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Special Issue Preface

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Autobiography of A. W. Castleman, Jr.

AUTOBIOGRAPHICAL SKETCH

Among my recollections of what constitute my "early childhood," are a few experiences that are still especially vivid in my memory. These might be taken as foretelling of what interests may have eventually governed the course of my professional life, one challenged by exploring as yet unresolved issues in science and technology. It is difficult to think back and recall what attracted my early interest. But as is the case with most children, it probably involved packing mud, together with wet sand and little stones, the beginning of my exposure to particle/(cluster)/science. Unknowingly, had we been exposed to this area of investigation for some 60+ years, perhaps we might have been able to start work on what eventually became a significant problem of critical angles in packing as demonstrated by de Gennes...ahh, the benefits of education and a prepared mind.

EARLY RECOLLECTIONS—CHEMISTRY ENTERS THE PICTURE

Other "phenomena" that did strongly attract me and that were beginning to show a significant chemistry component involved the burning of sparklers, where the oxidation of small metal particles played a role. Interestingly, I first had this experience when about 6 years of age, and recently, I returned to work in this area being undertaken through a current NAVY grant. Knowledge that the presence of water enhances the reaction process as does small particle size provides a key to understanding the kinetics of the reactions. My next ventures which led me toward photochemistry were taken jointly in a closet of a much older friend of mine who had some liquids with the intriguing properties of being light-emitting. The seasons in Richmond, VA, where I was born, change dramatically, and I soon lost the envy of not having these liquids myself. The reason is that using the abundant quantity of lightening bugs that readily became available, and putting them in contact with other substances, I too was able to create light at will, albeit less colorful than that of my playmate's liquids in the closet.

After a while, I became very curious about the wide variety of insects at my disposal, collecting and studying them in detail: some flew, others ran, and most climbed. Not all had the same number of legs. Coming across a praying mantis or a walking stick was always especially thrilling. This hobby lasted for a while but ended due in part to the attitudes of my classmates and a teacher. On a number of occasions, class assignments required us to present what we thought might be a possible future profession; in my case, there was more laughing than interest when I stated that in my later professional life, I would like to collect and study insects in Africa. Another topic might be determining the range of colors that could be acquired by mixing bug parts/juice with other ingredients. Then I wanted to see if I could generate a range of colors by other means, the kind I kept observing on my bedroom wall. After a while I ascertained that small holes in the window shade which allowed the sunlight to pass through were projecting various colors onto the opposite side of the room. This prompted me to keep poking more and more holes into it until my parents put a stop to the destruction of the shade. I did realize though that holes in shades were at least in part responsible for what I was seeing. To me, studies with colored matter (photophysics/chemistry) seemed to be an interesting avenue to pursue. As I grew older, I began to realize how many things there were to explore. In the area of chemistry, eventual additions to my various storehouses of chemicals enabled me to carry out an increasing number of reactions as also did my friends. We became especially enamored by "fast exothermic" reactions. On several occasions, my mother became horrified as a very loud noise rose from our basement, followed by a cloud of dense smoke. My hearing was certainly impaired for a few hours, which I did my best to hide. Despite our own concerns, we continued to explore the impact of differing formulations on the outcomes. However, we did confine our explosions to the backyard whenever we could.

Fortunately, not all of my hobbies had such dangerous potential outcomes. Along the way, I started raising tropical fish, and especially breeding a kind which is known to be difficult to accomplish. I also spent a period of time pursuing activities at the fringes of science. Fascinated by the Native Americans and their origin, I read every book about them that I could get my hands on. However, it was the more physical sides of science that eventually captured my interest. My observation that alloys of lead with differing compositions could be melted under quite different conditions was also exciting, but it gave me some difficulty when trying to keep some clean junctions in electric circuits. Given some unrefined crystals allowed me to make contacts, and attaching this assembly to some old ear phones led me to my biggest surprise, SOUND from some radio transmitter that was clearly not nearby, nor was the signal received by a conventional receiver. Little by little, reading and talking to others led me to make the crudest amplifier. And employing this together with a couple of hundred foot antennae in our backyard allowed me to listen to shortwave signals from Europe during the night, an activity that occupied many an hour. Other related pursuits led me to undertake learning Morris code, building a Hi-Fi, designing a multispeaker enclosure with reasonable resonance features, etc. And yet another hobby involved photography which I still enjoy; a year in Buffalo, NY provided me the opportunity to perfect my techniques through being subjected to monthly evaluations by senior individuals in the club sponsored by the Buffalo Science Museum. Prior to the digital age, the images arose from light-sensitive (halide) crystals, further evidence of connections to particle science and some of my interests.

OFF TO COLLEGE—A DIFFERENT EXPERIENCE

The fact that I enjoyed being involved with activities that had some original character rather than merely duplicating

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something others had done before me destined my future to include attending a college with strong technical curricula. Considering various aspects of potential college experiences to be of interest, many appeared as though they would be rather tedious. In consultation with advisors, I ultimately chose RPI which was and still is a rigorous hard-core engineering school; it took me quite a long time to find out what was going to be expected of me. For example, undergrads were expected, without notice or prewarning, to arrive a day or two early for their forthcoming semester, go around campus to find out the location of classrooms, look for comprehensive assignments in 4–6 courses typically consisting of about 5 h of effort each, hand them in on the first day and also be prepared to take an exam on the material—all before classes formally began. During the semester, typically some classes would be held on a Saturday morning on a rotating basis. This was quite a wake-up call and only a prelude of what was about to come. Furthermore, we students felt lucky to have a rigorous learning environment, and students never contemplated a day when we might rate faculty; instead, the reverse situation was in operation nearly 24 h a day.

At RPI, most intellectual activity had some technical content. There were some deviations to this dictum, mainly in my reading selection chosen mainly for relaxation. I have a great liking for Shakespeare's works, and to my pleasure, I could also fit them into my curricula. I am also fond of reading biographies and autobiographies of famous scientists, and my current "reading list" always contains a few awaiting completion.

■ SUMMER TIME AND WAITING FOR A FEW SELECTED COURSES

(**Undergrad Experiences**) As implied above, for me the undergraduate years were mixed, though in retrospect, largely positive experiences. Reflecting on courses to which I was exposed, a few clearly stood out. Perhaps the single most challenging yet interesting course was one in physics devoted to electricity and magnetism. I am grateful to the faculty member who taught it and expanded my early interest in this field, although I had prior experience in building shortwave radios, amplifiers, etc. Giving the next lab-class of students planning to enter the room a little shock was always worth a laugh if they failed to discharge the capacitors before touching the terminals.

Another subject I eventually found to be especially fascinating was that dealing with thermodynamics. Depending on the main topic, it was usually taught from several differing points of view; in my first encounter, I found it to be a subject for which I had great disdain to one becoming my favorite. Einstein's positive comments about this area were not the only reasons, though they certainly played some role. I realized how 'powerful' the classical subject was, and whenever there were opportunities to use it at a new level of depth, I did so. Little by little I acquired insights into this material to a level beyond that gained by many of my students and other colleagues. I employed numerous concepts which I used in my master's thesis that I picked up from Professors van Ness and Conti. My respect and love for the subject grew considerably when I got exposed to even more advanced ideas, especially as I could see possibilities emerging from statistical mechanics with some from quantum mechanics. I was very pleased that advanced course curricula allowed students to take courses with some content selected to their interests. In retrospect, I see some value in this, but students are not the best judges and may miss being exposed to some valuable concepts.

My summers were taken up with jobs, the most interesting of which involved several surveying projects, mainly laying out road-beds for new housing developments. My interest in calculating areas of odd shape made me a logical assistant for the transit operator; recall this was before the digital age and most calculations were done by hand and/or with the use of tables. Some course curricula provided opportunities for students to undertake totally independent projects during certain semesters, and I undertook two which had particular influence on the direction of my professional future. One of these was done under the guidance of Professor Sydney Ross, a well-known colloid chemist. I helped him develop an oscillating disk device which enabled some measure of the variation of viscosity near interfaces. I was fascinated with the outcome, which prompted me to occasionally spend extra time working on this project. This led Professor Sydney Ross to come rushing into the lab one evening with concern for my safety and the length of time I was devoting to the work; the instrument required large amounts of liquid nitrogen to be boiled away, and he feared that I might be lacking sufficient oxygen to stay awake, or worse.

Another research project was available under the tutelage of Professor van Ness of Chemical Engineering. It was expected to be a more challenging and comprehensive project and one generally worked on by two students in a partnership. Two of us approached van Ness, requesting a real challenge, in this case also having some relevance to surface chemistry/engineering. The project we finally settled on involved the formation of well-defined platinum films from which we could extract some fundamental information as the films changed upon reaction. As a consequence of our efforts in this project, an unexpected event occurred during our college graduation ceremony. As is quite typical, most students were not paying much attention to the presentations, it being to us a relaxing moment after four strenuous years. Suddenly, the person sitting next to me said, "they called your name and want you up on the stage". I thought this was a joke and sat still. But then my research lab partner's name was also called and we discovered we had been selected to receive the major undergraduate research award of the university for 1957, the Palmer C. Ricketts Award.

■ BNL—SOME OPPORTUNITIES

I graduated from RPI in 1957, only about 12 years after the first detonation of an atomic weapon ending World War II; the Cold War was well underway. These and related matters ensured the need for advances in military research. Even this modestly long time after the end of the second world war still witnessed numerous prominent scientists returning to universities from the national laboratories. And many older students were frequently around as well. These groups of individuals were often a storehouse of valuable knowledge. It was not necessary to have a prominent title in order for others to pay attention to your ideas; experience was what was needed and respected. For example, a brilliant and highly valued member of the mathematics division of BNL had not considered it worth his time to obtain a Ph.D. degree. (And later, among other possibilities, I became an expert in aerosols and had the opportunity and privilege to serve on a long-standing committee of the Atomic Energy Commission, namely, what became the Nuclear Regulatory Committee.) It was not long before the Sputnik age was ushered in. Science and engineering were areas with many opportunities, and jobs and research funding were relatively plentiful. But, at the same time, there was great concern for the threats imposed by the cold war. Upon graduating from RPI, within a few days I was able to garner attractive positions, and I took one at Olin Matheson Corporation working on the properties of boron fuels. The working conditions including safety, biological properties, and financial aspects were not particularly favorable compared to those at some of the various national laboratories, and during the year there, the pilot plant had an explosion that was heard miles away; fortunately the plant design minimized the need for safety concerns. The boron fuels I was working on at Olin Matheson had many unpleasant characteristics, including highly pyrophoric flammability and toxicity including some loss of nerve control. Dealing with nonconfined materials required the use of gas masks; the elimination of air reduced the number and severity of explosions we encountered (see: “The Green Flame”). It was a pleasure to move on after having had a valuable educational experience, which in fact laid the basis for some future research topics in the area of energetic materials (one topic currently under study in my laboratory supported by AFOSR and ONR).

Being offered a research appointment at Brookhaven National Laboratory was a great opportunity; I commenced working there in 1958. BNL was quite a different organization in terms of numbers of personnel, facilities, available research funds, and equipment, for example. In the following sections I try to give an idea of how the “red thread” of my career continued in the early/middle phase. Within the broad context of the mission of the laboratory and nuclear agency, I was generally able to pursue most areas of interest. I commenced by first learning new areas of instrumentation, particularly those involving radio chemical methods with which I had only limited expertise. Of particular value was learning the details of statistical analysis, which was of particular interest dealing with problems of diminishing concentration. A problem area of both fundamental and applied interest dealt with the transport of infinitesimal amounts of matter from the surface to gaseous state. Making measurements as well as interpreting the findings was nearly equally difficult, and learning the state in which the material was dispersed called for new approaches. After studying the problem for a while, I realized that a conventional chromatographic method would not solve the difficulties at hand, information about the state of bonding between the substrate and adsorbate being required. The instrument I ended up developing became known as a “thermochromatograph” and became used in the nuclear field to investigate fundamentals of fission product transport for trace radioactive materials among other topics.

During early phases of this work, I became interested in systems where the materials bound to the substrate revealed a statistical diffusion phenomena-release mechanism, especially for the case of nonmetals and gases bound at metallic interfaces. The subject was somewhat akin to that related to metal films studied as part of my B.S. research, endeavoring to learn more about the mechanisms of vaporization from the surface layer and especially the mass effect for diffusion in condensed systems, which became the theme of my graduate research. Studies of condensed phases continued to raise numerous issues about bonding and kinetics which I realized required a technique such as mass spectrometry to answer. Despite being the “young scientist on the block”, I was given nearly free reign to tackle problems of interest, and I was lucky to choose a few that provided some insights pertaining to open questions in fundamental science. One related to the diffusion problem mentioned above, while a few others touched on some environmental problems such as nuclear reactor safety, with interest in the physical and chemical mechanisms related to fission product release and the particle sizes of materials released as aerosols in a variety of cases. Cold War research had a lot to do with being able to determine the characteristics of various weapons being developed, and this was in turn coupled to aerosols formed via the nucleation of clusters, a problem in which I was particularly interested. As I proceeded to work on this research topic, the more I accomplished, the more new questions I uncovered. Sulfate aerosols which we were able to acquire at very high altitudes also revealed isotopic distributions that we could explain on the basis of the fundamental Lindeman mechanism, which accounts for available phase space considerations. Similar investigations on aerosols formed from nucleation/cluster growth began to be more than a side issue but instead started to become a major topic of study. Due to my success, I became a leader of the group despite the fact that I lacked the Ph.D. degree held by some other members of my group.

As time went on, I began to realize the number and variety of both fundamental and applied problems to which cluster research could make a significant impact, not only in nucleation phenomena, as pointed out earlier, and in understanding mechanisms of solvation and details of solid surfaces, among a potentially huge number of possible examples. Gaining new insights into liquids and solvation phenomena appeared to be another promising subject for study via cluster research, but this does require some caution due to the possible influence of surface effects. With appropriate care, this problem can be overcome. One key is acquiring well-defined equilibrium conditions while making experimental measurements, along with determination of cluster size distributions via mass spectrometry. The group was soon contributing significantly to knowledge of the thermodynamics of clusters of nearly all classes.

■ GRAD SCHOOL

Through a further expansion of my reputation, and of my interests in the field of clusters and aerosols, I had the opportunity to serve as an adjunct professor in the department of Earth and Space Science and the Department of Mechanics at the State University of New York, Stony Brook. During this time I had the occasion to supervise the master’s dissertation of a graduate student; prior to this I had already been considering my long-term goals which were clearly leading me toward academia. After consulting administrators at BNL and the Polytechnic Institute of Brooklyn (now: Polytechnic Institute of NYU), I found that pursuing a Ph.D. would likely be a possibility. The only stumbling blocks might be financial and especially the commitment of time. Although a direct Chemical Physics degree was not available, PIB was very flexible as long as I took a very comprehensive course load along with a meaningful dissertation, the sum total being equivalent to other programs in chemical physics.

At the very beginning of the 5/6 year period I had little realization what I had committed to; first a typical week involved a commitment of time to satisfy my regular full time BNL work appointment, meaning 8:00 am to about 4:30 pm every day; then, typically followed by a roughly 2 h drive through very heavy traffic to Brooklyn 2−4 days per week in order to take required courses (fortunately offered in the evening during selected semesters); returning home around

10:00 pm; with Saturdays and part of Sundays reserved for homework or efforts to accomplish my dissertation dealing with the mass effect on diffusion. I received my Ph.D. in 1969 and accepted a full professor appointment at the University of Colorado, Boulder in mid-1975 where I remained until mid-1982. One final move took me to Penn State University.

■ MY EXPANDING CAREER IN CLUSTER SCIENCE

As readily seen from this autobiographical sketch, much of my undertakings have led me progressively deeper into the field of cluster science, and for this I am eternally grateful to the students who have charted our course with me as well as to the funding agencies that made the voyages over the years possible. I cannot imagine any area that would offer more exciting, challenging, and fundamental scientific problems to work on, and I consider my opportunity to do so to be a true gift. Indeed it is a rare waking moment when some problem that I believe could be solved by cluster science does not enter my mind. It is well recognized that it is the significance of findings rather than the number that is the important criteria; though seeing a large number of publications of high quality is a measure worthy of note. I am proud of my group's contributions over the years as these are a measure of their dedication and enthusiasm and my success in motivating them.

During the 10 years at BNL, my group and I continued to investigate and consider what problems in cluster science, when solved, would make a major impact in the field. We were fortunate to also have had ideas for several new techniques which we fabricated and implemented. Realizing the value of our self-designed techniques and the potential significance of our research plans, the DOE research monitors of our scientific grant and a related individual at NSF supported my request for transfer of equipment and the program from BNL to the University of Colorado, Boulder. The coming several years were dominated by research on soft-matter, an area of interest that also encompasses aerosols and environmental science among other fields. Several students whom I had gotten to know on prior trips to Boulder were "awaiting" arrival of the equipment. In view of the fact that I had a large amount of equipment and that I was taking a joint appointment between Chemistry and CIRES, we were given considerable high quality space.

The years I spent in Boulder were very productive, the initial time being used to expand our activities in several new directions. Boulder had a number of stimulating individuals who were always anxious to discuss new ideas. Of particular note was the extensive interest in the fields related to the chemistry and physics of anions and cations. I took this opportunity to expand our work on ion molecule reactions. My group's studies of the fundamentals of cluster growth and nucleation phenomena were explored in detail, with some experiments designed to quantify the effects of ion charge and others about the "solvent's nature". The findings enabled improved understanding in several areas: behavior of charge states, ion characteristics of ion cloud chambers, and the effects of ion charge on certain atmospheric phenomena. Our findings provided a great amount of new knowledge about studies reported in the literature resulting from high altitude investigations. Extensive new thermochemical data on ion–ligand bonding was determined, values which in combination with theoretical calculations gave insight into factors governing specific structures of ion–ligand complexes.

A couple of years after arriving in Boulder, Caltech selected me for the prestigious Sherman Fairchild Distinguished Scholar Award. I accepted with pleasure, spending the Fall 1977 term there. After several additional years in Colorado, I was approached about possible interest in a position in the chemistry department at Penn State University. Following several visits accompanied by my wife, we decided that such a change would be mutually gratifying. We accepted and commenced preparing for the major resettlement. It required two of the largest moving vans to accommodate the entire lab equipment plus the content of our house along with the households and sports equipment of 10 post docs and grad students who followed me to Penn State. All of us including my wife and newborn son traveled through the country in several cars, and when we came across each other on occasion, the main questions of concern were if anyone had spotted the van carrying the precious equipment along the highway and if it was alright. Nobody really cared about the van carrying the personal belongings. The events associated with the move led to a wonderful camaraderie.

Recalling what has transpired over the years since our move in 1982, it is clear that this was a very appropriate decision. We have all worked well together, and I am very proud of the 79 students who have obtained their Ph.D. degrees under my guidance. Especially important to me is the fact that virtually all of them have been able to reach their goals through education, and my own aspirations have also been met. Throughout the years I have been very fortunate to have our accomplishments recognized through both my students' as well as my own honors and awards. As time has proceeded, I have acquired recognition through two of the ACS society awards (which are listed in my CV), a number of the society fellow awards, and most honorous the election to the National Academy of Sciences and the American Academy of Arts and Sciences, among others. I am also proud and pleased to have had the opportunity to work for 10 years as a senior editor, with my wife Heide, who served as editorial assistant of the Penn State office of *JPC*, in furthering the objectives of the journal.

As we made a planned transition in our studies at the time of moving to concentrate on problems in hard matter as well as soft matter, we spent some time to take stock in what we consider as some of our most recent significant findings. Our discovery of Met-Cars (uniquely bonded metal–carbon species with 8–12 stoichiometry and having exceptionally low ionization potentials) is high on our list. They have been found to readily form via certain selected hydrocarbon–metal cluster reactions, and these species continue to be of interest in many areas of cluster chemistry. Related studies of similar reactions have provided us new insights into the functioning of certain clusters as nanoscale catalysts comprised of metallic, oxides, and carbide species, another subject of considerable interest to us. In other work we have found factors beyond cluster cross sections that govern coulomb explosion phenomena via femtosecond laser pulses, developing this into a technique for investigating proton transfer reactions by direct observation, for example. Using time, energy, and intensity resolved pulses, we have devised a method to employ coulomb explosion to directly deduce mechanisms of reaction. We have learned how cluster size has a major influence on pulse duration and have explored the dynamics of solvation. Determining the number of solvent molecules responsible for ion-pair formation has been particularly interesting.

Another significant finding from our studies deserves particular mention. During the course of investigating reactions of selected metal clusters, we discovered that certain ones revealed unique electronic characteristics on the one hand and displayed chemical behavior on the other, similar to what is sometimes observed with specific elements. The first cluster where these aspects were identified was that comprised of aluminum, where, for example, Al_{13}^{-} was found being akin to a chlorine-like (super)halogen. Subsequent investigations via photoelectron spectroscopic velocity map-imaging revealed the surprising fact that many isovalent complexes comprised of certain atoms and molecules were quantitative mimics of various elements in terms of electronic properties and the united atom model. An overview of our discoveries and the origin of the 3-D periodic table are discussed in many of our papers; an example is seen on the cover where TiO is found to be close in electronic character to Ni. This class of element mimics we discovered was originally termed "united atoms". This has now been replaced by: "SUPERATOMS" (see publication 675). As Shakespeare has taught us, "A rose by any other name is still a rose".

Following my CV is a listing of my group's publications which point out the areas of cluster science where we consider we have made the biggest impact.

I have also made a large impact in terms of the considerable number of meetings I have attended, organized, chaired, and spoken at over the years. Among them, two stand out far beyond the others, and hence I mention them here. The first of these was a Nobel Symposium on Femtochemistry and Femtobiology held in Sweden in September 1996 where I was an invited participant. The second was also a symposium sponsored by the Nobel Foundation and held in Sweden in 2000; at that meeting I was invited to deliver a major lecture on the physics and chemistry of clusters.

All things considered, the most important factor in my life has been the support, love and interest received throughout the years from my wife Heide; also the enjoyment she and I have had together bringing up our son Clifton (and sharing the joy with him and his wife welcoming our first grand-son). Other pleasures for me include my wife's art, hearing her converse in several languages (but I for sure not understanding it unless it is in English!) and, last not least, visiting museums together and attending concerts.