11/2/98.

Thermodynamics

- the science of observation

  did some thermo to get 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.

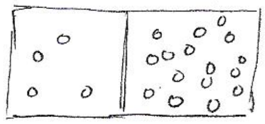
Observation :

A). state ①

partition

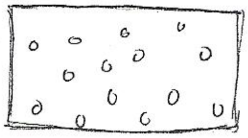
rigid, impermeable, themally insulating wall

$\underbrace{\text{themally insulating}}$ ↳ adiabatic



remove partion

state ②



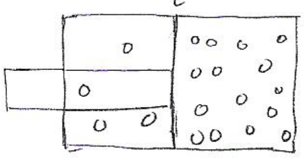
new state has greater uniformity "equilibration"

B). state ①.

partition.

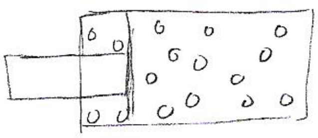
rigid, impermeable, adiabatic.

piston



allow piston to move

state ②



again, new state has greater uniformity.

Observation (A)

Internal energy E unchanged, } 2nd law of thermo

Entropy S - randomness, increased }

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

$\delta S \geq 0$ ← 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 ≡ energy

Work done by system corresponds to energy lost.

1st Law: Energy is conserved

$$dE = \delta Q - \delta W$$

change in internal energy

heat put into system
(thermal work ≡ atom vibrations).

work done by system.

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

S tends to a maximum. } can show ⇒ $T = \text{const}$

E tends to a minimum. } $P = \text{const}$

aside

Case A state ② has higher energy than case B, state ②.
(high T, P)

but $T = \text{const}$, $P = \text{const}$ true for both cases.

Define internal Energy:

$$dE = TdS - PdV + \sum_i \mu_i dN_i + \ldots$$

TdS = heat, T = temp, S = entropy

PdV = mech work, P = pressure, V = volume.

$\sum_i \mu_i dN_i$ = chemical work, μ_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.

$V' \to 2 \times V$, $N_i' \to 2 \times N_i$ and $S' \to 2 \times S$.

$E' \to 2 \times E$

$\Rightarrow$ $S, V, \{N_i\}, E$ are <u>extensive</u> or deformation variables.

would also double the energy

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

$T, P, \{\mu_i\}$ are <u>intensive</u> or force variables.

$$\left.\frac{\partial E}{\partial S}\right)_{V,\{N_i\}} = T \quad \left.\frac{\partial E}{\partial V}\right)_{S,\{N_i\}} = -P \quad \left.\frac{\partial E}{\partial N_i}\right)_{V,S,\{N_{j\neq i}\}} = \mu_i$$

$$\int dE \Rightarrow E = TS - PV + \sum \mu_i N_i$$

this internal energy is minimized when we control the entropy, volume and # of atoms in the system

i.e., case B.