THIRD LAW OF THERMODYNAMICS; RESIDUAL ENTROPY

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The entropy is related to temperature by

\[ \frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{N,V} \quad (1) \]

Using the chain rule, and keeping everything at constant \( N \) and \( V \), we can measure the change in entropy due to a change in temperature as

\[ dS = \frac{dU}{T} = \left( \frac{\partial U}{\partial T} \right)_{N,V} \frac{dT}{T} = C_V \frac{dT}{T} \quad (2) \]

where \( C_V \) is the heat capacity at constant volume:

\[ C_V = \left( \frac{\partial U}{\partial T} \right)_{N,V} \quad (3) \]

If we know \( C_V (T) \) as a function of temperature, we can therefore find the change in entropy for a finite change in temperature by integration:

\[ \Delta S = S_f - S_i = \int_{T_i}^{T_f} C_V (T) \frac{dT}{T} \quad (4) \]

The total entropy in a system at temperature \( T_f \) could theoretically be found by setting \( T_i = 0 \) in the integral

\[ S_f - S (0) = \int_0^{T_f} C_V (T) \frac{dT}{T} \quad (5) \]

In theory, at absolute zero, any system should be in its (presumably) unique lowest energy state so the multiplicity of the zero state is 1, meaning that \( S (0) = 0 \), and this integral does in fact give the actual entropy in a system at temperature \( T_f \). It’s also obvious that for this integral to be finite (and positive) \( C_V \to 0 \) as \( T \to 0 \) at a rate such that the integral doesn’t diverge at its lower limit. Thus we must have \( C_V (T) \propto T^\alpha \) where \( \alpha > 0 \) as
Either of these conditions is a statement of the third law of thermodynamics, which basically says that at absolute zero, the entropy of any system is zero.

In practice, as a substance is cooled, its molecular configuration can get frozen into one of several possible ground states, so that there is a residual entropy even when $T = 0 \text{ K}$.

**Example.** Carbon monoxide molecules are linear and in the solid form, they can line up in two orientations: OC and CO. Thus at absolute zero, the collection of molecules can be considered as a frozen-in matrix of molecules oriented randomly, so for a sample of $N$ molecules, there are $2^N$ possible structures. For a mole, the residual entropy is therefore

$$S_{res} = k \ln 2^{6.02 \times 10^{23}} = (1.38 \times 10^{-23}) (6.02 \times 10^{23}) \ln 2 = 5.76 \text{ J K}^{-1}$$

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