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Interview with Ralph G. Pearson

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Abstract

The following interview with Ralph Pearson was compiled over a period of days in the Fall of 1997 with the intention of including it with this *Coordination Chemistry Reviews* Volume on 'Inorganic Reaction Mechanisms' planned for publication during the year of Ralph's 80th birthday. © 1999 Elsevier Science S.A. All rights reserved.

Ralph G. Pearson was born in Chicago Illinois in 1919 to parents who had emigrated from Sweden in 1905. His childhood was spent in Chicago and New York City where he attended public schools. He went to college at the Lewis Institute in Chicago where he earned a B.S. degree in 1940. He then attended graduate school at Northwestern University in Evanston, IL and completed a Ph.D. in Physical Chemistry in 1943. After military service, he joined the Northwestern Faculty in 1946 and rose to the rank of Full Professor in 1957. In 1976, Ralph accepted a position in the Department of Chemistry of the University of California, Santa Barbara where he has remained since. In 1989, Ralph became Professor Emeritus at UCSB, but he continues to carry out research in theoretical studies to this day. He has published well over 200 papers as well as a number of textbooks and monographs that have been very influential in the development of physical inorganic chemistry. These include 'Kinetics and Mechanisms' co-authored in 1953 with A.A. Frost and published in two later editions and 'Mechanisms of Inorganic Reactions' with Fred Basolo in 1958 and 1967. His most recent book 'Chemical Hardness, Applications from Molecules to Solids' was published in 1997. Honors accorded to Ralph Pearson include a Guggenheim Fellowship in 1951–52 while he spent a year at Oxford University and the Royal Institute of Technology in Sweden.

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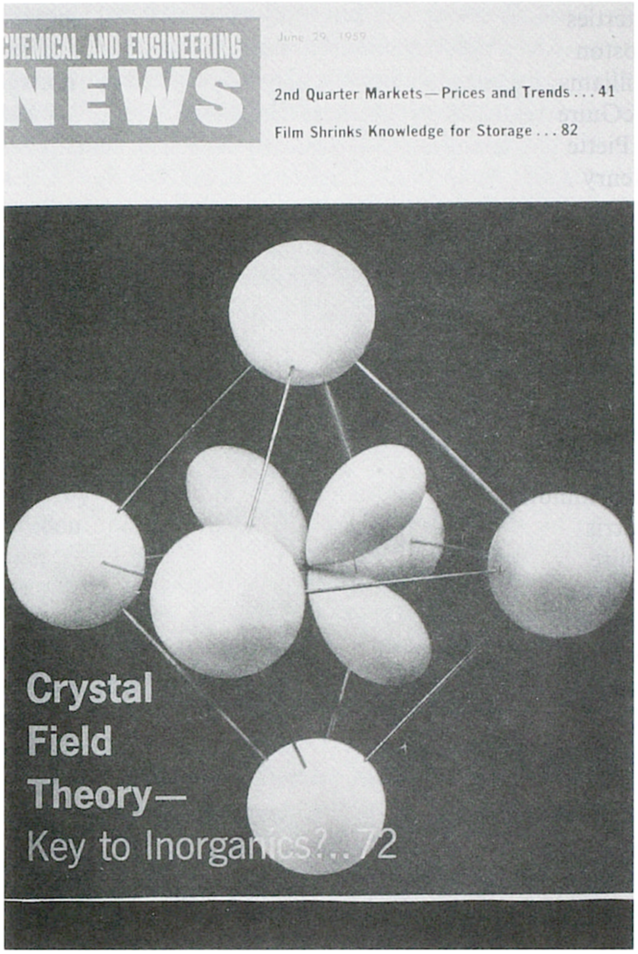
He has also been awarded the Midwest Medal of the American Chemical Society (1966) and the ACS Award for Distinguished Service to Inorganic Chemistry (1970). In 1974, he was elected to the US National Academy of Science.

(1) Ralph Pearson, ca. 1990.

(2) Attendees at a conference in Inorganic Reaction Mechanisms held at Northwestern University in 1957. Pearson is the sixth person from the left in the top row. Fred Basolo is the sixth person from the left in the second row.



(3) The cover of *Chemistry and Engineering News* June 29, 1959.

During his tenure on the faculties of Northwestern and UC Santa Barbara, Ralph mentored a number of outstanding undergraduate, graduate and postdoctoral students who have gone on to distinguished careers in industrial and academic settings. The names of his former students and postdoctoral researchers are listed below.

Former students and postdoctoral researchers of Ralph G. Pearson

Northwestern, 1946–1976
Robert L. Dillon
James M. Mills
Evan A. Mayerle
Angelo C. Sandy

Earl L. Muetterties
Charles R. Boston
Forrest V. Williams
William J. McGuire
Lawrence H. Piette
Patrick M. Henry
Leslie L. Alt
David H. Anderson
Robert E. Meeker
Debarata Banerjea
Ronald A. Munson
Donald C. Vogelsong
Ralph G. Wilkins
Harry B. Gray
Nancy C. Stellwagen
Hans-Herbert Schmidtke
Melvin L. Morris
John A. Maguire
Mary M. Anderson
Herbert R. Ellison
John W. Moore
Roger J. Mawby
Umberto Belluco
David N. Edgington
Steven K. Maples
Randolph Lanier
John V. Rund
Thomas Buch
Fabrizio Monacelli
Max Meier
John A. Broomhead
Ian S. Butler
J. Phillip Day
Mariel M. Muir
S. Peter Tanner
Peter Moore
Otto A. Gansow
Leon Kane-Maguire
Oren P. Anderson
Harold Sobel
Jon Songstad
Michael Hynes
Jean Dehand
Dwight A. Sweigart
Warren R. Muir

Robert W. Johnson
David G. Dewit
Jayaraman Rajaram
Carol G. Grimes
Wynand Louw
Paul C. Ellgen
Carl D. Gregory
Michel Laurent
Arthur T. Poulos
Phillip E. Figdore

UCSB, 1976–1989
Harold Walker
Charles T. Kresge
Heiko Mauermann
Georgia Kyriakrakoy
Charles H. F. Peden
Stewart F. Parker
Mats Almemark
Paul Reboa
Marca M. Doeff
Claude Amman
Katherine Jimison
Chris Tina Spillet

P.C.F.: Let's start with the early days.

I was born in Chicago in 1919. My parents had emigrated from southern Sweden in 1905. Their education was limited, about the equivalent of a 10th grade education in the US. My education, firstly in the public schools of New York City, and then Chicago, was not very good. My first chemistry teacher in high school was also the gym teacher. His training consisted of 1 year of college chemistry.

However, he allowed me free access to the laboratory and my interest was awakened by doing experiments on my own. Earlier I had brought a Gilbert Chemistry Set second hand from a neighbour. Changing water into wine and wine into ink was pretty exciting! I worked two summers as a mail boy for Central Scientific Co., supplier of chemicals and laboratory equipment. I built up a rather nice little home laboratory, bought at a discount.

Nevertheless, when I went to college in 1936 I did not want to be a Chemistry major, but an English major. My dream was to write important novels. The Great Depression was at its height in 1936, and I decided that Chemistry offered a better chance of a job upon graduation.

I attended Lewis Institute in Chicago, later a part of the Illinois Institute of Technology. I won a scholarship and was offered a part-time job in the chemistry store-room; otherwise, I could not have afforded college. The department was small and friendly. The faculty did no research, but were all very good teachers. I took a year each of general chemistry, organic chemistry and analytical chemistry. But only one semester of physical chemistry was offered. There was no biochemistry, but I had a course in food analysis, which included some biochemistry.

I graduated in 1940 and had several offers of graduate appointments, including one from John Bailar at Illinois. I decided to go to Northwestern, because I had a girlfriend who lived in Chicago. Besides, I could live at home, which was cheaper. The reason I went to graduate school was again economic. The job market was poor, and I knew I would earn more with a Ph.D.

My research director was Ward V. Evans, a physical chemist. He was not well known for research, but he was a famous expert on explosions, often testifying as an expert witness. I earned extra money by doing some analyses for him. Evans was the only scientist on the committee that examined J.R. Oppenheimer to see if he should be given a security clearance. He voted in favor of Oppenheimer, but the other two members voted against him.

I worked on the electrolysis of Grignard reagents, a process in which organic free radicals were produced at the anode. After 1 year Doc Evans told me to write a paper, because he liked to publish at least one paper a year. I wrote one on the electrolysis of arylmagnesium bromides, which was published in the *Journal of the American Chemical Society* in 1941.

Evans's work on the electrolysis of Grignard reagents included the discovery that, if a lead anode was used, a lead tetraalkyl was formed. This was made into a commercial process by the National Aluminate Corporation (now Nalco). They made millions of dollars from the rate of lead tetraethyl. Doc Evans never saw a penny of this, but Northwestern was given a few thousand dollars.

P.C.F.: How did you become a member of the Northwestern University faculty? Isn't it unusual to stay at the same school where you did your graduate work?

It was accidental. My plan had been to use my Ph.D. degree to get a good paying job at Du Pont or Dow. But World War II had started halfway through my graduate career. When I finished in 1943 I had several offers which would have kept me out of the army, including one from the Manhattan Project. But I felt uneasy about avoiding military service, so I let myself be drafted in early 1944, after teaching at NU for a few months. In 1946, when I was discharged, I went back to Northwestern because, by law, they had to give me back the job I had when I left. Because of the large number of returning G.I.s, they were glad to have me, and I stayed on.

P.C.F.: What was your research program at this time?

This was a serious problem because I had not really planned on becoming an academic. I scrambled around to find something, both in the way of ideas and equipment. I had an interest in organic reaction mechanisms, mainly because of L.P. Hammett's book on Physical Organic Chemistry. I found a very precise conductivity bridge that had been bought for some other purpose, perhaps for Malcolm Dole or Frank Gucker. I realized I could study the kinetics of reactions where ions were formed or destroyed. At this time I had never done a kinetics experiment in my life, but I had taken a graduate course from Arthur Frost. It seemed like kinetics would be an easy area to work in, and this proved to be the case.

At this time there was no start-up money for a new faculty, and very few places where you could apply for money. You could get chemicals and basic equipment from the chemistry stockroom, and you could rummage around for bigger equipment that you might use. In a pinch you could try to get money from the department, but $100 would be about the limit. Nevertheless, I published two papers in 1947 and 1948, all work done by myself.

In 1948 I was fortunate enough to get $3000 from the Research Corporation. I nursed this for 3 years. I picked up my first graduate student, Bob Dillon, in 1948. Most graduate students were supported as teaching assistants. A few had graduate fellowships, but these were grants given to individual professors who had contacts with a particular company. In 1940 I received $60 per month, courtesy of Universal Oil Company, whose president was a friend of Ward Evans. In 1940 a postage stamp cost two cents, and a loaf of bread ten cents, so $60 wasn't bad.

P.C.F.: How did your association with Fred Basolo begin?

Fred had also come to Northwestern in 1946, from Rohm and Haas. He approached me in 1948 with the suggestion that we jointly study the mechanism of ligand substitution reactions, using the stable chlorammine complexes of cobalt(III) as a start. In 1949 Earl Muetterties was an undergraduate senior, who wanted to do some honors research. So we put him to work on *cis*-$Co(en)_2Cl_2^+$, studying aquation and Hg^{2+} catalyzed aquation. I'm surprised that he became an inorganic chemist after this introduction. All three of us were very much confused and frustrated by his observations.

After working with organic compounds, I was horrified to find out how little was known about the reactions of coordination compounds, and how hard it was to find out anything. What we had available was my conductance bridge, a Beckman DU spectrophotometer, a pH meter, and a Rudolph polarimeter. Fred also knew how to analyze these compounds, providing we could get enough to analyze. At this time there were no commercial infrared spectrometers, no NMR instruments, no chromatography, and no X-ray machines that you could buy.

We persevered, however, and in 1952 we published our first paper. Fortunately the Atomic Energy Commission decided they needed to know much more about coordination chemistry. In 1950 Fred and I received a grant of $7000 for 2 years, and in 1952 we obtained money from the newly created National Science Foundation. The AEC also began giving fellowships to graduate students. As a result of all this, we attracted as many graduate students as we needed. In fact, inorganic chemistry, which previously had been as dead as a dodo, became the hottest area of chemistry, at least in some places.

The reason for this, I believe, is that a number of very able people became interested in the reaction mechanisms of coordination compounds, and in their unusual properties such as spectra. Just as physical–organic studies increased in the interest in organic chemistry in the 1930s, so physical–inorganic chemistry rejuvenated inorganic chemistry in the 1950s. Of course the influx of Federal money also helped. After 1957, when Sputnik was launched by the Russians, money for research became even more plentiful.

P.C.F.: Who were the others who helped create physical inorganic chemistry?

There were, of course, a few people all over the world, who did work that could be called physical–inorganic, in the 1920s and 1930s. But the people who started in the late 1940s and early 1950s were the ones I knew best. Names that come to mind are John Edwards, Henry Taube, Arthur Adamson, Ed King, Cliff Garner, Bob Connick, Gordon Harris, Wayne Wilmarth, and Ralph Wilkins. Many of us met for the first time in 1950 when the AEC sponsored a conference on the properties of coordination compounds, held at the University of Chicago.

The highlight of that meeting was a talk by Taube in which he explained the kinetic behavior of both inert complexes, like those of Co(III), and labile complexes, like those of Al(III), and Ti(III), using valence bond theory. At that time Pauling's ideas dominated inorganic chemistry, two of his books, *The Nature of the Chemical Bond*, and *Introduction to Quantum Mechanics* (with E.B. Wilson) were very influential in shaping my ideas during graduate school. I still consult *Quantum Mechanics* from time to time, but not *The Nature of the Chemical Bond.*

In the 1940s, valence bond theory (VBT) and molecular orbital (MO) theory were competing with each other. The chief spokesman for VBT was Pauling, who was one of the creators, along with Heitler, London, and Slater. MO theory was sponsored mainly by R.S. Mulliken, who created it, along with Hund and Hückel. Since Pauling knew much more chemistry than Mulliken and was a much better speaker, he had more influence, particularly in inorganic chemistry. The organic chemists, however, found MO theory much more useful in discussing aromatic compounds.

P.C.F.: The people you mentioned were all young, mostly American, and did work on reaction mechanisms of complex ions. Ingold and Nyholm in England also entered this field in 1950. You and Basolo had a dispute with them on the mechanism of base hydrolysis of cobalt(III) complexes. Any comments on this?

I won't go into details, since the story is well known. Ingold was the, more or less, undisputed king of organic reaction mechanisms. I believe he thought he could clear up inorganic reactions quickly with a few well-planned studies. He had the very able R.S. Nyholm to help him out, though Nyholm had no interest in reaction mechanisms. However, at University College, London, you didn't say no to C.K. Ingold!

Ingold got into trouble, I believe, because of his inexperience with water as a reaction medium. In fact his choice of solvent was methyl alcohol, which was at least partly organic, but it was enough like water so that basic anions like acetate and azide gave some methoxide ions, which are very reactive. He could have prevented this, as we did, by simply adding a little of the conjugate acid to his solutions. While he realized his mistake later, he never backed down from the S_N2 mechanism he proposed, based on faulty data.

Nonetheless, the fact that Ingold published some papers on reactions of the cobalt(III) haloamines was a big stimulus to the fledgling field of inorganic reaction mechanisms. Martin Tobe continued the studies at University College and did outstanding work. In fact, Britain became one of the leading centers for physical inorganic chemistry.

P.C.F.: You mentioned how Pauling's books made an impression on you when you were a graduate student. Two books that greatly influenced me in graduate school were Kinetics and Mechanisms by Frost and Pearson, and Mechanisms of Inorganic Reactions by Basolo and Pearson. In the latter, I learned about crystal field theory, CFT, a competitor of VBT. How did you become aware of this development?

CFT had its early beginnings in physics. It entered chemistry in 1951, in a paper by Hartmann and Ilse dealing with the spectra of transition metal complexes. It was well known that these spectra contained valuable information about the structure and nature of the complexes, but it was impossible to understand them using VBT. In 1954 Leslie Orgel gave a lecture on CFT at Northwestern. I was spellbound, but just to make sure, I asked him after the lecture if he was explaining why *cis*-$Co(en)_2Cl_2^+$ was violet, and the *trans*-isomer was green. He replied that he was.

I was very instrumental in spreading the gospel of CFT. I gave numerous lectures on the subject. The book by Basolo and myself appeared in 1958, complete with a detailed discussion of CFT. In 1959 I wrote an article for *Chemical and Engineering News*, which set some kind of record by generating over 5000 reprint requests. Not only inorganic chemists, but all kinds of chemists, found CFT a simple way to understand transition metal chemistry. One wit said that "we went from crystal ball theory to crystal field theory".

An outstanding feature of the *Chemical and Engineering News* articles was pictures of all the d orbitals. These were of models made by Bob Gould. At that time there were no pictures or diagrams of d orbitals in either beginning or advanced books on inorganic chemistry. There were pictures of s and p orbitals, but only pictures of d^2sp^3 or dsp^2 hybrid orbitals. This was a result of the great influence that Pauling had.

Of course CFT quickly became ligand field theory, and finally was recognized as MO theory applied to coordination compounds. Today molecular orbital theory is by far the most widely used by all chemists, and the most successful. It is used to explain structures, physical properties, chemical reactions of all kinds, and chemical bonding.

In my opinion, valence bond theory and the things that go with it, such as hybrid orbitals and resonance theory, have had their day. They are still taught in introductory chemistry courses, but an examination of the literature will rarely find them mentioned. MO theory is used instead, both in theoretical papers and to explain experimental results. Density functional theory (DFT) is also an MO theory, and will complete the takeover.

P.C.F.: Let's get back to the Basolo and Pearson joint efforts on reaction mechanisms.

The 10 years from 1951 to 1961 were probably the most exciting and productive years of both of our research lives. What we established, essentially, was that octahedral complexes reacted by dissociation, or S_N1, mechanisms, and that square planar complexes reacted by a displacement, or S_N2, mechanism. Much later Chad Tolman pointed out to me that we could have predicted these results in advance, if we had only remembered the 16–18 electron rule for complexes.

After 1960, Fred and I drifted a little apart in our interests. He started work on organometallics, which was virgin territory, and I started studying rapid reactions, particularly the ligand substitution reaction of labile complexes. But we never completely stopped collaborating until I left NU in 1976. Altogether we published over 70 papers jointly. Jim Ibers joined the faculty at Northwestern in 1964, and I published some papers with him also.

P.C.F.: Besides reaction mechanisms, what have been some of your research interests?

I continued to do quite a lot with organic reaction mechanisms during the 1950s but this tapered off after 1960. It never completely stopped, but I published my last paper in this area in 1989.

Theoretical chemistry has always been of great interest to me. I published my first paper on the subject in 1948. This was the only one which was purely computational, and it was not very good. My interest really lies in concepts, and particularly the strength of the chemical bond. I have always tried to find correlations between different properties of the same molecule. I call these papers 'theoretical' only in the sense that they needed no laboratory work on my part, they usually rely heavily on the experimental work of others.

P.C.F.: This sounds like the Principle of Hard and Soft Acids and Bases.

That is correct. HSAB is the prototype for my theoretical work in many ways. It is an idea that was inspired by a fortunate collaboration with John Edwards in 1962, and it started with a paper which appeared in 1963. The HSAB Principle states that hard acids prefer to coordinate to hard bases, and soft acids prefer to coordinate to soft bases. Initially hardness and softness were related to polarizability.

'Hard and Soft' certainly has generated more interest than anything else I have ever done. I wrote about 25 papers dealing with the original concept. Two of these papers have been selected as citation classics by *Current Contents*. The papers citing them have been of two kinds. Most were favorable, when the authors had a useful experience with the Principle, which is really a very good one. But a few were unfavorable, when the author's experience was a bad one.

In my opinion, most of the unfavorable cases were due to a misunderstanding on the part of the authors. They, and many other chemists, seem to think that the Principle claims that only hardness or softness determines the strength of a coordinate bond. But, as I clearly stated in 1963, all that was implied was a preference, which is not a very strong word. Chemical bonds are very complicated, and many factors determine their strength.

P.C.F.: The HSAB Principle got you involved in another disagreement with Pauling.

Yes, Pauling had proposed a bond energy equation as a way of measuring the electronegativity (EN) of the elements. This equation is very famous and is used in a number of cases to discuss bond energies. But I had noticed that in exchange reactions of the kind: $A{:}B + A'{:}B' \rightarrow A{:}B' + A'{:}B$, the Pauling equation failed, almost always. Not only was the calculated value of ΔH off by many kilocalories, but the sign was wrong!

Now the HSAB Principle is very good at predicting the correct sign for ΔH, but not its magnitude. In 1968 I published a paper pointing out this failure of Pauling's equation. It created quite a stir in the public press for a few days. The *New York Times* had column headlines saying "Pauling's Equation Found to be Useless". The reaction amongst the chemical community was almost nil. Obviously very few chemists could believe that Pauling had done something less than perfect. (Actually Pauling managed to get the right values for the ENs of the elements even with a flawed equation. This is a tribute to his insight).

P.C.F.: The concept of 'hard and soft' has had a renaissance in more recent years?

One of the problems I had with HSAB was my inability to define exactly what I meant by hardness and softness. In the eyes of many scientists this was a very damning failure, essentially invalidating the whole idea. Fortunately, in 1983 Bob Parr spent a sabbatical at the Institute for Theoretical Physics at UCSB. One day we met and he was able to explain to me what hardness and softness were. We came up with an exact definition, and with an operational definition for measuring hardness. Softness was simply the inverse of hardness.

This was in 1983. I had published my last paper on HSAB in 1970, and had become interested in symmetry rules for chemical reactions. This was inspired, of course, by the work of Woodward and Hoffmann. But I also want to acknowledge the stimulus I received from reading Al Cotton's book, *Chemical Applications of Group Theory*. I wrote a book myself, in 1976, on symmetry rules, but it was not very successful. In fact chemists in general lost interest in the role of symmetry in chemical reactions, rather quickly. I suppose this was because so few molecules have much symmetry.

At any rate, in 1983 I was ready for a new interest, and the new understanding of HSAB fitted in perfectly. Actually it was DFT which provided the definitions for chemical hardness, and also a new definition of absolute EN. These two properties of any chemical system give a lot of information about how the system would behave chemically. This has become the focus for most of my research in the last 14 years, and I have published about 30 papers on chemical hardness, one way or another.

This has also caused me to try to understand the related subject of physical hardness, which is the resistance to changes in shape or volume of a solid object. Chemical hardness is the resistance to change in the electron distribution in a molecule. It appears, based on many lines of evidence, that an equilibrium system is characterized by a maximum value for both the chemical hardness and the physical hardness. There is a Principle of Maximum Hardness (PMH), and a Principle of Maximum Physical Hardness (PMPH). These Principles seem to have important consequences.

I'm afraid that I irritated Pauling one last time by espousing absolute EN, as defined by Parr. Actually, absolute EN is quite different in its meaning from Pauling EN. I feel that it fills a definite need in our understanding of chemical systems, whether they be atoms, radicals, ions, molecules, or a crystal of a solid. It is unfortunate that the same word 'electronegativity' is used for both concepts.

I should say that both Pauling and Ingold were very kind to me in our personal contacts. They were quite similar, both being very self-confident and very charming. They had every reason to be self-confident, of course, but they also were a little arrogant.

P.C.F.: You retired in 1989 at the age of 70. Obviously you have kept busy since then.

I come in to the University every weekday and put in a few hours reading and writing. I definitely enjoy my retirement, since I am healthy, have a generous collection of pensions, and can do pretty much as I please. I do miss contact with the students and lecturing, though I give a guest lecture now and then.

I do not miss writing research proposals, making up and grading exams, making out grades, and departmental meetings. My research since retirement, as I said, has been pretty much on chemical and physical hardness. Along the way, I had to learn something about the solid state. I found this to be a very interesting field and have published some papers, though I do not claim to be an expert. I have very recently written a book entitled *Chemical Hardness*, published by VCH Publishers. It contains sections on DFT, the solid state and physical hardness, which I hope will be of interest.

P.C.F.: We agreed to avoid discussing individual students. Are there any general remarks you would like to offer?

Over the years I have had many young people work with me, and I am very proud of how they have turned out. I don't think I taught them very much, certainly not in the lab where my expertise dates back to the 1940s or 1950s. Occasionally I would astonish them by explaining results that they have obtained and were baffled by. I don't think my explanations were always correct, but they served their purpose at the time.

At any rate, the successes that my former students have had are entirely due to their own abilities and hard work. I take some pride in noting that almost all of them are working in areas that have little to do with the kinds of research that they did with me.

P.C.F.: Ralph, you always have such great stories when we let down our hair a bit. Are there any you would like to record for posterity?

Starting in 1951, I have done a lot of consulting for the chemical industry, especially Dow Chemical. My role was mainly as a good listener. I would encourage ideas that I thought were right, and discourage those that seemed wrong to me. My most memorable experience had to do with cesium. The Dow people had made the purest cesium metal ever, and were unhappy because it was yellow, a color associated in the minds of organic chemists with impurity. Besides the textbooks all said cesium was silver–white. I told them that people who write books often don't know what they are talking about. Cesium is yellow!

P.C.F.: OK—one last question—what's the most interesting referee's report you've received?

One referee suggested that my manuscript should be either reduced by 50% or oxidized completely! I usually did not find most referee reports very humorous at the time I received them; they often seemed to be written by the mentally challenged. Looking back, I am more tolerant now and believe that most of my papers were improved because of reviewer's comments. I'm sure I often did a poor job as a referee myself when given papers where I was not familiar with the latest developments.

P.C.F.: Thank you, Ralph.