#1)

The Route of Physics

(Interpretation of equilibrium condition)

How systems exchange E?

Does E flows from higher E to lower E?

Not always!

Considering this issue leads to LT(!)

when 2 systems in contact (isolated):

$$\underbrace{E_{tot}}_{\substack{\text{control}\\ \text{parameter}}} = E_1 + E_2 = \text{const.} \Leftarrow \text{from Init. Conditions}$$

E_j – not fixed

Question: how do they go to "equilibrium"? i.e., E_1^*, E_2^*

Answer: depends on $S_{tot}(E_{tot} | E_1, E_2)$ entropy of whole system subject to partition (E_1, E_2)

focus on →
neglect interaction E!

$$\begin{cases} S_{tot} = S_1 + S_2 \\ S_1 = S_1(E_1) \\ S_2 = S_2(E_2) \end{cases}$$

carries info how probable is initial partition

$\Rightarrow$ not trivial because $S_1^* \neq S_1(E_1, E_2)$!

For what partition $S_{tot} = \max$?

$$\Rightarrow \left.\frac{dS_{tot}}{dE_1}\right|_{E_1^*} = 0 \Rightarrow \left.\frac{dS_1}{dE_1}\right|_{E_1^*} = \left.\frac{dS_2}{dE_2}\right|_{E_2^*} \quad \text{since } dE_1 = -dE_2$$

$\Rightarrow$ The most probable partition is when

$\beta_1(E_1^*) = \beta_2(E_2^*)$ → need to relate $\beta \to T$!

How? For any system $S[E(\beta)]$

$\Rightarrow$ We know $Z(\beta)$ – normalization factor to $\Omega(E)$ for micro canon.

$\Rightarrow$ Associated potential: $LT(S) \to \mathcal{A}(\beta) = \beta E - S[E(\beta)]$.

Thermodynamics

Definitions of thermo variables

Steady state:	Time independent
Equilibrium:	Steady state + no macroscopic curre
State functions: (or state variable)	equilibrium quantity depends on thermo variables but independent of history
Extensive	state function $\propto N$
Intensive	independent of N
Thermodynamic limit	$V \to \infty$ $N \to \infty$ $\frac{N}{V} \to$ finite
Spontaneous process	Does not involve change in external constraints (internal dynamics)
Quasistatic	Infinitely slow
Reversible	Quasistatic + allows a path in state space which maybe reversed

In equilibrium: state variables connected by EOS

Zeroth Law

A in equilibrium with B

B in —"—"—"—"— C

⇒ A in —"—"—"—"— C

Alternatively: intensive quantities constant throughout system

⇒ $T = \text{const.}$ ⇒ thermal eq.; $P = \text{const.}$ → mech eq.

$\mu = \text{const}$ → chem. eq.

First Law

Conservation of energy

dE = increase in internal energy

$$dE = dQ - dW$$

dW – work done by the system

dQ – heat added to the system

x_i – state variable (V, M) ⇒ generalized displacements

X_i – conjugate —"— (P, H) ⇒ generalized forces

$$dW = -\sum X_j \, dx_j$$

Adiabatic

$dQ = 0 \Rightarrow dW = -dE$

no heat exchanged!

between system and surrounding

Second Law

a state variable : entropy such that for any process

$$dQ \le T\,dS$$

Equality ⇒ reversible process

For adiabatic process ($dQ=0$) :

$$\rightarrow \qquad dS \ge 0$$

Helmholtz Free Energy

what is the maximal amount of work extractable in an isothermal process

state function ⇒ $A \equiv E - TS$ "A" related to E via LT

Then $dA = dE - TdS - \underbrace{SdT}_{=0}$ isothermal process

$$dA = \underbrace{dE - \overbrace{TdS}^{dQ}}_{=-PdV \to -dW}$$

→ isothermal (from I law) $dE = dQ - dW$

$$dW = dQ - dE = (dQ - TdS) - dA$$

Use 2nd law : $dQ \le TdS$

$$\Longrightarrow dW \le -dA$$

⇒ { the max work that can be extracted at T = const.

(equality for reversible process!)

⇒ "A" is the available amount of energy which can be converted to work.

If all the external parameters are fixed:

$dW = 0$ → { for $T = \text{const.}$ spontaneous process can only decrease A ⇓ Equilibrium at $\begin{matrix} T = \text{const} \\ W = \text{const} \end{matrix}$

⟹ $-dA \geq 0$

or $\{dA \leq 0\}$

Free energy is minimized for isothermal process if all external parameters fixed. ⟹ min A

Note: For ~~p~~ such processes the intensive parameters, conjugated to those kept fixed, have to change

e.g. V fixed ⟹ $\underbrace{P \text{ changes}}_{\text{intensive (conjugate) para.}}$

Gibbs Free Energy ⟹ $G = A + PV$
↳ state function

Sometimes useful to keep these conjugates fixed, rather than the parameters

$$G \equiv \underbrace{E - TS - \sum_i X_i x_i}_{A - \sum_i X_i x_i}$$

If X_i, T fixed:

$$\Longrightarrow dG = dE - TdS - \sum_i X_i dx_i$$

By definition, $dG = dQ - TdS$

$\Rightarrow \{dG \leq 0\}$ in spontaneous process with $\begin{cases} T = \text{const} \\ P = \text{const} \end{cases}$

When all the X_i are not fixed, subtract only these, e.g., when μ fixed, but not others

grand potential $\Omega_G = E - TS - \mu N \Rightarrow d\Omega_G = -S\,dT - P\,dV - N\,d\mu$

$$\underbrace{\boxed{d\Omega_G \leq 0}}$$

Various thermo. potentials determine equilibrium under different physical conditions

isolated	$dS \geq 0$
T fixed	$dA \leq 0$
T, P fixed	$dG \leq 0$
T, μ fixed	$d\Omega_G \leq 0$

$A(T)$	LT of	$E(S)$
$G(T,P)$	— " —	$A(T,V)$
$\Omega_G(T,\mu)$	— " —	$A(T,N)$