

### THIRD LAW OF THERMODYNAMICS; RESIDUAL ENTROPY

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 3.9.

The entropy is related to temperature by

$$(0.1) \quad \frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{N,V}$$

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

$$(0.2) \quad dS = \frac{dU}{T} = \left( \frac{\partial U}{\partial T} \right)_{N,V} \frac{dT}{T} = C_V \frac{dT}{T}$$

where  $C_V$  is the heat capacity at constant volume:

$$(0.3) \quad C_V = \left( \frac{\partial U}{\partial T} \right)_{N,V}$$

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:

$$(0.4) \quad \Delta S = S_f - S_i = \int_{T_i}^{T_f} \frac{C_V(T)}{T} dT$$

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

$$(0.5) \quad S_f - S(0) = \int_0^{T_f} \frac{C_V(T)}{T} dT$$

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)  $C_V \rightarrow 0$  as  $T \rightarrow 0$  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  $T \rightarrow 0$ .

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.** 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

$$(0.6) \quad S_{res} = k \ln 2^{6.02 \times 10^{23}} = (1.38 \times 10^{-23}) (6.02 \times 10^{23}) \ln 2 = 5.76 \text{ J K}^{-1}$$

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