This Week's Citation Classic

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Frank H S & Evans M W. Free volume and entropy in condensed systems. III. Entropy in binary liquid mixtures; partial molal entropy in dilute solutions; structure and thermodynamics in aqueous electrolytes. *J. Chem. Physics* **13**:507-32, 1945. [Dept. Chemistry, Univ. California, Berkeley, CA]

Equations based on Parts I[1] and II[2] of this series are derived for entropy changes when gases dissolve to form dilute solutions. Data for nonpolar solutes in normal liquids agree with these predictions and define normal behavior. Departures from this for nonpolar solutes in cold water are interpreted in terms of quasifrozen patches, or 'icebergs,' about nonpolar molecules or groups. Ions, depending on size and charges, may weaken water structure as well as produce freezing, or saturation, of the water nearest them. [The *SCI*® indicates that this paper has been cited in over 1,220 publications since 1961.]

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"In retrospect, my principal feeling about this paper is of great good fortune, both in the circumstances of its writing and in the factors that have caused it to be cited so often. The original impetus to work in this field came from a 'doubletake' while walking the deck in June 1939 on the 5.5. *President Coolidge* on the voyage back to the US on a furlough from my post at Lingnan University, Canton, China. The inspiration consisted of the sudden realization that the thermochemistry of an aqueous salt solution is dominated by changes in the local entropy of the solvent water in the immediate neighborhood of the ions (see, for example, reference 3).

"Most of the 19391940 furlough year was spent in Pittsburgh, where it was possible to work with A.L. Robinson, and our computation of the entropies of dilution for a number of salts[4] yielded results that gave credence to the idea that some ions (e.g., Li^+, Na^+) intensify the structure of neighboring water, while others (e.g., I^-, Cs^+, NO_3) disrupt it.

"Back in Hong Kong, where Lingnan University was then located, attention could be turned to the physical interpretation of entropy in condensed systems and, picking up an idea from Mayer and Mayer,[5] a general theorem could be formulated, relating entropy to a suitably defined free volume. Started on the back of an envelope in a Hong Kong movie house, and continued, after Pearl Harbor, in the Stanley Internment Camp, calculations on this subject were carried forward during repatriation on the first 'Gripsholm' exchange.

"One decisive piece of good fortune was the securing of a post in the chemistry department of the University of California at Berkeley to do some of the teaching left uncovered by the diversion of permanent faculty members to war work. The situation there gave me a free hand to do my own research from fall 1942 to summer 1945, when I left to spend a year in the State Department in Washington. Following the Berkeley tradition, this work, since it was unclassified, was fair game for discussion, both at the weekly department research conferences and between times. It was Lewis who proposed the use of the word 'iceberg' for a structured patch (of whatever origin or geometry) in water. My coauthor, Marjorie Woodard Evans, was a graduate student whose thesis work (which was classified) did not distract her mind sufficiently from the fact that her husband was on a submarine in the Pacific. To get additional distraction, she volunteered to spend evenings performing the exacting calculations (precomputer) which Part III contains.

"Parts I, II, and III of the series 'Free volume and entropy in condensed systems' were completed just before I left Berkeley, and were published while I was in Washington. As to why Part III should have been so widely cited, there seem to be three special reasons. First, of course, is that since the properties of aqueous solutions are fundamental to so many areas, any advance in understanding them will have to be 'used by everybody.' Second is that for a long time the only aqueous systems of which the solution properties had been intensively studied had been electrolytes and, from about 1920 on, electrolyte theory had been 'doing so well,' without apparent need for structural ideas, that an establishment had grown up which, for the most part, was neither accustomed nor hospitable to them. This made all the more effective the positive influence of the third factor, namely, favorable notice and practical application in such influential new works as the monographs of Robinson and Stokes[6] and Kauzmann[7] This field has expanded in many directions; see, for example, reference [8]."

1. **Frank H S.** Free volume and entropy in condensed systems. I. General principles. Fluctuation entropy and free volume in some monatomic crystals. *J. Chem. Physics* **13**:478-92, 1945. (Cited 20 times.)
2. .....Free volume and entropy in condensed systems. II. Entropy of vaporization in liquids and the pictorial theory of the liquid state. *J. Chem. Physics* **13**:493-507, 1945. (Cited 50 times.)
3. **Falkenhagen H.** *Elektrolyte.* Leipzig: S. Hirzel, 1932. p. 1567.
4. **Frank H S & Robinson A L.** The entropy of dilution of strong electrolytes in aqueous solutions. *J. Chem. Physics* **8**:93-38, 1940.
5. **Mayer J E & Mayer M G.** The cell method of calculating liquid partition functions. *Statistical mechanics.* New York: Wiley, 1940. p. 319-26.
6. **Robinson R A & Stokes R H.** Properties of ionizing solvents. *Electrolyte solutions: the measurement and interpretation of conductance, chemical potential and diffusion in solutions of simple electrolytes.* New York: Academic Press, 1955. p. 1 22.
7. **Kauzmann W.** Some factors in the interpretation of protein denaturation. *Advan. Prot. Chem.* **14**:163, 1959. (Cited 1,765 times.)
8. **Franks F.** The hydrophobic interaction. (Franks F, ed.) *Water. A comprehensive treatise. Volume 4. Aqueous solutions of amphiphiles and macromolecules.* New York: Plenum Press, 1975. p. 194.