Thermodynamics

The science of observation did some thermo to get a concentration of pt. defects now do things more formally.

Objective: answer the question if we put a bunch of elements in a box, what would they like to do? e.g. form a compound, form a simple mixture, explode.

Use thermo to predict
- what can happen
- not what will happen.

Observation

A) state 0 partition

rigid, impermeable, thermally insulating wall → adiabatic

remove partition

state 1

new state has greater uniformity "equilibration"

B) state 0

partition

rigid, impermeable, adiabatic

piston

allow piston to move

state 2

again, new state has greater uniformity.
Observation (A) 

Internal energy, unchanged, \[ E \] 
Entropy, \( S \), randomization, increased

2nd Law: For given \( E \), \( S \) will be maximized at equilibrium,

\[ \Delta S \geq 0 \quad \text{for all changes in state} \]

Also, \( S \) of any system is a positive #

Observation (B)

Our system did work on the outside world (via piston)

Work done by system corresponds to energy lost.

1st Law: Energy is conserved.

\[ dE = dQ - dW \]

\( \Delta E \) = change in internal energy

\( h \) = heat put into system

(Thermal work = atom vibrations)

Combined: if our system can minimize its \( E \)
(by doing work on the outside world) it will

\( S \) tends to a maximum, \( \text{can show } T = \text{const} \)

\( E \) tends to a minimum, \( \Rightarrow P = \text{const} \)

Aside:

Case A, state @ has higher energy than case B, state @.

\( (\text{height, } P) \)

but \( T = \text{const, } P = \text{const} \) true for both cases.
Define internal energy:
\[ \text{d}E = T \text{d}s - P \text{d}V + \sum_i \mu_i \text{d}N_i + \ldots \]

- \( T \text{d}s \): heat, \( T \): temp, \( S \): entropy
- \( P \text{d}V \): mech work, \( P \): pressure, \( V \): volume
- \( \sum_i \mu_i \text{d}N_i \): chemical work, \( \mu_i \): chem potential of species \( i \)
- \( N_i \): # of atoms of species \( i \)

Other types of work: magnetic, electrical, gravitational, etc.

If we double the size of the system, by adding 2 identical systems,
\[ V' \rightarrow 2 \times V, \quad N_i' \rightarrow 2 \times N_i, \quad \text{and} \quad S' \rightarrow 2 \times S. \]
\[ E' \rightarrow 2 \times E \]

\( S, V, \sum_i N_i, E \) are extensive or deformation variables.

\( E = E(S, V, \sum_i N_i) \)  \( E \) is a natural function of the extensive variables.

\( T, P, \sum_i \mu_i \) are intensive or force variables.

\[ \frac{\partial E}{\partial s} (s, N_i, \sum_i N_i) = T \quad \frac{\partial E}{\partial V} (s, N_i, \sum_i N_i) = -P \quad \frac{\partial E}{\partial N_i} (s, N_i, \sum_i N_i, \sum_j N_j) = \mu_i \]

\[ \text{Sd}E \rightarrow E = TS - PV + \sum_i \mu_i N_i \]

This internal energy is minimized when we control the entropy, volume and # of atoms in the system, i.e., case B.