Autobiographical Notes of Aron Kuppermann[†]

I shall attempt in these notes to identify those aspects of my life that most influenced my scientific career. As a result, they have a strong personal flavor.

My father was born in Warsaw, Poland, and left home at the age of 18, spending four years in Germany before immigrating to Brazil. My mother was born in Trostenetz, a small shtetl in Ukrania, and immigrated to Newark, New Jersey, with three older half-brothers when she was about 14. Her mother immigrated a few years later to São Paulo, Brazil, with the remaining four children and step-children. After my mother became an adult and a citizen of the United States, she traveled to Brazil to visit her mother whom she had not seen since leaving home. There she met and married my father. However, she could not get used to living in the provincial environment of São Paulo of the mid 1920s and, when I was six months old, the three of us moved to New York. Neither of my parents had a college education, and my father eked a meager living during the depression years as a laborer in a small factory making women's purses. When I was three months old my mother was diagnosed with breast cancer, spent the remaining three years of her life in hospitals, and died at the age of 34. I spent those years in foster homes and orphanages and after her death my father moved us back to Brazil, where he remarried a few years afterward. He opened a small haberdasher's shop, where my stepmother helped him out. Such were my early beginnings.

Despite my parent's very limited means, they made sure I always attended good schools. I clearly remember the day I became excited about mathematics. I was in sixth grade, and was being exposed to pre-algebra word problems. The teacher posed one such problem and said, after challenging the class to solve it, that it had no solution. That sounded counter-intuitive to me. The problem involved two unknown quantities, whereas we had been accustomed to one only. However, two pieces of information were given, rather than the usual one, making the problem soluble. I went to bed thinking about it and awoke in the middle of the night with the correct solution in my head. I was very excited and the next day presented it to the teacher. He initially challenged it but eventually had to accept it, and graciously presented it to the class. That was the first inkling of how exciting and fulfilling the activity of solving challenging problems was for me. That excitement has been with me ever since.

It is interesting to speculate on which circumstances determine one's choice of career. In my case, and in many others I suspect, there is a high element of randomness. I had a cousin who was my namesake, one year older than I, and whom I greatly admired. One day when I was about 10, he asked me what I wanted to be when I grew up. Not having thought about the matter previously, I told him I did not know, and asked in turn what he wanted to be. He answered that he wanted to be a chemical engineer. "What does a chemical engineer do?" I asked. "He manufactures soap," was his answer. "That sounds interesting," I replied. And I decided then and there to become a chemical engineer, which he never did. As the time to enter college approached, I was able to rationalize that choice as offering a combination of science and mathematics, which I greatly enjoyed, and providing a profession which would allow me to earn a living. I was admitted to the Polytechnic School of the University of São Paulo to pursue that career. That school was modeled after the École Politechnique in Paris, founded by Napoleon. The course was a very demanding one, consisting of five years of studies involving 40 hours or more of classroom and laboratory work per week for its entire duration.

In my third year I took a course in Organic Chemistry, and was exposed to Markownikoff's rule, which dated back to 1870. According to it, the addition of hydrogen chloride to the double bond of propylene occurs with the chlorine atom adding to the middle rather than the end carbon atom, resulting in isopropyl chloride rather than propyl chloride. I asked the professor, a chemist of the old descriptive school, what the reason was for that behavior. He answered that that is the way nature is. That unsatisfactory answer led me to repeat the question to the Physical Chemistry professor, who was equally unhelpful. However, his assistant directed me to Pauling's *The Nature of the Chemical Bond*, from which I progressed to Eyring, Walter, and Kimball's Quantum Chemistry book for a more quantitative description. To my chagrin, I found that my preparation in Mathematics and Physics was insufficient to cope with that book. I had had two years of Calculus and Physics each. The Chemical Engineering curriculum, as all other curricula in Science and Engineering at the University of São Paulo, was entirely prescribed and did not include elective courses. I had done very well in my classes, but the Calculus ones did not include partial differential equations and the Physics ones were limited to Classical Physics. I came to the conclusion that to learn Quantum Mechanics I had to become a Physics major. That required taking new entrance examinations and starting from scratch in the Physics curriculum, as if I had never been at the University. That I did, and while I was in my last year of the Chemical Engineering program I was concurrently a freshman Physics major. Since that department was in a totally different part of town than the Engineering School, this entailed a very time-demanding commuting effort. After graduating as a chemical engineer, I spent two years as a chemistry instructor at the newly created Aeronautical Technological Institute, modeled in part after MIT. I continued my Physics studies, however, and found the experience extremely worthwhile. I learned Mathematical Physics from Abrahão de Morais, a top-notch theoretician, and Quantum Mechanics from David Bohm.

The year was 1952. David Bohm had just published his superb Quantum Mechanics book and his two papers on a reinterpretation of Quantum Mechanics, a topic that is reemerging as a useful tool for viewing quantum phenomena from a different perspective. His contract as an Assistant Professor of Physics at Princeton University had not been renewed because he had refused to testify during the McCarthy era hearings of the House Un-American Activities Committee and he had been declared in contempt of Congress. He left the United States in 1951 to take a position at the University of São Paulo, and I took his course the following year. That put my grasp of Quantum Mechanics on a good basis.

By then I had married my wonderful wife, Roza. I had decided that I would like to become a research scientist, a very

[†] Part of the special issue "Aron Kuppermann Festschrift".

10.1021/jp004063f CCC: $20.00 © 2001 American Chemical Society
Published on Web 03/15/2001

incipient profession in Brazil. I believed that that required spending some time abroad. I applied to the Institute of International Education, an agency affiliated with the U.S. government, and to the British Council, for one-year fellowships. I received them both, and decided to take them in succession. In Britain, we spent a year at the University of Edinburgh, a university I selected because it offered both Radiation Chemistry and Quantum Mechanics. Training in the former, which I confused with Radiochemistry, was intended to help me secure, upon my return to São Paulo, a position at the newly created Atomic Energy Institute. The latter was aimed at improving my background for becoming a theoretical chemist. I took a fascinating course with Max Born, who had found refuge in Edinburgh from Nazi Germany, and was rapidly approaching retirement. From him I learned firsthand the historical development of the ideas of Quantum Mechanics, which has been invaluable to me ever since.

After our exciting stay in Edinburgh, we went to South Bend, Indiana, under the second fellowship, where I intended to do some research in Radiation Chemistry at the University of Notre Dame for one year. In my application to the Institute of International Education I had stated that I was interested in studying Theoretical Chemistry and Radiochemistry and indicated Caltech as my first preference, followed by Berkeley and Harvard. Many years later I was told by Linus Pauling that my application wound up on his desk, as chairman of Caltech's Division of Chemistry and Chemical Engineering. He responded that although there was an opportunity for studying Theoretical Chemistry at Caltech, there was no program in Radiochemistry. He recommended that my application be sent to Notre Dame, where there were both. Just as had happened with me, he confused Radiochemistry with Radiation Chemistry. Notre Dame had one of the founding fathers of the latter, Milton Burton, as well as an excellent theoretical chemist, John Magee. I learned a lot from both. During our first year in South Bend, Roza taught freshman Chemistry at St. Mary's College, across the road from Notre Dame, and helped support us. During the second year our first son, Baruch, was born. Although I was supposed to stay for only one year at Notre Dame, Burton convinced me that it would be better for my career to obtain a Ph.D. degree, even though those degrees were rare in Brazil, especially at the Atomic Energy Institute. After slightly less than two years of doing experimental research on the chemical effects of electrical discharges, as well as theoretical work on diffusion kinetics in Radiation Chemistry, I completed that degree. Once more, Burton convinced me that it would be useful for my career to acquire some academic experience in the United States before returning to Brazil. He informed me of an opening at the University of Illinois at Urbana-Champaign at the instructor level. I applied and received an offer, joining the Chemistry Department in the fall of 1955. And so began my academic career in the United States. I am grateful to Burton for his professional guidance, which profoundly affected my career and life.

During my graduate studies I learned that excited triplet states of molecules produced by collisions with low energy electrons played an important role as precursors of free radicals. However, little was known about them because of the forbidden nature of optically-induced transitions from ground singlet states. This stimulated the design and construction of a low energy electron impact spectrometer at Illinois. The technique eventually led to the identification of hundreds of triplet states of molecules before laser-based techniques were developed. I had also read that the nitric oxide-inhibited pyrolysis of saturated hydrocarbons occurred via the unimolecular decomposition of vibrationally-excited states, and the study of the rates of these processes accounted for most of the experimental knowledge about unimolecular reactions at the time. Having learned how to prepare per-deutero butane and to use analytical mass spectrometers, one of my first Ph.D. students and I were able to show that the extent of isotopic scrambling in the pyrolysis of mixtures of ordinary and per-deutero butane was the same and statistical in both the presence and absence of the nitric oxide inhibitor. The results clearly showed that the reaction occurring in the presence of the inhibitor was not unimolecular, since if it were it should have produced no isotopic scrambling at all. Finally, the existence of Illiac I at the University of Illinois, one of the very early programmable electronic digital computers, permitted us to accurately solve for the first time the free radical diffusion-reaction equations which had been postulated to describe the radiation chemistry of dilute aqueous solutions. The results of these calculations were in excellent agreement with experiment and put this theory on a firm ground. These three projects launched my career as an independent researcher. They were based on a strong desire to understand the behavior of macroscopic chemical systems on a molecular level, using experimental and/or theoretical techniques, depending on which one was most appropriate for the problem under consideration. That perspective has guided my research until this day.

For four years I shared an office with Martin Karplus. He arrived in Urbana in the same year that I did, and from him I learned Quantum Chemistry. We interacted strongly and became close friends.

After a few years at Urbana-Champaign, I decided to spend a year in São Paulo as a test for a permanent return to our grass roots and family environment. I was offered a job to develop a Radiation Chemistry program at the Atomic Energy Institute. By then, Roza and I had three children, Miriam and Nathan having been born in Urbana. We arrived in late 1959 but, after six months, the difference in the atmosphere and resources for doing research in Brazil and the United States came clearly into focus. At that time, over 40 years ago, I realized that two options were available to me: I could either live in Brazil *or* be a research scientist, but I could not do both. It also became clear that my commitment to science was so deeply ingrained that to give it up was not a realistic choice. As a result, we returned to Urbana and shortly thereafter I was given tenure. The move to Caltech occurred in 1963 and our fourth child, Sharon, was born in Pasadena three years later.

The years at Caltech have been very fruitful and stimulating. My research expanded in the direction of elementary reactions under non-Boltzmann conditions. We developed experimental techniques for studying the reactions of monoenergetic hydrogen or deuterium atoms of variable energy with simple molecules, and were able to determine the threshold of such reactions from these studies, directly confirming the existence of activation barriers. We built a crossed molecular beam apparatus and demonstrated the existence of quantum oscillations in the interactions between diatomic molecules. We also built a variable angle photoelectron spectrometer that showed that electrons photoejected from sigma and pi orbitals had significantly different angular distributions.

We had started doing classical trajectory calculations for unimolecular decompositions of simple triatomic molecules while still at the University of Illinois, but the attractiveness of using accurate quantum mechanics to do such calculations for simple bimolecular reactions was irresistible, as this would directly explore the foundations of absolute reaction rate theory. At Caltech, we developed techniques for performing, for the first time, accurate ab initio quantum mechanical calculations of state-to-state integral and differential cross sections for the reactions of atoms with diatomic molecules. Such techniques and calculations are currently being extended in our group to tetraatomic systems. They have involved extensive use of massively parallel computer codes, which we developed before such computers became commercially available. As time went on, it became clear to me that the questions regarding simple chemical reactions which I was interested in exploring could better be answered using advanced theoretical and numerical techniques and state-of-the-art computers than by doing experiments on those systems. Such questions were of a stereochemistry nature and involved the effect of the relative orientation of the reagents and the polarization of the products in such reactions. In addition, I was interested in determining the sensitivity of dynamic resonances, whose existence we had first discovered in quantum calculations of collinear reactions, to the details of the potential energy surfaces in the strong interaction region. The freedom of changing these surfaces at will in theoretical calculations permits a deeper understanding of their relation to reaction dynamics. For these reasons, I switched my research efforts completely to theoretical quantum reaction dynamics, which is where I currently stand.

As a result of emigrating from Brazil where I had done my undergraduate studies, I became interested in helping the development of Chemistry in that country, as best I could. The first opportunity came when Carl Djerassi, of Stanford University, initiated in 1969 a collaboration program between the U.S. National Academy of Sciences and the Brazilian Conselho Nacional de Pesquisas-CNPq (their equivalent of our National Science Foundation) to strengthen graduate education and research in Chemistry at the Universities of São Paulo and Rio de Janeiro. That program paired about ten American academics with an equal number of Brazilian ones and started new research efforts at those universities. The transfer of scientific know-how was accomplished through young postdoctoral fellows, trained mainly in one of the participating Americans' research groups, and who then spent three or more years living and working in Brazil. Each American professor visited Brazil once or twice per year for about one week at a time. Some of these postdocs now have permanent academic positions in Brazil. The program lasted for seven years, and I was its chairman for the last three. It was very successful and strongly influenced chemical research in Brazil. As a result of that program, I later became involved in Science and Technology programs of the World Bank for developing countries. In the late 1970s and early 1980s, the World Bank concluded that modern technology could be an important tool for accelerating the economic development of such countries. To introduce such a tool required, however, that there be a local population of people highly trained, at international standards of graduate education and research, in areas of Science and Technology of economic importance. One such program was developed through a loan requested by the Brazilian government in 1983 to help improve University graduate research throughout Brazil in the areas of Chemistry, Biochemistry, Geosciences, and Mineral Technology. The mechanism chosen was the funding of research programs in those areas through an objective peer review mechanism, protected against conflicts of interest. Since the Bank had no significant experience in such activities, they asked for my help as a consultant. That first Brazilian project started in 1985, and the third one is currently underway. Since then, similar programs have been developed in other countries, and I have been involved in those in China, Mexico and Chile. They have been instrumental in introducing objective mechanisms for the evaluation of research proposals and have helped raise the level of the scientific research performed in those countries. This activity has been, and continues to be, a source of great satisfaction for me.

I cannot finish these remarks without mentioning three additional major sources of satisfaction. I have derived enormous pleasure from the interaction with my graduate students, 44 of whom received their Ph.D. degrees while doing research in my group. Some of them were truly outstanding and are now world-class scientists in their own right. I could not have made whatever contributions to science I was involved in without their collaboration. I am very proud to have received last year's Graduate Student Council's Award as the best mentor in recognition of my activities as a research advisor. The second source of satisfaction has been teaching undergraduate and graduate courses at both Illinois and Caltech. I truly enjoy that activity and have recently been honored by two Badger Awards in teaching given by the Chemistry Division and another one given by the Graduate Student Council of the Institute, as the best teacher of the year. The third source of satisfaction has been my interaction with the 35 postdoctoral fellows who over the years have been part of my research group. They have brought to it experience from other groups and have greatly broadened my horizons.

I wish to express my gratefulness to my wife and children, who have given me love and support at times when such gifts were greatly needed. As those of us in academia know, even though our professional life is mostly very satisfactory, there are times of stress which require a supportive and understanding family. I am also very gratified by the high levels of accomplishment of my family members. Roza has retired as a star high school chemistry teacher at Westridge School in Pasadena, and my three oldest children are Associate Professors in various medical schools of the University of California. Our youngest, who has Down Syndrome, has given me joy and added a different and more understanding perspective to my life, including my professional life.

Finally, I am most thankful to Joel Bowman, Jack Kaye, George Schatz, and Don Truhlar, who went to great lengths to put together the festivities of my 75th birthday, including this special issue of *The Journal of Physical Chemistry*.