Statistical Molecular Thermodynamics

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Video 7.2

Third Law of Thermodynamics

Absolute Entropy Values

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_P(T)dT}{T}$$

If $T_1 = 0\ \mathrm{K}$

$$S(T_2) = S(0) + \int_{0}^{T_2} \frac{C_P(T)dT}{T}$$

Thus, we can calculate the entropy of a substance at *any temperature* T_2 if we know the entropy at 0 K and the constant pressure heat capacity

What about 0 K?

Walther Nernst 1864-1941
Nobel Prize in Chemistry in 1920

Nernst suggested that the change in entropy for chemical reactions approached 0 as the absolute temperature approached 0

$$\Delta_r S \rightarrow 0 \text{ as } T \rightarrow 0$$

I think that the entropy of a pure substance approaches 0 at 0 K!

Max Planck, again

The Third Law: Every substance has a finite positive entropy, but at zero Kelvin the entropy may become 0, and it does so in the case of a perfectly crystalline substance.

Statistics and the Third Law

The third law was formulated before the full development of quantum theory. However, statistical thermodynamics gives us *molecular insight* into the third law.

$$S = k_B \ln W$$

At 0 K we expect that all systems in the ensemble will be in the lowest energy state, i.e., $W = 1$, $S = 0$.

or

$$S = -k_B \sum_j p_j \ln p_j$$

If $p_0 = 1$ and $p_j = 0$ for all other j then $S = 0$.

What about ground-state degeneracy?

Ground-State Degeneracy

$$S = -k_B \sum_j p_j \ln p_j$$

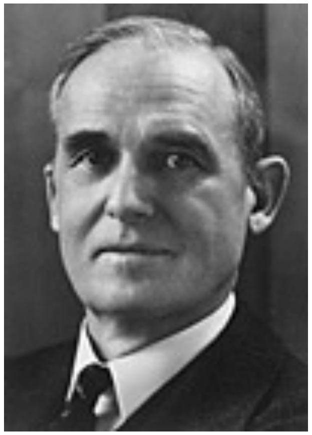
If the ground state is *n*-fold degenerate, there will be equal ($1/n$) probability of being in any one of the degenerate states and thus

$$S = -k_B \sum_{j=1}^{n} \frac{1}{n} \ln \frac{1}{n}$$

$$= -k_B n \left(\frac{1}{n} \ln \frac{1}{n} \right) = k_B \ln n$$

Recalling $k_B = 1.38 \times 10^{-23}$ J•K^{-1}, this is a very small entropy even for a very large degeneracy *of a single system*

Third Law History



William
Giauque
1895-1982

Chemistry Nobel in 1949:
"for his contributions in the field of chemical thermodynamics, particularly concerning the behavior of substances at extremely low temperatures”

He reached 0.25 K and much, much lower temperatures have since been achieved by adiabatic demagnetization.