

## This Week's Citation Classic®

**Kauzmann W.** The nature of the glassy state and the behavior of liquids at low temperatures.  
*Chem. Rev.* 43:219-56, 1948.

[Department of Chemistry, Princeton University, NJ]

Below the so-called "glass transformation temperature,"  $T_g$ , supercooled liquids undergo a transformation in which the specific heat, compressibility, and coefficient of expansion decrease markedly. Simple extrapolations of thermodynamic properties at higher temperatures lead to the expectation that at temperatures somewhat below  $T_g$  the supercooled liquid in true thermodynamic equilibrium would have a lower energy, entropy, and volume than the crystal. This impossible state of affairs is the so-called "Kauzmann Paradox." [The *SC*<sup>®</sup> indicates that this paper has been cited in more than 485 publications.]

### The Kauzmann Paradox: A Thermodynamic Quandary

Walter Kauzmann  
Department of Chemistry  
Princeton University  
Princeton, NJ 08544

In 1937 Westinghouse decided to embark on a strong basic research program in physics and chemistry. E.U. Condon, then an associate professor of physics at Princeton University, was recruited to direct this effort. This was the start of Condon's illustrious and stormy career of service in industry and in government.

In order to attract young physical scientists to this program Condon persuaded Westinghouse to establish postdoctoral positions with the title "Westinghouse Research Fellowships." These involved a two-year commitment at an attractive salary and permitted the recipient the choice of any research areas from among the extremely broad fields of interest covered by Westinghouse (ranging from nuclear physics to analytical and polymer chemistry—a far broader range of possible interests than exist in any academic department even now).

While at Princeton, Condon had strong interactions with Henry Eyring. I received my PhD in 1940 under Eyring's tutelage, and this combination of circumstances led to an offer of one of these fellowships, which I accepted.

Among the problems I studied during my two-year stay in East Pittsburgh was the application of Eyring's absolute rate theory to dielectric relaxation. Eyring had the notion (since shown to be probably incorrect) that molecular motions in electrical and mechanical relaxation involve large jumps (of the order of intermolecular distances and large angles) over barriers on the potential energy surface of the system in question. In principle this approach, as applied to the temperature and pressure dependence of the relaxation rates, could give new insights at the molecular level. My research involved, among

other things, a survey of large masses of data on dielectric relaxation at radio frequencies.

For entirely practical reasons dielectric relaxation is rarely studied at frequencies less than 60 cycles/sec. But it is a simple matter to extrapolate the behavior at higher frequencies and higher temperatures to lower frequencies and lower temperatures. The question then arises as to the thermodynamic behavior of, say, a liquid in which the dielectric relaxation time becomes much longer than the time required to make a thermodynamic measurement—say hours or days or weeks or even years or geological ages.

My reading of the literature soon brought me to the fact that something called the "glass transformation" is observed in all supercooled liquids that fail to crystallize spontaneously at low temperatures. This transition involves a considerable decrease in the heat capacity and the coefficient of thermal expansion over a narrow range of temperatures (centered on the "glass transformation temperature,"  $T_g$ ). The plots of enthalpy, entropy, and volume vs. the temperature are, however, continuous, showing only a marked change in slope at  $T_g$ . By the early 1940s numerous workers had realized that the "glass transformation" was not a true thermodynamic transition but rather a consequence of the slow molecular motions below the glass transformation temperature. My observations on dielectric relaxation times confirmed this.

It had, however, evidently not been noticed by earlier workers that if the "true" thermodynamic differences such as the entropy and enthalpy differences between the liquid and the crystal for glycerol and glucose and many other substances are extrapolated below  $T_g$ , these properties would go through zero and become negative if some thermodynamic or other effect did not intervene. The temperatures at which the enthalpy and entropy differences would pass through zero are different, however; the extrapolated free energy difference between the liquid and the crystal becomes in all instances increasingly larger as the temperature is lowered below  $T_g$ ; the crystal would always be thermodynamically more stable than the liquid, even after the very, very long times that would be required for "true" equilibrium to become established.

This puzzling behavior was described in my 1948 paper. Although the existence of the puzzle had become clear to me during the 1940-1942 period at Westinghouse, World War II had intervened and more pressing work had taken priority. It was Austen Angell who gave the name "Kauzmann Paradox" to these observations. He<sup>1</sup> and others<sup>2</sup> have made further studies of the phenomenon, which remains unresolved.

1. Angell C.A. Thermodynamic aspects of the glass transition in liquids and plastic crystals. *Pure Appl. Chem.* 63:1387-92, 1991.

2. Cahn R.W. Missing atoms and melting. *Nature* 356:108-9, 1992.

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