Statistical Molecular Thermodynamics

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Video 7.7

Review of Week 7
Critical Concepts from Week 7

- Entropy variation with temperature may be determined as

\[
\left( \frac{\partial S}{\partial T} \right)_X = \frac{C_X(T)}{T} \quad X = V, P
\]

- So, just as integrating heat capacity can be used to determine enthalpy, integration of heat capacity divided by temperature can be used to determine entropy.

- The Third Law states that at non-zero temperatures, all substances have positive entropies, while at 0 K the entropy of a perfect crystal is equal to zero.

- An entropy of exactly zero depends on there being a single, non-degenerate ground state \((W = 1 \text{ or } p_j = \delta_{ij} \text{ for ground state } i)\).
William Giauque generated temperatures very near absolute zero, and well below what is possible through adiabatic gas expansion, by adiabatic demagnetization.

Entropy at a given temperature $T$ can be computed as:

$$S(T) = \int_{T_{\text{fus}}}^{T} \frac{C_p(T) \, dT}{T} + \frac{\Delta_{\text{fus}} H}{T_{\text{fus}}} + \int_{T_{\text{fus}}}^{T_{\text{vap}}} \frac{C_p(T) \, dT}{T} + \frac{\Delta_{\text{vap}} H}{T_{\text{vap}}} + \int_{T_{\text{vap}}}^{T} \frac{C_p(T') \, dT'}{T'}$$

At very low temperatures

$$\bar{S}(T) = \frac{\overline{C_p(T)}}{3}$$
Critical Concepts from Week 7

- Measured third-law entropies are in near quantitative agreement with results predicted from the partition function using

\[ S = k_B \ln Q + k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} \]

- Degrees of freedom contributing to entropy are, in order of quantitative importance: translation > rotation > vibration > electronic excitation

- Increasing particle mass increases \( S_{\text{trans}} \) logarithmically

- Stiff, insulating solids, have very low entropies near 0 K; conductors approach such low values less rapidly.
Critical Concepts from Week 7

• In general, the more atoms a molecule has, the greater its entropy at a given temperature (increased mass, moments of inertia, and degrees of vibrational freedom)

• Residual entropy can be associated with a system failing to experimentally access a perfect crystal at 0 K; CO is a good example

• As for enthalpy (or any other state function), entropies of reaction are additive

• Entropies of gases are much, much greater than those of their corresponding condensed phases