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# KENNETH SANBORN PITZER 1914 – 1997

A Biographical Memoir by ROBERT F. CURL

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Biographical Memoir

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# KENNETH SANBORN PITZER

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BY ROBERT F. CURL

The research career of Kenneth S. Pitzer, physical chemist, is truly awe inspiring. In 1936, his first year as a graduate student, with J. D. Kemp, another graduate student, he discovered that a barrier to internal rotation was required to explain the third law entropy of ethane. This discovery had an enormous impact upon organic chemistry and thermodynamics. This was just the first of his many important contributions to thermodynamics and later to quantum chemistry. The unique aspect of much of his most important work was the development of powerful models for the thermodynamics of whole classes of systems through insights derived from statistical thermodynamics. His equations for accurately describing the thermodynamic properties of ionic solutions from dilute solutions to fused salts have found wide application in a number of fields. His extension of the method of corresponding states for fluid properties is also used extensively. In the field of quantum chemistry Pitzer applied his unique talents to the development of improved core potentials for relativistic systems.

Pitzer's grandfather, Samuel Collins Pitzer, settled in Pomona, California, in the 1890s. Samuel Pitzer's offspring consisted of three boys and one girl. Kenneth's father, Russell Kelly Pitzer, was the youngest. He arrived in Pomona in time to attend high school and then Pomona College, which was located in Claremont, graduating in 1900. He then went to law school in San Francisco. He never really practiced law but instead became involved in citrus orchard activities following the career path of his father and older brothers. He later served actively on the board of the local savings and loan bank. Over time he became quite wealthy—wealthy enough to found Pitzer College in Claremont.

Kenneth's mother, Flora Anna Sanborn, went to Pomona College, graduating a year after Russell, and then attended the University of California, Berkeley, for a year. She then returned to Pomona and taught high school mathematics. Kenneth Pitzer was the only child of this union and a rather late one—his parents were in their mid-30s when he was born. Flora Pitzer taught her son kindergarten and first grade at home, with a heavy emphasis on mathematics, so that he entered school in the second grade. She died of cancer when Ken was in junior high school.

In high school Ken became increasingly interested in mathematics, physics, and chemistry. This led him to attend Caltech. He did well enough as a freshman to be selected as one of the few students to do summer undergraduate research at A. A. Noyes's private laboratory near Balboa Harbor. This summer research gave him his first two publications on higher oxidation states of silver and credit for the required sophomore quantitative analysis course, thus freeing up more time for undergraduate research with both Don Yost and Linus Pauling. This work resulted in his first single author paper—the determination of the crystal structure of tetramminocadmium rhenate.

## BERKELEY I

Upon receiving a bachelor's degree from Caltech in 1935, Pitzer married Jean Elizabeth Mosher, whom he had known

since childhood, and started graduate school at the University of California, Berkeley. He chose Wendell Latimer as his research director primarily because Latimer gave his students great freedom to choose their own research directions. J. D. Kemp, a graduate student of William Giauque, was working with Ralph Witt, a postdoctoral, to measure the heat capacity of ethane from low temperatures to room temperature, thereby obtaining its third law entropy. The room temperature entropy could be calculated by the methods of statistical thermodynamics given the rovibrational energy levels appreciably populated at room temperature. When Kemp carried out such a calculation, he found that the statistical thermodynamics entropy was higher than the one he obtained from the third law calculations. Such a result is possible if ethane formed a glass at very low temperatures freezing in entropy, but Kemp knew the melting point of ethane was sharp, making glass formation highly unlikely. Could there be something wrong with the statistical thermodynamics calculation?

He took this puzzle to Pitzer. The only unusual feature of the statistical mechanics calculation was that internal rotation could take place about the CC bond. Orthodox belief at the time was that such internal rotation was essentially free. Pitzer and Kemp realized that the entropies calculated by the two methods could be brought into agreement by introducing a substantial barrier to internal rotation, and Pitzer had the mathematical ability and the knowledge of quantum mechanics needed to calculate the internal rotation energy levels as a function of barrier height, thereby determining that the barrier to internal rotation was about 3 kcal/mol.

This research, with Pitzer and Kemp as the only authors, was the subject of his first and second papers as a graduate student and his fourth and fifth papers overall. This seminal work had a revolutionary impact upon both organic chemistry and the thermodynamics of organic compounds. This research and a number of other accomplishments by Kenneth Pitzer won him a faculty appointment at Berkeley upon his graduation in 1937.

The Pitzer's three children, Ann, Russell, and John, were all born in Berkeley. The oldest, Ann, resides in California at La Jolla and had a career in software development management. Russell is on the faculty at Ohio State University and lives in Columbus, Ohio. John is a noted national income economist and lives in Arlington, Virginia. All three children have been successful though Russell is the only chemist of the three.

Pitzer's work with Kemp was published in 1936, more than a year before the birth of Pitzer's son Russell, who much later provided a new chapter in the ethane story. Like his father, Russell grew up to be a physical chemist. As a graduate student at Harvard, Russell calculated the barrier to internal rotations of ethane obtaining a value very close to what his father had proposed more than 20 years before. This was quite an accomplishment because previous calculations always produced a much smaller number. Russell has had a distinguished career as theoretical chemist at the Ohio State University. As we shall see, much later the research interests of father and son crossed paths again.

During the years before the Second World War, Pitzer's research was primarily focused on thermodynamics. His publications included several that exploited the internal rotation results and several on the thermodynamic properties of ionic salts, ions, and ionic solutions. While his interest in the effect of internal rotation on thermodynamic properties lessened and essentially ended by the mid-1940s, the interest in the thermodynamic properties of ionic solutions was a lifelong interest that resulted many years later in his most cited publications. A single paper in 1939 on the theory of corresponding states for fluids also foretold an interest that would be revived and greatly amplified after the war.

California, particularly Berkeley, will be a recurring theme in this narrative. The Pitzers were deeply rooted in California. Pitzer loved the California landscape, especially the Sierra Nevada, and took great pleasure in outdoor activities, especially sailing. His interest in sailing went far beyond the pleasure of moving across the water. It extended to the design and construction of boats, including using unorthodox sails at times. In terms of personal environment Pitzer almost certainly would have been content to remain at Berkeley throughout his life, but events and opportunities would repeatedly draw him away. Always he would return. The first event that pulled the Pitzers from Berkeley was World War II.

## WORLD WAR II

In the early years of the war Latimer received a contract from the Office of Scientific Research and Development to study gas flow patterns relevant to chemical warfare. Pitzer joined him in this work carrying out experiments on a field in the Yolo Bypass near Sacramento. In 1943 he was invited to help run a laboratory to support the Office of Strategic Services near Washington, D.C., for the National Defense Research Council. Most of the work was in support of behind-the-lines activities, such as sabotage and espionage, in a role like the James Bond gadget man, Q. Originally he was a deputy technical director, but his chief was pulled off for another role, and Pitzer became first acting technical director and then shortly thereafter technical director.

Although most of his time was consumed by war matters, it should be noted that two of Pitzer's 10 most cited publications were published either during the war years or shortly thereafter. The earliest of these, published in 1942 with Bill Gwinn, was concerned with the calculation of the energy levels and thermodynamic functions of molecules with internal rotors. The other, published in 1943 with D. W. Scott, applied this work to the thermodynamic functions of benzene and its methyl derivatives.

The most important paper Pitzer published during the war years appeared as a letter to Science in 1945. It was entitled "Strain Energies of Cyclic Hydrocarbons" and was concerned with the balancing of the energy required to distort CCC bond angles against the energy required to move up barriers to internal rotation about CC bonds. If such barriers are neglected, the expected bond angles of cyclopentane seem ideal for a planar ring. When internal rotation barriers are included one of the carbon atoms pops up out of the plane of the others. In this letter Pitzer correctly predicted the cyclopentane would not be planar. For six-membered rings CCC bond angle distortion is relieved by distortion of carbon atoms out of planarity. There are two ways this can logically be achieved. One of these structures vaguely resembles a boat and the other vaguely resembles a chair. In the 1930s Hassel's electron diffraction experiments found the chair form. Pitzer explained that the chair form would be the more stable because it had the lower internal rotation energy. Although not discussed in this paper, internal rotation barriers affect other hydrocarbon ring sizes. Thus for the four-membered ring, cyclobutane, there is a small barrier to planarity even though displacement out of planarity of the carbon atoms is vigorously opposed by the distortion of bond angles. It lies far down Pitzer's citation list, with 99 citations to date.

Altogether Pitzer published 32 papers from 1942 to 1947. Some of these were undoubtedly from work done prior to or after the involvement of the United States in World War II, but 11 of these papers have publication dates from 1943 to 1945.

### BERKELEY II

After the war the Pitzers returned to Berkeley for what turned out to be a relatively short stay. His scientific interests during this period focused primarily upon thermodynamic properties of a number of species, most of which were hydrocarbons. Returning to cyclopentane, Pitzer considered again the result that the most stable conformation has one C atom out of plane. Since all five carbon atoms are equivalent, there are five equivalent minima. The resulting fivefold degenerate energy level should then be split by tunneling between equivalent minima. However, the barrier between adjacent energy minima turned out to be virtually negligible so that there is no need to invoke tunneling, and the atom that is out of plane can appear to rotate around the ring. Since there is no angular momentum associated with this rotation, this is not a "real" rotation. Pitzer called it "pseudorotation."

His other significant interests during this period were infrared spectroscopy and the nature of the hydrogen bond in the F-H-F anion. Another highly cited paper from this time was on repulsive forces. His publication rate increased compared with the war years, with 18 publications dated 1948-1949. During this period he was adviser to George Pimentel, one of his most famous students.

Pitzer was never far from administrative duties. In fact, he regarded them as an obligation for scientists with a talent for them. Upon his return to Berkeley after the war, he was asked to become assistant dean in the College of Arts and Sciences and accepted. This was a job advising freshman and sophomore chemistry majors. Pitzer was a faculty member in the College of Chemistry, but undergraduate chemistry majors belonged to the College of Arts and Sciences. At this time upper-level chemistry majors were advised by the College of Chemistry, but lower-level (prospective) chemistry majors were not advised by anyone. Pitzer agreed to step into the breach. This was a minor job with a big title. A much more important activity he was involved in was work on the Budget Committee of the University Senate. It was at this time that the Pitzers acquired their much enjoyed place at Clear Lake, where the family would swim, sail, and water ski, and Pitzer could experiment in his orchard.

# ATOMIC ENERGY COMMISSION 1949-1951

Kenneth Pitzer was called back to Washington in 1949 to be director of research of the Atomic Energy Commission (AEC). The first big agenda item that came up was an anticipated shortage of uranium. At that time essentially all uranium was being imported. This seemed to Pitzer to be a bad situation. He wanted very much to encourage uranium prospecting in North America and thought the best way to do it would be to offer a large enough price for local uranium. This proposal upset the procurement people, who had been trained to get the best price. In order to make this happen Pitzer supported a proposal by E. O. Lawrence for a material testing accelerator (MTA) that could be put to use making plutonium. A suitable site for this had to be found. It turned out some land owned by the federal government and unused near Livermore looked ideal, and in due course this land was turned over to the AEC. The prospect of the MTA apparently frightened the procurement people enough that they began to encourage prospecting, and it was never built. The land near Livermore thus acquired became the site of Lawrence Livermore National Laboratory.

The dominating issue of Pitzer's time at the AEC was the question of whether there should be a crash program

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to develop thermonuclear weapons. He was definitely on the side of such a program, and J. Robert Oppenheimer was definitely opposed to it. Pitzer was alarmed by the rapid success of the Soviet Union in developing an atomic weapon. He felt that it would be a dereliction of duty not to make every effort to explore the feasibility of a thermonuclear weapon in the face of this development, and he worked to make sure that such a program was undertaken. Pitzer produced only a relatively small amount of research on topics of his personal interest during his tenure of the AEC position.

## BERKELEY III

In 1951 Pitzer returned to Berkeley to become the dean of the College of Chemistry. The first order of business was to develop chemical engineering. Schutz had already been appointed professor of chemical engineering in the College of Chemistry. This effectively preempted the College of Engineering from forming a Department of Chemical Engineering, so Pitzer divided the College of Chemistry into a Department of Chemistry and a Department of Chemical Engineering and hired additional faculty in chemical engineering.

With much more time available for research Pitzer set to work. He published 70 papers from 1952 to 1962. In 1938 he published a paper on corresponding states of "perfect liquids;" Pitzer now returned to this theme. Qualitatively he looked at how the effects of a molecule being globular like neopentane, or being asymmetric like a normal hydrocarbon, or having a small dipole moment like H<sub>2</sub>S affects the intermolecular potential and found the effects were similar. From these considerations he proposed an extension of corresponding states for fluids by adding a third parameter for each substance in addition to critical temperature,  $T_c$ , and critical pressure,  $P_c$ . He called this parameter the "acen-

tric factor,"  $\omega$ . He defined  $\omega$  in terms of the reduced vapor pressure at  $T_r = 0.7$  as  $\omega = -\log P_r - 1$ . For a "perfect fluid," such as Ar, Kr, Xe, or  $CH_4$ ,  $\omega = 0$  since the reduced vapor pressure of these substances at Tr = 0.7 is 0.1. Pitzer therefore created a class of "normal fluids." Two normal fluids with the same value of  $\omega$  will have the same compressibility factor  $Z = PV_M/(RT)$  at the same value of reduced temperature,  $T_r$  (= T/T<sub>c</sub>), and reduced pressure  $P_r$  (= P/P<sub>c</sub>). His next step was to consider a power series expansion of Z in terms of  $\omega$ . Since the differences between the Z's of la normal fluid and the Z's of a perfect fluid are small at the same reduced temperature and pressure, this expansion could be terminated at the linear term (i.e.,  $Z(T_r, P_r, \omega) = Z^{(0)}(T_r, P_r) +$  $\omega Z^{(1)}(T_r,P_r)$ . Thus, the PVT behavior and the dependence of thermodynamic quantities upon pressure for a wide variety of substances can be determined from two sets of tables and values of  $T_c$ ,  $P_c$ , and  $\omega$  for the particular substance of interest. This development proved to be of considerable use to chemical engineers needing a rapid estimate of PVT or pressure dependence of thermodynamic quantities.

Other especially notable works from this period are the paper with W. E. Donath on the energetics of cyclopentane and its derivatives, the 1959 paper with Enrico Clementi on the species expected to be present in carbon vapor (linear chains with even numbers of carbon atoms dominant), and the 1960 paper with Oktay Sinanoglu on the force between two molecules adsorbed on a surface.

At this time Pitzer became a trustee of Mills College and Harvey Mudd College. These activities were the first offered to him by his California community in recognition of his wisdom and stature. Such service was important to him. He served for many years as a trustee of both Mills College and Pitzer College. He also served twice on the Council of the National Academy of Sciences and on several boards of both non-profit and for profit institutions.

#### RICE UNIVERSITY 1961-1968

In early 1961 J. Newton Rayzor, a Rice Institute trustee, approached Pitzer about whether he would be interested in the presidency of that school. Pitzer had taken a course at Caltech under William V. Houston, the retiring president of Rice and had great respect for him. He also knew several faculty members at Rice. Since Rice was a small place, he would have time to keep some research going, and he could see some possibilities for making Rice a player on the national scene. Yes, he was interested. When George R. Brown, board chair, went to the trouble of coming to San Francisco to see him, Pitzer knew that the interest was mutual. He immediately told Brown that his interest was contingent upon Rice opening admission to all races. Brown replied that would not be a problem.

At the same time that this was going on Pitzer was being offered the position of chancellor of any one of several University of California campuses. He decided that it would be more likely that he could make significant progress at Rice. In 1961 Rice had been in existence for less than 50 years. Its first president, Edgar Odell Lovett, envisioned Rice as developing into a great university. He worked hard to make this vision a reality. The institution got off to a good start with a high-quality faculty. The biologist Julian Huxley, for example, was an original member of the faculty. However, a great university is not created overnight, and then the Depression intervened creating great stress on all universities. The Rice Institute became a small, elite institution differing from liberal arts colleges in emphasizing science and engineering. Because Rice did not charge tuition, it was able to skim the cream of potential matriculants in Texas and neighboring states and consequently developed a reputation for producing highly capable graduates.

When Pitzer came into the presidency of Rice, the Depression was long over and he recognized George R. Brown as an individual who could help him raise Rice to another level. Brown had a well-deserved reputation as a wheelerdealer, but he was also a man of vision with broad interests and real devotion to Rice. He was also enormously wealthy. Together Pitzer and Brown set out to make Lovett's vision of Rice as a great university a reality. The name was changed from Rice Institute to Rice University, students of all races were welcomed, and Rice began to charge tuition. Pitzer quickly began to demonstrate the name change meant a real change by developing the humanities and social sciences. The charging of tuition was introduced because this initiative required lots of money. The tuition itself was modest, but charging it did allow Pitzer to demonstrate to foundations he approached that Rice was utilizing every resource available to it.

Pitzer was somewhat surprised to learn that Rice had no formal tenure system and persuaded the Board of Trustees to introduce one. He found that there was no institutionalized system for providing a faculty voice in university governance and created one. Then he set about plotting a direction and a mechanism for transforming Rice in the direction of becoming a national university. This required both a plan for development and the financial means to carry it out. Working with others, he created a 10-year plan for the university and persuaded the board to begin a successful \$33 million capital campaign. In his efforts to bring Rice to national prominence he worked closely with George Brown. There is no doubt that Pitzer's efforts lifted both the aspirations of Rice and improved Rice's quality enormously.

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At Rice, Pitzer also had time to maintain a vigorous research program. He set up a research office and laboratory in the chemistry building and spent most of his early mornings there. He took no graduate students but always had several postdoctoral fellows. These included Stewart Strickler, Jürgen Hinze, Jerry Kasper, Harry Hopkins, and T. S. S. R. Murty. The author of this memoir had the pleasure of working closely with the middle three of this list during this period. While at Rice, Pitzer worked on bonding in xenon halides, continued work on small carbon clusters, and began working on nuclear spin isomerization in methane. The gas phase theory work on nuclear spin isomerization of methane was completed while he was at Rice, but he continued work on the spin isomerization behavior of solid methane after returning to Berkeley from Stanford.

# STANFORD UNIVERSITY 1968-1971

During his time at Rice, several first-tier universities approached him about becoming their president. He was uninterested primarily because he wanted to realize his aspirations for Rice. Then George Brown retired from the board, and the makeup of the board shifted in the direction of being less visionary and bold. Pitzer disliked repetitive tasks, and the situation at Rice seemed to offer less scope for creative initiatives. When he was approached by Stanford about its presidency, the time seemed right to make a move. Stanford was clearly a world-class university, the return to his roots in California was attractive, and so was the opportunity to deal with new challenges in a much bigger institution. In 1968 Pitzer became president of Stanford.

He knew that the Viet Nam War would create problems in the new job, but he took the job at Stanford, estimating that student unrest would be decreasing. The invasion of Cambodia, however, provoked new protest. Pitzer was opposed to the war. While at Stanford, he signed a lengthy public statement to that effect. This did nothing to reduce the almost nightly turmoil on the Stanford campus, which involved both students and nonstudents. During this time, being president of Stanford became a full-time job of emergency management. This was not the job that Pitzer wanted. While turmoil may have many exciting aspects and present critical challenges to a university president, if your interests are in the development and intellectual management of a university, turmoil becomes just a distraction taking away from the real business of a university. After three years, Pitzer left Stanford. He was 57 years old and had abandoned any type of research program when he moved to Stanford.

# BERKELEY IV 1971-1997

The Berkeley Chemistry Department immediately invited him back as a professor. Pitzer was touched profoundly by this offer. It seemed that at 57 his best years as a researcher were likely to be behind him, especially as he had been out of research at Stanford. He set out to prove that his colleagues' faith in him was not misplaced. The result was astonishing: 211 of his 405 papers were published and his three most highly cited papers were produced after this final return to Berkeley. The main themes of his research in this period, in order of number of publications, were:

- 1. developing and using a new method for describing the properties of ionic solutions;
- 2. developing and using quantum chemical calculations for molecules where relativistic effects are important;
- 3. continuing the work started in the mid-1950s on the properties of fluids; and
- 4. describing the thermodynamics of various systems. Pitzer also published a variety of papers during this period that are not so neatly categorized.

Pitzer's first research publications after returning to Berkeley were concerned with developing an empirical method for predicting the thermodynamic properties of ionic solutions. Debye-Hückel theory describes the limiting behavior of electrolytic solutions, but it becomes inaccurate at rather low ionic strengths even for 1:1 electrolytes. Various approaches had been proposed for extending descriptions of ionic solutions, but all suffered either from limited accuracy or required too many empirical parameters. Pitzer examined the theoretical underpinnings carefully and proposed a formula for describing the thermodynamic behavior of ionic solutions requiring a minimal number of empirically determined parameters. He followed this paper with another giving the values of his parameters for 227 pure electrolytic solutions and yet another describing how mixed electrolytes should be treated. These three publications are his most highly cited in the order just listed. This method for treating the thermodynamics of ionic solutions is widely used in many fields, particularly geology.

This work highlights a major aspect of Pitzer's creativity in which he used statistical mechanics to gain insight into the best way to develop empirical methods that work. In the case just described he did this for ionic solutions. The approach he used for ionic solutions of a theory paper followed by useful tabulations is remarkably similar to one that he used in extending corresponding states to obtain a more accurate treatment of the properties of fluids. It is interesting to note that two of the papers on corresponding states of fluids are among his 10 most highly cited. In total there were 12 papers in this initial series on ionic solutions and many other papers on electrolytes not labeled as part of the series, totaling far more than the number in the corresponding states of fluids series. After returning to Berkeley, Pitzer published well over 100 papers on the properties of ionic systems.

About this time Pitzer began to be more deeply interested in the effects of relativity on quantum chemical calculations. He began with a paper on the effect of the f-shell filling on atoms. At that time there were good nonrelativistic and relativistic Hartree-Fock calculations on the row from Hf to Bi. He set out to distinguish the effects of relativity from those resulting from screening by the f-shell. To explore f-electron screening he carried out nonrelativistic Hartree-Fock calculations comparing the results on normal atoms to those on pseudo-atoms without the f-shell electrons with the nuclear charge reduced by 14. These were ground-clearing calculations; his real interest was in the effects of relativity on chemical bonding. He explored this by considering the reactivity of several heavy elements and the stability of their compounds finding one of the major effects arises from spin-orbit splitting (a relativistic effect) of p electrons. The relativistic orbitals  $p_{1/2}$  and  $p_{3/2}$  are not bonding. In order to get full *p* electron bonding the linear combination  $p_{1/2}/\sqrt{3} + p_{3/2}\sqrt{2/3}$  must be used. This requires a promotion energy corresponding to 1/3 of the spin-orbit splitting.

Around this time the need to have methods for carrying out quantum chemical calculations on systems with many electron atoms became apparent. Goddard and his students attacked the problem of doing such calculations by developing effective core potentials, which did not contain relativistic effects. Y. S. Lee, W. C. Ermler, and Pitzer then developed an effective core potential methodology that included relativistic effects. A few years later his son Russell became interested in carrying out calculations on molecules containing many electron relativistic atoms and utilized his father's approach developing a method to utilize molecular symmetry to eliminate complex Hamiltonian matrix elements for most molecules having symmetry, greatly reducing computation times and improving calculational efficiency. Starting in 1975 and continuing into the early 1990s, Pitzer was deeply involved in *ab initio* quantum chemistry calculations primarily those involving molecules with heavy atoms. His paper production in this area peaked around 1983. All together Pitzer published 31 quantum chemistry papers after returning to Berkeley.

Not all of Pitzer's work after returning to Berkeley was in theory and calculation. He established a program in lowtemperature calorimetry to investigate nuclear spin species conversion in methane. This harked back to the low-temperature spectroscopy on spin species conversion in methane that he did at Rice. A careful investigation of solid methane containing a small amount of O<sub>2</sub> to catalyze the spin species conversion revealed a thermal anomaly centered around 1 K that could be followed down to about 0.5 K. The entropy change associated with this conversion indicated that about <sup>3</sup>/<sub>4</sub> of the molecules were being converted. At that time several structures for solid methane had been proposed. One of these had ¼ of the molecules in a very symmetrical site and <sup>3</sup>/<sub>4</sub> in unsymmetrical sites. Thus, the fact that about <sup>3</sup>/<sub>4</sub> of the molecules underwent conversion at the thermal anomaly provided excellent evidence for this particular structure. Experiments without O<sub>2</sub> catalyst did not exhibit the 1 K thermal anomaly.

Much later Pitzer developed an experimental program in measuring the critical properties of electrolyte solutions and collaborated extensively with experimental groups measuring the properties of electrolytes. However, it seems fair to say that Pitzer was always primarily interested in theory and calculations but always theory and calculations related closely to experimental data.

His research during the last years of his life was exclusively in thermodynamics and almost exclusively in the properties of ionic systems. There are an enormous number of electrolytic solutions. A number of these systems exhibit interesting behavior, and he found encouragement in the success of his approach in describing this behavior. Perhaps the strongest encouragement for continuing this line of research was the enthusiastic reception given this work by workers in geology and oceanography, who found his quantitative description of electrolyte solutions extremely useful to their research.

I remember Kenneth Pitzer remarking a few years before his death that most of his still living contemporaries had abandoned research. I felt this remark reflected both pride in still being productive and perhaps a little puzzlement that someone would willingly give up the source of so much pleasure and satisfaction. Kenneth Pitzer was vitally involved in the research enterprise until his death.

MANY SPECIFIC PIECES OF personal information related here were obtained from a series of interviews with Kenneth and Jean Pitzer conducted by Sally Hughes and Germaine LaBerge. These, together with a number of interesting short pieces and fragments concerned with Kenneth Pitzer, are available as a single PDF file from the Bancroft Library, University of California. Ann Pitzer and Russell Pitzer, consulting with John Pitzer, provided new information and corrections. Melissa Kean, the Rice historian, reviewed the manuscript and suggested many editorial changes that I happily adopted.

# HONORS AND AWARDS

- 1943 American Chemical Society Award in Pure Chemistry
- 1949 Elected to the National Academy of Sciences Precision Scientific Award in Petroleum Chemistry of the American Chemical Society
- 1950 U.S. Junior Chamber of Commerce Award as one of the Ten Outstanding Young Men in the Nation
- 1951 Alumnus of the Year Award, University of California, Berkeley Guggenheim Fellowship
- 1954 Member, The American Philosophical Society

1958 Clayton Prize, Institution of Mechanical Engineers, London

Fellow, American Academy of Arts and Sciences

- 1962 D.Sc. (hon.) Weslayan University, Middleton, CT
- 1963 Priestley Memorial Award, Dickinson College, Carlisle, Pennsylvania
  - Doctorate of Law , University of California, Berkeley
- 1965 Gilbert Newton Lewis Prize, California American Chemical Society
- 1966 Alumni Distinguished Service Award, California Institute of Technology
- 1969 LL. D. (hon.) Mills College, Oakland, CA Priestley Medal, American Chemical Society
- 1975 National Medal of Science
- 1976 Gold Medal, American Institute of Chemists Willard Gibbs Medal, Chicago Section, American Chemical Society
- 1978 Centenary lecturer, Royal Society of Chemistry, United Kingdom
- 1984 Berkeley Citation Robert A. Welch Award in Chemistry
- 1986 Honorary fellow, Indian Academy of Sciences Mack Award, Ohio State University
- 1987 Pitzer Lecture, University of California, Berkeley
- 1988 Rossini Lecture, 10th IUPAC Conference on Chemical Thermodynamics, Prague
- 1991 Clark Kerr Award, University of California, Berkeley
- 1994 Gold Medal Award, Association of Rice University Alumni Hall of Fame, Alpha Chi Sigma
- 1996 Robert J. Bernard Award for Outstanding Service to the Claremont Colleges

# SELECTED BIBLIOGRAPHY

#### 1936

With J. D. Kemp. Hindered rotation of the methyl groups in ethane. J. Chem. Phys. 4:749-749.

## 1939

With W. M. Latimer and C. M. Slansky. The free energy of hydration of gaseous ions, and the absolute potential of the normal calomel electrode. *J. Chem. Phys.* 7:108-111.

### 1943

With D. W. Scott. The Thermodynamics and Molecular Structure of Benzene and Its Methyl Derivatives. J. Am. Chem. Soc. 65: 803-829.

## 1942

With W. D. Gwinn. Energy levels and thermodynamic functions for molecules with internal rotation. I. Rigid frame with attached tops. J. Chem. Phys. 10:428-440.

#### 1945

Strain energies of cyclic hydrocarbons. Science 101:672.

# 1946

Energy levels and thermodynamic functions for molecules with internal rotation. 2. Unsymmetrical tops attached to a rigid frame. *J. Chem. Phys.* 14:239-243.

#### 1947

- With Frederick D. Rossini, Raymond L. Arnett, Rita M. Braun, and George C. Pimentel. Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds. Pittsburgh, PA: Carnegie Press.
- With C. W. Beckett and R. Spitzer. The thermodynamic properties and molecular structure of cyclohexane, methylcyclohexane, ethylcyclohexane and the 7 dimethylcyclohexanes. J. Am. Chem. Soc. 69:2488-2495.

- With J. E. Kilpatrick and R. Spitzer. The thermodynamics and molecular structure of cyclopentane. J. Am. Chem. Soc. 69:2483-2488.
- With C. W. Beckett. Tautomerism in cyclohexane derivatives—reassignment of configuration of the 1,3-dimethylcyclohexanes. J. Am. Chem. Soc. 69:977-978.

## 1948

Repulsive forces in relation to bond energies, distances and other properties. J. Am. Chem. Soc. 70:2140-2145.

#### 1953

Quantum Chemistry. New York: Prentice-Hall.

## 1955

- The volumetric and thermodynamic properties of fluids. 1. Theoretical basis and virial coefficients. J. Am. Chem. Soc. 77:3427-3433.
- With D. Z. Lippmann, R. F. Curl, C. M. Huggins, and D. E. Petersen. The volumetric and thermodynamic properties of fluids. 2. Compressibility factor, vapor pressure and entropy of vaporization. J. Am. Chem. Soc. 77:3433-3440.

#### 1958

With R. C. Millikan. The infrared spectra of dimeric and crystalline formic acid. J. Am. Chem. Soc. 80:3515-3521.

## 1959

- Intermolecular and intramolecular forces and molecular polarizability. Adv. Chem. Phys. 2:59-83.
- With E. Clementi. Large molecules in carbon vapor. J. Am. Chem. Soc. 81:4477-4485.
- With W. E. Donath. Conformations and Strain Energy of Cyclopentane and its Derivative. J. Am. Chem. Soc. 81: 3213-3218.

#### 1960

With O. Sinanoglu. Interactions between molecules adsorbed on a surface. J. Chem. Phys. 32:1279-1288.

#### 1961

With L. Brewer. Thermodynamics. (Revision of Lewis and Randall's book). New York: McGraw-Hill.

#### 1967

With R. F. Curl and J. V. V. Kasper. Nuclear spin state equilibration through nonmagnetic collisions. J. Chem. Phys. 46:3220-3228.

# 1973

- Thermodynamics of electrolytes. 1. Theoretical basis and general equations. J. Phys. Chem. 77:268-277.
- With G. Mayorga. Thermodynamics of electrolytes. 2. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent. J. Phys. Chem. 77:2300-2308.

## 1974

With J. J. Kim. Thermodynamics of electrolytes. 4. Activity and osmotic coefficients for mixed electrolytes. J. Am. Chem. Soc. 96:5701-5707.

## 1975

- Are elements 112, 114, and 118 relatively inert gases? J. Chem. Phys. 63:1032-1033.
- With G. J. Vogt. Spin species conversion and heat capacity of solid methane near 1 degree K. J. Chem. Phys. 63:3667-3668.

# 1979

With P. A. Christiansen and Y. S. Lee. Improved ab initio effective core potentials for molecular calculations. J. Chem. Phys. 71:4445-4450.

#### 1980

Electrolytes—from dilute solutions to fused salts. J. Am. Chem. Soc. 102:2902-2906.

#### 1984

Relativistic calculations of dissociation energies and related properties. Int. J. Quantum Chem. 25:131-148.

#### 1987

With R. T. Pabalan. Thermodynamics of concentrated electrolyte mixtures and the prediction of mineral solubilities to high temperatures for mixtures in the system Na-K-Mg-Cl-SO<sub>4</sub>-OH-H<sub>2</sub>O. *Geochim. Cosmochim. Acta* 51:2429-2443.

## 1989

With R. R. Singh. Relationships in the approach to criticality in fluids, including systematic differences between vapor liquid and liquid systems. *J. Chem. Phys.* 90:5742-5748.

#### 1990

With R. R. Singh. Near-critical coexistence curve and critical exponent of an ionic fluid. J. Chem. Phys. 92:6775-6778.

#### 1992

Ed. Activity Coefficients in Electrolyte Solutions. Boca Raton: CRC Press.

## 1993

Ed. Molecular Structure and Statistical Thermodynamics: Selected Papers of Kenneth S. Pitzer. Singapore: World Scientific.

## 1995

Thermodynamics, 3rd ed. New York: McGraw-Hill.

## 1999

With B. S. Krumgalz and A. Starinsky. Ion-interaction approach: Pressure effect on the solubility of some minerals in submarine brines and seawater. J. Solid State Chem. 28:667-692.