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The Third Law of Thermodynamics and the Residual Entropy of Ice: "Stillwater" or $\Delta S^{H_2O}_{f,T=0} = 0$

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As the temperature of water gets closer and closer to absolute zero, its internal motions become less and less until finally a state is reached which, for the purposes of this article, we will call "Stillwater." This paper will explore the connection between the Third Law of Thermodynamics and the residual entropy of ice. The guiding principle to all physical behavior at low temperatures is the Third Law of Thermodynamics. The first complete statement of this law in a text was given in 1923 by Gilbert Newton Lewis (1) of the University of California in his book *Thermodynamics and the Free Energy of Chemical Substances* (2). He and his coauthor Merle Randall state

> Every substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero and does so become in the case of perfect crystalline substances.

The historical basis of this law is rooted in the theoretical work of Walther Nernst at Goettingen for which he later received the 1920 Nobel prize. By the early 1900's, there were many unexpected experimental results. For example, with decreasing temperature, the emf of galvanic cells becomes linearly proportional to the internal energy change of the cell reaction. Another puzzling observation was that at low temperatures the specific heats measured by James Dewar at the Royal Institution in London were much smaller than anticipated. Nernst stated (3) that the difference between the free energy and the total energy of a chemical reaction goes to zero tangentially at absolute zero. Alternately, Nernst's law can be stated: in a reaction between pure solids or liquids, the change in entropy approaches zero at $T = 0$ (4). At the turn of the century, it was thought that energy, not entropy, went to zero at complete rest. The zero point energy is at a minimum, but not zero. Although enigmatic at first, this zero point energy was a direct manifestation of the basic principle of quantum mechanics. The earliest verification of zero point energies was in an X-ray crystallographic experiment on rock salt by R. W. James and Elsie Firth (5) in 1927 at Manchester in William Lawrence Bragg's laboratory. The experiment was performed at the temperature of liquid air. Since the atomic vibrations were too large to be entirely accounted for by thermal energy, this was a direct measure of the zero point energy.

Nernst made an unusual application of his thermodynamic studies in the area of animal husbandry. After a Christmas day visit to his cow shed, he noticed it was rather warm in there and attributed the heat to the metabolism of the cows. He immediately had the cows sold, a pond dug, and carp installed. His reason was that the entropy of the cows was higher than that of the carp, and therefore, the feed he gave the cows increased their entropy rather than increasing his farm profits (6).

Forty years after Nernst's paper, Max Planck gave a stronger statement of the Third Law (7)

> As the temperature diminishes indefinitely, the entropy of a chemically homogeneous body of finite density approaches indefinitely near to the value of zero.

A modern definition of entropy derived from statistical mechanics would have to contain safeguards against metastable states such as supercooled liquids and gases. Little is known about the entropy of the nucleus which ultimately must be considered. Since absolute zero is unattainable, the properties must be smoothly extrapolated to zero degrees from the lowest attainable temperature. Sometimes the entropy does not go to zero, as for example, in the case of configurational randomness. Results of the Third Law have been extended to both gases and solids. In the case of a crystal, Ludwig Boltzmann first showed that (in modern terms) if W is the number of quantum states available in a closed system with fixed values of energy and volume, then $S = k \ln W$ where k is Boltzmann's constant with $k = R/N$ (R is the gas constant and N is Avogadro's number). Another consequence of the Third Law is that the associated specific heats also become zero at absolute zero.

The title of this paper refers to the entropy of formation. The calculation of the entropy of formation is an experimental procedure which permits verification of the Third Law. Let T equal a given temperature. ΔS_R and ΔS_P are determined by calorimetric measurements. ΔS_T can be calculated by a Second Law method; for example, $\Delta S_T = (\Delta H - \Delta G)/T$ where ΔH is the enthalpy change and ΔG is the free energy change. Now the final calculation at absolute zero is $\Delta S_0 = \Delta S_R + \Delta S_T - \Delta S_P$, which will show experimentally, within the accuracy of the experiment, whether the Third Law is verified.

The entropy difference between a given temperature, for example room temperature, and absolute zero can be measured both calorimetrically and spectroscopically. The calorimetric entropy is measured from experimental heat capacities and heats of phase transitions. Spectroscopic entropy can be calculated using spectroscopic data as the source of moments of inertia, vibrational frequencies, and ground state electronic degeneracies. Gases such as argon, nitrogen, oxygen, carbon dioxide, and ammonia give excellent agreement between spectroscopic and calorimetric measurements. Where there are discrepancies, the calorimetrically measured values are always lower than the spectroscopic values. The spectroscopic measurements in combination with associated theory are considered closer to the "true" entropy values because, among other factors, of the inclusion of the number of quantum states. For example, in the case of CO, its symmetry, small dipole moment, and the fact that it is isoelectronic with nitrogen, combine in the actual crystal to produce a random crystal of CO and OC. Thus, even at zero K the entropy of CO will not be zero.

The authors have taken a liberty in the title of this article. Indeed, the residual entropy of water, although small, is not zero [8]. In 1933, W. F. Giauque and M. F. Ashley at Berkeley, California, [9] measured the residual entropy of ice. Their data combined with that of A. R. Gordon [10] gave an experimental value of 0.87 entropy units (eu) which is 3.6 J K^{-1}. The first
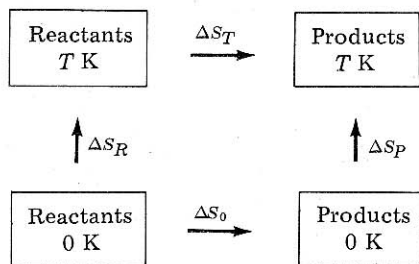
major theoretical interpretation is due to Linus Pauling [11] in 1935. His calculations were based on the interpretation of the randomness of the hydrogen bonds in water. Indeed, many of the unusual properties of water [12, 13] are due to hydrogen bonding: (1) the negative volume of melting; (2) density maximum in the normal liquid range (at 4°C); (3) isothermal compressibility minimum in the normal liquid range (at 46°C); (4) at least nine crystalline polymorphs; (5) high dielectric constant; (6) anomalously high melting, boiling, and critical temperatures for a low-molecular-weight substance that is neither ionic nor metallic; (7) increased liquid fluidity with increasing pressure and (8) high-mobility transport for H$^+$ and OH$^-$ ions.

If Pauling's argument on residual entropy is to be understood, the structure of ice must also be considered. The arrangement of the oxygen atoms is known from X-ray diffraction [14, 15]. Each oxygen is tetrahedrally surrounded by four other oxygen atoms; all the oxygens are hydrogen bonded. Pauling's assumptions [11], derived from the Bernal-Fowler ice rules [16], are (1) the water molecule, HOH, remains intact in ice; (2) the hydrogen atoms are directed more closely to two of the four nearly tetradehrally surrounded oxygen atoms; (3) the orientations of adjacent water molecules are such that exactly one hydrogen atom lies on each oxygen-oxygen axis; (4) interactions beyond nearest neighbor interactions may be neglected.

From assumption 2, there are six possible tetrahedral configurations of HOH. Now consider the adjacent water molecule. The probability that one of the two more closely bonded sites is occupied is $1/2$. Since each oxygen in water has two associated hydrogens, the probability that both of the two more closely bonded sites are occupied is $1/4$. Thus the total number of configurations, W, for Avogadro's number of molecules, N, is $W = (6 \times 1/4)^N = (3/2)^N$. Substituting in $S = R/N \ln W$ for one mole, $S = (R/N) \ln(3/2)^N = R \ln(3/2)$, which yields $S_0 = 0.805$ eu (3.37 J K^{-1}) where S_0 is the entropy at absolute zero.

In 1936, the year following Pauling's calculations, W. F. Giauque and J. W. Stout [17] improved their calorimetric measurement and experimentally found $S_0 = 0.82 \pm 0.15$ eu (3.4 ± 0.6 J K^{-1}). Thus, the measured and theoretical values agreed within the limits of experimental error.

Pauling's work remains embedded in modern theory. His estimate is incredibly accurate due to the fact that a large number of closely lying quantum states are nearly equally populated. In 1964, E. A. DiMarzio and F. H. Stillinger [18] calculated that the Pauling estimate was 1% too low. Then in 1966, J. F. Nagle [19] calculated $S_0 = R \ln 1.5069 = 0.8151$ eu (3.410 J K^{-1}). Both Pauling's and Nagle's values lie well within the 1936 experimental limits. Pauling's calculations are based on the assumption that all Bernal-Fowler ice structures have the same energy and therefore have equal a priori probabilities. However, these structures are not precisely equal in energy, but spread out over a band of states. Consequently the probabilities are not equal, and S_0 should be correspondingly reduced. Perhaps sufficiently precise calorimetric experiments could distinguish between Nagle's and Pauling's theories. If Nagle's work were verified, this would implicitly demonstrate the energy dispersion.

A complicating experimental feature is that crystal imperfections such as vacancies, dislocations, grain boundaries, and impurities would tend to increase S_0. Their influence would have to be very carefully assessed. Perhaps this suggests a series of S_0 determinations on ice samples with different formation conditions, such as freezing rate, impurity doping, and annealing.

The last calorimetric measurements of the entropy of ice were made in 1936. With new theoretical results the issue is far from closed. The time is now ripe for a modern experimental redetermination of the residual entropy of ice.

Acknowledgment

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Misconceptions

What misconceptions about science and chemistry do your students have? We all have some that plague us in our teaching. From the field of physics, for example, it is commonly believed by beginning students that rockets need something to "push" against, that satellites stay aloft because gravity is weak high above the earth, and that a dam's strength must be in proportion to the size of the lake formed. Biology students believe that Balsa is a softwood. A post-doctoral researcher was recently heard to say that a solution whose pH = 2 is twice as acidic as one whose pH = 4! Equilibrium is often used when "steady-state" is meant, or vice-versa.

If you have a favorite misconception concerning science in general and chemistry in particular, and would like to share it (or them) in an effort to eliminate such misconceptions from the minds of your students, please mail them to: Dr. R. L. Neman, Department of Chemistry East Central University, Ada, OK 74820. They will then be compiled and made available to anyone who wants them.