M02T.3—Pauling's Ice Rule

Problem

One of the all-time classic experiments was the measurement of the residual entropy S of ordinary water-ice by Giauque and Stout. This is the entropy that ice has at a temperature of zero kelvin. This entropy is not zero.

a) What 'law' does this violate? How would you make such an absolute determination of this entropy?

Pauling proposed a model to explain this entropy and the problem here will be to calculate S according to this model. The crystal structure of ice is such that each oxygen atom has 4 nearest neighbor oxygen atoms. On each 'bond' between nearest neighbor oxygen pairs sits a hydrogen atom, but it does not sit in the middle. It sits in one of two positions close to one of the two oxygens at the end of the bond.

b) Assume there are N water molecules. If all hydrogen configurations are equally likely, what is S?

Not all configurations are equally likely. Pauling introduced his "ice rule": There are precisely two hydrogen atoms close to each oxygen atom, reflecting the molecular structure of water. Otherwise, all configurations are equally likely. This limits the number of configurations, but presents a horrific combinatorial problem. Pauling simplified matters further with his Pauling approximation: He estimated the fraction of allowed configurations by taking the hydrogen configuration surrounding one oxygen atom to be independent of those surrounding all other oxygen atoms.

c) Compute S on the basis of the Pauling approximation.

(This answer agrees well with the experimental number $0.44k_B$ per molecule. The original Pauling paper is J. Am. Chem. Soc. **57**, 2680 (1935).)