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

$$\left(\frac{\partial S}{\partial T}\right)_X = \frac{C_X(T)}{T} \qquad X = V, P$$

- 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 ($W = 1$ or $p_j = \delta_{ij}$ for ground state i).

Critical Concepts from Week 7

- 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

$$S(T) = \int_0^{T_{fus}} \frac{C_P^s(T)dT}{T} + \frac{\Delta_{fus}H}{T_{fus}} + \int_{T_{fus}}^{T_{vap}} \frac{C_P^l(T)dT}{T} + \frac{\Delta_{vap}H}{T_{vap}} + \int_{T_{vap}}^{T} \frac{C_P^g(T')dT'}{T'}$$

- At very low temperatures

$$\overline{S}(T) = \frac{\overline{C}_P(T)}{3}$$

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_{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