

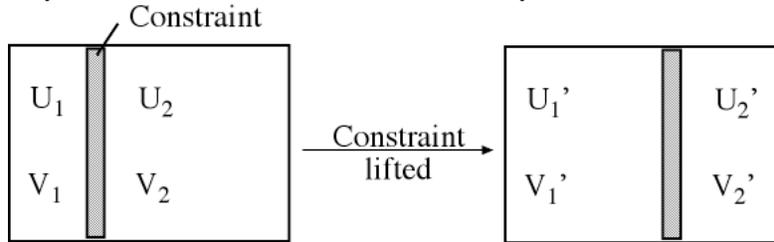
The postulates of thermodynamics:

P0:

Simple systems have equilibrium states that are fully characterized by a unique set of extensive state functions $\{U, X_i\}$, where U is the internal energy (energy for short) and the X_i are other required extensive state functions (e.g. V, A, L, n_i , etc.).

Lemma: A composite system also has a unique set $\{U, X_i\}$ where $U = \sum_k U_k$ and $X_i = \sum_k X_{ik}$; however, this set does not fully characterize the composite system unless the internal constraints are specified.

ex: Both composite systems below have identical U and V , but they are still not identical.



P1:

The quantity U is conserved for a closed system.

Notes: - U is usually a relative energy; for P2 and P3, only relative energies are important
 -Relativistically mc^2 is not conserved by itself; chemically, m is assumed conserved

P2:

For a set of simple systems $\{S_k\}$, there exist single-valued, continuous, and differentiable extensive state functions $S_k(U_k, X_{ik})$, defined for stable local equilibrium states, such that for a closed composite system $\{S\} = \sum_k \oplus \{S_k\}$, the state functions U_k and X_{ik} take on those values which maximize the entropy $S = \sum_k S_k$ of the closed composite system, subject to its internal constraints.

Notes: - $S_k = S_k(U_k, X_{ik})$ are called the “fundamental relations” for the subsystems. S_k are the entropies of the subsystems, and S is the entropy of the composite closed system.
 -The total energy $U = \sum_k U_k$ of the composite system is conserved even while S is maximized.
 -“Stable” means $d^2S < 0$ so a well-defined maximum exists

P3:

S is a monotonically increasing function of U and $\lim_{(\frac{\partial U}{\partial S})_{X_i} \rightarrow 0} S(U, X_i) = 0$.

Note: -Monotonicity allows U and S to be freely interchanged, so we can write $U=U(S, X_i)$ instead
 -This will later be seen to be equivalent to the statement that $\lim_{T \rightarrow 0} S=0$