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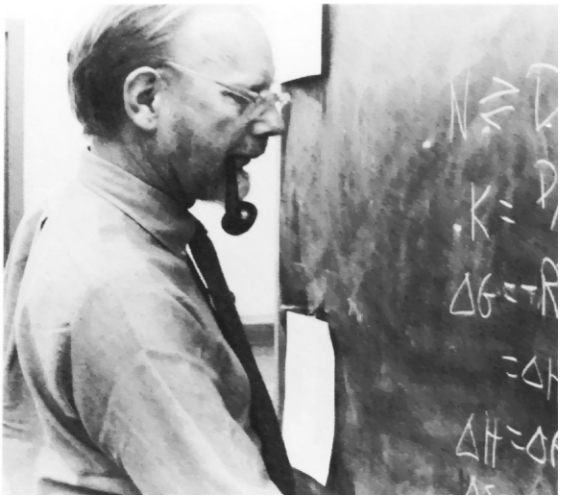
Foreword

This Festschrift of *Biophysical Chemistry* was put together to honor Walter J. Kauzmann's many lifetime contributions to physical and biophysical chemistry. Despite the proximity in time to the recent issues of *Biophysical Chemistry* honoring John Edsall and John Schellman, both of whose research interests often overlapped with Kauzmann's, the response by the physical/biophysical chemistry community has been tremendous. The participants range from former Princeton undergraduate students, graduate students, post-doctoral fellows, faculty colleagues, collaborators, lifelong friends and admirers. It is clear that, during his long career as teacher, mentor, researcher, collaborator, scholar, writer, editor, department chairman and friend, Walter Kauzmann has influenced the lives of innumerable people, many of whom have contributed to this special issue.



We count 41 research papers and seven personal recollections that make up the Walter Kauzmann Festschrift. The articles reflect his broad research interests over the years and the scientific impact he has had in those areas. The present papers cover topics as diverse as the physics of phase transitions and glasses (Stillinger and Debenedetti) to biochemical correlations with, and possible underlying causes of, immune thrombocytopenic purpura (Beardsley et al.) and diabetes (Khalifah et al.).

The personal recollections highlight not only Walter's enormous breadth and depth of knowledge, both of and outside physical chemistry; his phenomenal recall of references and his scientific and career-guiding influences; but also his ever-present willingness to share that information with students and co-workers and his genuine kindness, open-mindedness, integrity and modesty shown to all who interacted with him. As Walter Kauzmann's last graduate student, the guest editor was able to experience all of that firsthand and would like to take this opportunity to add a bit to the legend. Since we are fortunate to have several, enjoyable reminiscences about Walter Kauzmann included in this special issue, just a couple of memorable experiences are given here. These demonstrated, in the guest editor's mind, some of Walter's many admirable and impressive qualities.

We remember the time we were developing a random network model of liquid water and wrestling with rationalizing our introduction of temperature-dependent lattice vibrational force constants and frequencies at constant volume despite originally assuming that the lattice modes were totally harmonic (Einstein oscillators) [1]. The tempera-

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ture dependence of some lattice frequencies of ice had been observed experimentally, and presumably results from the structural character of ice and its anharmonic lattice potentials, allowing for the presence of hot bands [1]. One could certainly see how the same situation might also exist in water. However, temperature-dependent force constants for harmonic oscillators imply temperature-dependent potentials, which in turn imply temperature-dependent energy levels at constant volume. The latter lead to statistical thermodynamic inconsistencies, with one of the consequences being that the heat capacity can take on extremely large values at high temperatures, instead of leveling off at R per mode [1]. As we were discussing this conundrum, Kauzmann paused in thought for a while, as he often would do, and then suddenly, and quite amazingly, recalled an obscure paper by Rushbrooke-from over 40 years earlier [2]. In that paper, Rushbrooke showed how an apparently temperature-dependent potential could arise, classically at least, if one were to separate the set of system variables into two or more subsets and then do a preliminary Boltzmann averaging over one subset of variables [2]. Because our model of water was based on a separation into configurational and lattice vibrational contributions, Rushbrooke's analysis was indeed quite relevant and lent some theoretical justification for having constant-volume, temperature-dependent frequencies in water. Just to close the story quickly for any interested readers: since we could not deal with the anharmonic lattice modes, the heat capacity problem was circumvented by starting not with the free energy of harmonic vibration but by substituting the temperature-dependent frequencies into the usual expression for vibrational energy and differentiating that with respect to temperature at constant volume.

Another aspect of Walter Kauzmann that impressed people was his open-mindedness and willingness to listen to and not harshly criticize other points of view, even if they might be in opposition to his own. An example of this was Kauzmann's role as manuscript referee. Being highly regarded in many areas, he was frequently called upon to review various journal manuscripts. Kauzmann often invited the guest editor to review some of the submitted manuscripts he had received and discuss them with him. Occasionally, there would be a paper that argued against Kauzmann's own views or one that might be considered highly controversial, to say the least. While some other reviewers might perhaps be tempted initially to reject such papers, Kauzmann always held that, as long as there were no obvious violations of the laws of physics (thermodynamics), and the papers were logically presented and reasonably readable, he could not recommend that such papers be rejected. He often said that he was not smart enough to know when a new idea or approach to a problem might turn out to be correct and have a major impact on the field. All of this is not to say that Walter did not raise pointed questions, make detailed comments and suggest revisions. He certainly did all that and let you know when you had reinvented the wheel or made an obvious error, but his comments were always made in a constructive fashion. Kauzmann, who is a long-time student of the history of science and technology, often cited the tragic battle between Ludwig Boltzmann and Ernst Mach and Wilhelm Ostwald over the atomistic view of matter, as an example of where overly strong resistance to a new (correct) theory delayed progress in chemistry and physics.

Next we present a brief summary of Walter Kauzmann's life as a scientist. To do so, we draw heavily from his own article, 'Reminiscences from a life in protein physical chemisty', published in 1993 in *Protein Science* [3] as a prelude to his receiving the 1993 Stein–Moore Award in protein science.

Walter Kauzmann was born in August 1916, in Mt. Vernon, NY, a city a little north of New York City. Europe was at war that year, and no Nobel Prize was awarded. The early ('classical') quantum theory was still in its critical developmental period. As so many scientists have during their youths, young Walter possessed a chemistry set and microscope, which stimulated his interest in chemistry and biology. With an excellent grounding in physics, Walter set off for Cornell University, obtaining a bachelor's degree in chemistry in 1937 [3].

While still an undergraduate, Kauzmann had decided to go into organic chemistry. His decision was influenced partly by the fact that the training

in organic and inorganic chemistry offered at Cornell at that time was much superior to the overall training given in physical chemistry. Kauzmann has written [3] that, except for his brief exposure to thermodynamics and statistical mechanics taught by John Kirkwood, the coverage of physical chemistry at Cornell was well behind the times as a result of the dominance of chemistry professor Wilder Bancroft.

Bancroft, who founded the *Journal of Physical Chemistry* and served as its editor until 1933, was an obstacle to the real advancement of physical chemistry, according to Kauzmann [3]. While studying under Ostwald for his Ph.D., Bancroft gained a mistrust of atomic theory (vide supra), and later vehemently argued that proteins were colloids, not polymers. Bancroft avoided the use of advanced math in his own work and resisted the increasing influence physics and theory had on chemistry at that time. As editor of the *Journal of Physical Chemistry*, he routinely rejected purely theoretical papers, especially in the burgeoning field of quantum chemistry and this directly led to the formation of a new journal, the *Journal of Chemical Physics* (JPC) [3]. Ironically, many years later, Kauzmann would serve on the editorial advisory board of the *Journal of Physical Chemistry*.

One could say that Bancroft's editorial misjudgments, which resulted in the creation of JPC, also led to Kauzmann's attending graduate school at Princeton University. During his senior year at Cornell, Walter discovered the *Journal of Chemical Physics*, which had been publishing many interesting papers by Henry Eyring of Princeton University's Chemistry Department. He thought to himself that, even though Eyring was not an organic chemist, it would have to be a positive, learning experience to be in the same place as Eyring, and so he applied to Princeton University [3].

With an eye towards organic chemistry, Walter started his graduate studies working for Eugene Pacsu, the carbohydrate chemist. However, it became clear to Pacsu that Kauzmann was not cut out to be an organic chemist, and he reported this to Hugh Taylor, the department chairman. Taylor, a well-known physical chemist himself, had, on the basis of Kauzmann's scores on the mathematical portions of the Graduate Record Examination, recommended that he work for Henry Eyring. Perhaps it is most fitting, then, that Walter ended up working for the person who had originally attracted him to Princeton in the first place. Kauzmann's thesis work under Eyring involved the theory and measurement of optical activity of molecules, and this subject remained a long-time interest of his [3].

Upon finishing his Ph.D. in 1940, Kauzmann accepted a 2-year fellowship with Westinghouse Electric Co., in Pittsburgh, PA. It was from this period that many of the ideas Walter incorporated into his seminal paper on the glassy state and the so-called 'Kauzmann Paradox' originated [3]. When the Westinghouse fellowship was up, he joined the NDRC laboratory in Bruceton, PA, outside of Pittsburgh, and worked under Louis Hammett. One of Kauzmann's colleagues at the time was Rufus Lumry, who has kindly contributed two papers to our Kauzmann Festschrift. Following one and a half years at Bruceton, Walter spent 2 years (1944–1946) at Los Alamos. His main project involved finding the best way to controllably implode the atom bomb container so as to cause the fission chain reaction of ^{235}U to runaway.

In 1946, Henry Eyring, a devout Mormon and under pressure from his wife, decided to move to the University of Utah. He recommended to Hugh Taylor that Kauzmann replace him, and that is how Walter ended up in his teaching position at Princeton University. Kauzmann could now follow, full-time, his interest in applying physical chemistry to the study of proteins, and he soon had several graduate students working in related areas [3].

Incidentally, while not officially Kauzmann's graduate student, Howard Schachman likes to make the claim that he was Walter's first grad student because of all the time they spent together discussing Schachman's thesis research. And Charles Tanford, who was not Walter's grad student while at Princeton either but had had many lengthy discussions with Kauzmann on proteins during Walter's first couple of years as a professor, decided to switch from flame chemistry to protein chemistry and took a postdoctoral position with Cohn at Harvard. Kauzmann likes to think of Tanford as one of his most important discoveries [3].

Besides studying the many aspects of the physical chemistry of proteins, Kauzmann, during his

tenure at Princeton, investigated, although did not always publish on, a broad range of subjects that included the theory of optical rotary dispersion, plastic flow of metals, static electrification of textile filaments, the role of *d*-hybridization in pi bonding, water and aqueous solutions, effects of pressure on spectral solvent shifts and weak acid ionizations, how muscles function and, in retirement, molten silicates and oxides.

Given his main interest in protein chemistry, Kauzmann naturally was interested in the properties of life's solvent, liquid water and theories to explain its unusual behavior. We take the opportunity here to note that, in addition to the monograph he and David Eisenberg co-authored on water [4], Kauzmann [5] also wrote a highly cogent, but underappreciated (in the guest editor's opinion), paper that basically shows how mixture models of liquid water cannot account for the unusual thermodynamic properties of water in any consistent fashion. The paper was published in a journal not readily accessible to American researchers and, consequently, probably has not been read as widely as it should be. We return to the subject of publications shortly.

Two of the most important developments in Kauzmann's career were his sabbatical visits to the Carlsberg Laboratory in Denmark and his interactions with one of the pioneers of protein chemistry, Linderstrøm-Lang. Three of Walter's sabbatical leaves were spent overseas, partly because he enjoyed expanding himself both intellectually and culturally. From Kauzmann's time spent at Carlsberg sprang the genesis and clarification of his thoughts on the hydrophobic bond [3], most of which is set forth in his well-known 1959 publication in *Advances in Protein Chemistry* [6].

Interestingly, despite the impact of his scientific writings and the recognition he has gained over the years, Walter Kauzmann was not, as one might expect, a prolific author in terms of the total number of published papers. This may be due in part to the fact that Kauzmann started his academic career when there were, in general, fewer papers published, and there was perhaps less pressure in the academic world to 'publish or perish'. But it also reflects, to some degree, Walter's character traits of integrity, modesty, continued striving for perfection and his dedication to his profession as both researcher and teacher. For example, Kauzmann took his role as teacher very seriously, and he considered it just as important to write and edit books and reviews for students at all levels as to produce original research papers. His books on the thermal properties of matter [7,8] and quantum chemistry [9] are considered excellent, highly readable introductory texts, and his monograph on water [4], written with David Eisenberg, was still being published in various languages 30 years after its first printing. Kauzmann was quick not to take credit for something he did not do; he would decline to have his name listed as a co-author on papers for which he felt he did not contribute substantially. Partly as a result of this personal policy, Walter did not routinely co-author papers with his grad students on their doctoral work and encouraged them to publish on their own. Before seeking to publish a paper of his, it seems Walter had to be convinced strongly that the paper truly represented a new and significant contribution to the scientific literature. Kauzmann's 1959 article in *Advances in Protein Chemistry*, in which he described and highlighted the role of the hydrophobic bond (interaction) in protein structure [6], and his 1948 article in *Chemical Reviews* [10] on the glassy state are two of the most frequently cited references in their respective fields. Both references to this day still serve to stimulate research in those areas as evinced by several of the papers in this Festschrift.

In closing the foreword, the editors of *Biophysical Chemistry* would like to thank all of those who have contributed to this special issue, making it a treasured collection that is a truly worthy tribute to Walter Kauzmann. We are sure that the rest of the physical chemistry and biosciences communities join us in recognizing and honoring Walter Kauzmann for his many achievements and contributions to science as teacher, mentor, researcher, scholar, writer, colleague, collaborator, editor and friend.

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