Thermodynamics of a Rubber Band

Fundamental energy equation $(dN=0)$

$$dU = TdS - pdV + f\,dL$$

(f: force; L: length)

natural variables: S, V, L

variables we like better: T, P, L ($S \leftrightarrow T$, $V \leftrightarrow P$)

$$U - TS + PV \equiv G$$

← canonical transformation to arrive at a free energy in our variables

$$dG = dU - TdS - SdT + PdV + VdP$$

$$dU = TdS - pdV + f\,dL$$

$$dG = -SdT + VdP + f\,dL$$

$$\therefore \quad f = \left(\frac{\partial G}{\partial L}\right)_{T,P} = \left(\frac{\partial H}{\partial L}\right)_{T,P} - T\left(\frac{\partial S}{\partial L}\right)_{T,P}$$

because $G = H - TS$ also!

$\therefore$ f has both enthalpic & entropic contributions

$\left(\frac{\partial S}{\partial L}\right)_{T,P}$ is going to be impossible to measure, so we need a maxwell relation:

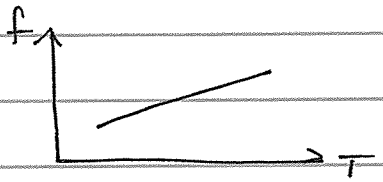
$$S = -\left(\frac{\partial G}{\partial T}\right)$$

$$\frac{\partial S}{\partial L} = -\frac{\partial}{\partial L}\left(\frac{\partial G}{\partial T}\right) = -\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial L}\right) = -\left(\frac{\partial f}{\partial T}\right)_{P,L}$$

$$\therefore \quad \left(\frac{\partial S}{\partial L}\right)_{T,P} = -\left(\frac{\partial f}{\partial T}\right)_{P,L}$$

← how does force of rubber band change with temperature

So the entropic part of the force can be determined by holding the rubber band at a fixed length L and measuring how the retractive force varies with T:

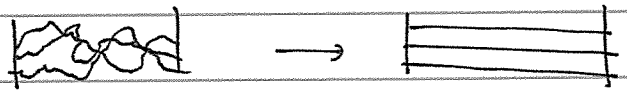


← you can actually do this experiment!

$$\left(\frac{\partial f}{\partial T}\right)_L > 0 \quad \therefore \quad \left(\frac{\partial S}{\partial L}\right)_T < 0$$

↑ stretching a rubber band orders the material! Metals (and gases) are exactly the opposite.

Stretching rubber decreases the multiplicity of polymer conformations



↑ entangled chains → ↑ aligned chains!

Mixtures:

Consider a system with only one component

molar volume: $v = \frac{V}{n}$ ← # of moles

molar free energy: $g = \frac{G}{n}$

But what if your system has more than one species:

$\vec{n} = n_1, n_2, \ldots n_M$

Mixtures

For more than 1 species we can define

partial molar volume

$$\nu_j = \left(\frac{\partial V}{\partial n_j}\right)_{T,P,n_{i\neq j}}$$ ← how much does the volume change when you add dn_j moles of type j, with all other components held constant

$$dV = \sum_{j=1}^{M} \left(\frac{\partial V}{\partial n_j}\right)_{T,P,n_i} dn_j$$

$$= \sum_{j=1}^{M} \nu_j \, dn_j$$

Ideally, partial molar volumes are independent of the composition of the mixture, and equal to the molar volumes of the individual pure components

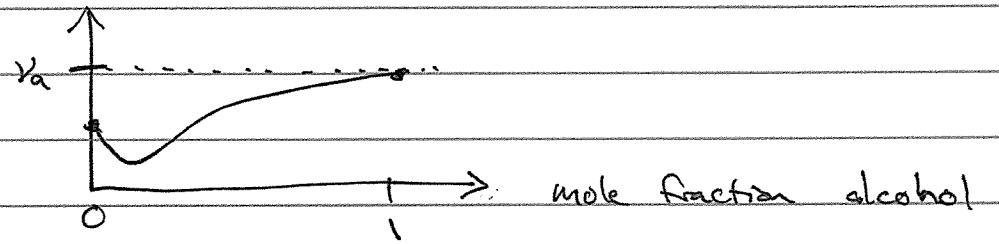
Let's mix V_a of ethanol with V_w of water

Ideally:

$$V = V_a + V_w$$

In reality, we measure an apparent molar volume

$$\nu_{apparent} = \frac{V - n_w \nu_w}{n_a}$$ ← fixed to molar volume of pure water



At low concentrations in water, the apparent molar volumes of alcohols are smaller than for pure liquids

$$V_{actual} < V_a + V_w$$

Likewise we can measure partial molar free energies or chemical potentials

$$\mu_j = \left(\frac{\partial G}{\partial N_j}\right)_{T,P,N_{i\neq j}}$$

$$= \left(\frac{\partial H}{\partial N_j}\right)_{T,P,N_{i\neq j}} - T\left(\frac{\partial S}{\partial N_j}\right)_{T,P,N_{i\neq j}}$$

$$= h_j - Ts_j$$

partial molar enthalpy & entropy.