A brief intro to some thermodynamic terms: (5-1)

A <u>system</u>: a collection of matter in any form delineated from <u>surroundings</u> by real or imaginary boundaries

Defining a system often depends on what problem you are trying to solve

Much of thermo is careful bookeeping - accounting for energy or matter exchange across the boundaries (or volume changes).

<u>Open</u> systems: can exchange energy, volume, or matter with the surroundings (e.g. the <u>earth</u>, a <u>cell</u>, etc.)

<u>closed</u> systems: energy can cross the boundaries, but not matter (e.g lightbulbs, balloons, pistons, bomb calorimeters)

<u>isolated</u> systems: Neither energy nor matter can cross the boundaries, and the volume doesn't change. This makes U (the internal energy) <u>constant</u>

<u>Semipermeable</u> membrane: restricts the flow of some types of particles, allowing others to flow.

<u>adiabatic</u> boundary: prevents heat from flowing (e.g. a picnic cooler is approximately an adiabatic boundary)

Thermodynamic state functions (like entropy) can be functions of other state variables

$$S = S(U, V, \vec{N})$$

tells us S depends on these quantities

U: energy (also a state function)

V: volume (a state variable)

$\vec{N} = N_1, N_2, N_3 \ldots N_M$ (composition) or # of moles of component i

Thermo doesn't provide the explicit dependence of S on these other variable, equations of state come either from experiment (empirical) or from microscopic models (e.g. Statistical Mechanics)

But, we can use functional dependence to figure some things out:

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,\vec{N}} dU + \left(\frac{\partial S}{\partial V}\right)_{U,\vec{N}} dV + \sum_{j=1}^{M} \left(\frac{\partial S}{\partial N_j}\right) dN_j$$

Alternatively we can choose U as the dependent function

$$U = U(S, V, \vec{N}),$$ which means

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,\vec{N}} dS + \left(\frac{\partial U}{\partial V}\right)_{S,\vec{N}} dV + \sum_{j=1}^{m} \left(\frac{\partial U}{\partial N_j}\right)_{S,V,N_i} dN_j$$

total differential (how does U change with changing values of $S, V, \vec{N}$)

Each of the partial derivatives corresponds to a physically measurable property:

$$T \equiv \left(\frac{\partial U}{\partial S}\right)_{V,\vec{N}} \qquad P \equiv -\left(\frac{\partial U}{\partial V}\right)_{S,\vec{N}} \qquad \mu_j \equiv \left(\frac{\partial U}{\partial N_j}\right)_{S,V,N_i}$$

Conjugate properties:

$$T \longleftrightarrow S$$
$$P \longleftrightarrow V$$
$$\mu \longleftrightarrow N$$

intensive $\longleftrightarrow$ extensive

So:

$$dU = T\,dS - p\,dV + \sum_{j=1}^{m} \mu_j\,dN_j$$

No magic here, these are just the definitions of these state variables. (T, P, μ_j)

Or if we solve for dS:

$$dS = \left(\frac{1}{T}\right)dU + \left(\frac{P}{T}\right)dV - \sum_{j=1}^{m}\left(\frac{\mu_j}{T}\right)dN_j$$

Which gives us 3 more definitions

$$\left(\frac{1}{T}\right) \equiv \left(\frac{\partial S}{\partial U}\right)_{V,\vec{N}} \qquad \left(\frac{P}{T}\right) \equiv \left(\frac{\partial S}{\partial V}\right)_{U,\vec{N}} \qquad \frac{\mu_j}{T} \equiv -\left(\frac{\partial S}{\partial N_j}\right)_{U,\ldots}$$