THIRD LAW OF THERMODYNAMICS - RESIDUAL ENTROPY

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The entropy is related to temperature by

$$\frac{1}{T}=\left(\frac{\partial S}{\partial U}\right)_{N,V} \tag{1}$$

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

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

where C_V is the heat capacity at constant volume:

$$C_V=\left(\frac{\partial U}{\partial T}\right)_{N,V} \tag{3}$$

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:

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

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

$$S_f-S(0)=\int_0^{T_f}\frac{C_V(T)}{T}dT \tag{5}$$

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 required 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 $C_V(T)\propto T^a$ where $a>0$ as $T\to 0$. 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 $T = 0$ K.

Example 1. 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

$$S_{\text{res}} = k \ln 2^{6.02\times 10^{23}} = \left(1.38\times 10^{-23}\right)\left(6.02\times 10^{23}\right)\ln 2 = 5.76 \text{ J K}^{-1} \tag{6}$$

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