the last academic year I spent at Yale.

I moved all the shock tube and flash photolysis apparatus to Chicago, and with all that, an idea for a new kind of experiment. I'd decided to try to merge two beams of ions, one negative and one positive, to study low-energy collisions that produced mutual neutralization of the ions. I'd become interested in atomic and molecular collisions, particularly in vibronic coupling, and began a line of work that continues still. Low-energy neutralization collisions were the basis of John Weiner's thesis. He continued to be interested in all sorts of low-energy phenomena, and has dropped all the way down to Bose-Einstein condensates.

A year in Copenhagen expanded the collision studies when, in our first conversation, Svend Erik Nielsen and I realized that vibronic coupling in bound states is intimately related to associative ionization and dissociative recombination, and that all these processes could be treated with a common approach. In that first conversation, we laid the basis for eight or 10 years' work.

Moving to Chicago stimulated another line of activity for me, a line I would never have guessed or predicted. Chicago in the 1960s suffered from a very, very polluted atmosphere. I thought I was psychologically prepared for this, but it turned out I was not. I became very angry about it, and wrote an angry letter to Mayor Richard J. Daley, with a copy to our alderman, Leon Despres. The alderman and I were invited to visit the city's pollution control facilities. They were so clean and orderly that it was obvious that not much was being done. I joined a community effort to try to change things, beginning with getting the existing laws and regulations enforced, and then, we hoped, getting the laws and regulations made stricter. This was, in retrospect, a fascinating time because environmental protection and minimizing pollution were changing from subjects only for subrosa grumbling into topics of public debate. It was a time of fundamental political transformation. Our economists, looking backward, would say it was the time that the costs of regulation had fallen below the costs of living with pollution—but they did not recognize it at the time. As a scientist, I was able to help answer some of the questions of the lay public, and to read and understand technical publications about pollution and pollutants. I was primarily a concerned, active citizen, but was also a little bit of an expert too. In any event, the laws and regulations did change, and with them, Chicago's air and water turned clean. By 1970, Florence (Mrs. Willard) Stout could point out to me that Chicago's snow stayed white for 3 days!

Despite the reduction in air pollution coming primarily from the change from coal to gas as fuel, I began to wonder how one might go beyond addressing immediate symptoms and examine deeper causes. By the summer of 1969, I thought one should examine the possibilities of improving the efficient use of energy, because energy consumption was responsible for most polluting processes. A summer's work, originally intended to "solve" the problem, turned out to be a good pilot study for the research that Margaret Fels and I did, on the energy and free energy used in producing and disposing of a single major consumer product, the automobile. We collected all sorts of data from factories and engineering process texts, and compared the actual consumption of energy and free energy, step by step, with the ideal thermodynamic limits. This, we decided, would reveal those steps that should return the greatest increase in efficient use of energy if they were improved technologically. The approach, which we called "energy analysis" (at the suggestion of Thomas V. Long in our group) and was later called "life cycle analysis," was adopted by many others studying energy use, and was applied to many systems and processes. Dow Chemical used a limited form of it, just examining what happened within its plants, to improve the efficiency of its operations. Their work and ours were essentially simultaneous, and as soon as we learned of each other, we established a stimulating dialogue.

Then, the unexpected happening: I was asked, “Why do you compare the actual consumption with the ideal thermodynamic limit? That limit corresponds to a reversible (infinitely slow) process, and who would order a car from a manufacturer who makes them reversibly?” This question led to perhaps the most unexpected, yet perhaps the most widely-reaching line of research I had undertaken. I would never have guessed, in previous times, that I might actually do research in thermodynamics. Nonetheless that challenging question led to a set of more precise, scientifically addressable questions that formed the basis of many subsequent years of research. That work took shape when it became clear that one could ask, “What would be necessary and sufficient conditions for the existence of quantities analogous to thermodynamic potentials, but for systems whose definitions included constraints on the time or rate of their operation?” (These analogues of potentials would have the properties that their changes would equal the extremal work or heat that the system or process could exchange under the specified conditions.) The next natural question was, “If they exist, how can one construct and evaluate such potentials?” One step further, one asks, “How can one find the pathway of operation that makes the system operate as near the ideal limit as possible?” Peter Salamon, Bjarne Andresen, and others, including Abraham Nitzan and Morton Rubin in early days, worked with me on this topic. A few years after we had been publishing, Lev Rozonoer and Anatoly Tsirlin, in Moscow, independently started along the same lines. As soon as we discovered each other’s work, we began corresponding and eventually, collaborating. Many students and postdoctoral associates worked on problems in finite-time thermodynamics, as we came to call the approach. This is another line of work that continues even until now, most recently with Tsirlin and Stanislaw Sieniutycz, from Warsaw.

During the mid-1950s, Stuart Rice, Dudley Herschbach, Bill Klemperer and I talked frequently about what the “big problems” of physical chemistry would be in the coming decades. We agreed on several; among them were the exploration of the new approach of reactions in colliding molecular beams, the nature of liquids, the problem of excluded volume of polymers, and the nature and consequences of electron correlation. These conversations obviously shaped the thinking and career paths of all of us. In time, I found myself working on electron correlation. We had developed a graphic method for displaying two-electron wave functions at about the time that doubly excited helium atoms became known. David Herrick and his postdoctoral associate (and my former student) Michael Kellman found that the energy level pattern of doubly excited helium was extremely like that of a rotor-vibrator, with collective rotations and bending vibrations. When we learned of this, we immediately examined the wave functions of these states with our graphic approach, and then with more quantitative tools. From there we turned to the valence electrons of the alkaline earth atoms. In these, we found that the ground and low-lying excited states exhibit so much correlation that most of their commonly found states are far better described by collective, rotor-vibrator models than by the independent-particle, Hartree–Fock model that we had all been taught was the natural starting point for these systems. The stretching modes, however, do not fit a harmonic model at all; they must be represented by symmetric and antisymmetric combinations of local modes. After all, what could be less like a parabolic, harmonic well than a Coulomb potential?

My interest in nonrigid molecules never disappeared. We returned to it in the early 1980s, when Michael Kellman, Francois Amar, and Gregory Ezra developed a way to construct energy level correlation diagrams linking the vibrational spectra of traditional rigid molecules with nonrigid models of floppy molecules containing the same number of atoms. The goal was finding how the spectral pattern of the vibrations of a somewnat nonrigid molecule would reveal the mechanism and pathways of the nonrigid motions. Again something unexpected occurred; Jamie Burton, then at Notre Dame, gave a seminar at The University of Chicago on his simulations of clusters of rare-gas atoms. His molecular dynamics showed that small clusters could exhibit well-defined solidlike and liquidlike forms, and, at suitable energies, pass quickly between these two forms. Burton, in a publication on this work, suggested that these clusters might even be exhibiting a first-order phase transition. This, of course, was heresy to us, who were taught that small systems must exhibit gradual, smooth transitions between, for example, solid and liquid phases. It was immediately clear that our correlation diagrams gave us an easy way to estimate densities of states for solid—i.e., rigid—and liquid—i.e., nonrigid—forms of clusters. And with these densities of states, we could readily compute the thermodynamic properties of the phase-like forms of clusters. All we had to do was postulate that the two forms could, at some condition or conditions, both be locally stable. Julius Jellinek, Grigory Natanson, and I made such calculations and showed that one could reproduce the thermodynamic characteristics embodied in Briant and Burton’s simulations, and in others done about the same time.

Then the challenge became finding necessary and sufficient conditions for the simultaneous local stability of two phase-like forms. We succeeded in doing this, and in demonstrating that *more* than two phase-like forms could be locally stable, and that minority phases of small systems could be found in observable amounts. It was not long before we could show the connections, the similarities and differences of phase equilibria of small systems and bulk systems. Several students and postdoctorals made this work move rapidly. We were soon examining the dynamics of several kinds of clusters and how these dynamics could be related to the topographies of the effective multidimensional potential surfaces that governed the particles’ motions. A trigger for the next step was John Rose’s finding that as alkali halide clusters cool from liquid forms, they find their way to rocksalt crystal structures, even though the locally stable amorphous structures on their potential surfaces outnumber the crystalline forms by many orders of magnitude. In contrast, rare gas clusters cool from their liquid states to amorphous structures. The alkali halides are “structure-seekers,” and the rare gases are “glass-formers.” From this knowledge, it was natural to ask what characteristics of the topographies of the potentials made the crucial difference. This emerged from the work of several people, most notably Ralph Kunz, then a graduate student at the Technische Universität, Berlin, who had spent a year with us in Chicago working on phase changes of clusters.

Recognizing the similarity of the behavior of structure-seeking clusters to that of folding proteins was unavoidable. Soon we were trying out the results from clusters with a simple protein model. We found that the same general rules do indeed apply: a topography with some sharp, large drops, as in a bumpy staircase, makes for structure-seeking, in contrast to a more sawtooth-like topography, that traps systems in random, amorphous structures. Shortly after these results appeared, I received a message from Ariel Fernandez, wondering whether the work he and his student Andreas Colubri had started could be related to what we had been doing. That triggered a collaborative study of protein dynamics that has now become one of the central components of our research.

What does this little history tell us? I will be arrogant enough to extrapolate from my own experience and perspective. Perhaps foremost is the centrality for research of being receptive to those new bits of information that awaken an awareness that a new question needs to be articulated. One recognizes, in a diffuse way, that there is some kind of puzzle there; then begins the most exciting phase of science, turning that diffuse notion into one or more questions that one can address with the tools of science and mathematics—or for which one might be able to invent the tools. But doing science this way can be a bit lonely, sometimes. One finds oneself going in directions, whether in unexplored fields or in unconventional directions in well-populated fields, that others may only recognize slowly. But if one's motivation is the satisfaction, the excitement of realizing one is adding a tiny, new morsel to the vast heap of scientific knowledge, that one has laid the groundwork to change the thinking of other people, then the questions of "loneliness" or slow acceptance are irrelevant. So long as the work is done competently and convincingly enough to merit publication, that is enough.

Each of us has a personal style of doing science. In contrast to my late colleagues Subramanyan Chandrasekhar and Richard Bernstein, who planned courses of research for many, many years into the future, my personal style has followed a different kind of path. While I see a continuity in much of what I have done, following two or at most three paths, each of these paths has taken unexpected, sharp twists that have led my colleagues and me in new directions, directions we could not have predicted when we embarked along these paths. I would never have guessed that I would devote years to research in thermodynamics, or that I would delve into problems of molecular biology. Yet following these paths, with their twists and turns, has been the most natural way for me to try to make a creative life from the fascination and bewilderment that the world around us stimulates in me.