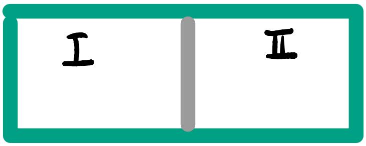
2-2 walls / constraints.



isolated

- rigid wall: mechanical work
- adiabatic wall: ✗ heat
- diathermal wall: ✓ heat

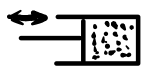
2-3 First Law of thermo.

1> $\underline{dU} = đQ + đW$ ($\uparrow \Delta U$; $\underbrace{đQ + đW}_{\text{Transitory}}$)

W_M
W_E
W_C

U → a definite state

$đW = -p\,dV$



$\begin{cases} dW > 0 & \text{sys gains energy.} \\ dW < 0 & \text{sys loses energy} \end{cases}$

$đQ = dU - đW = dU + P\,dV$

2> $dU_{total} = 0 = dU_{sys} + dU_{surr.}$

$\Rightarrow dU_{sys} = -dU_{surr.}$

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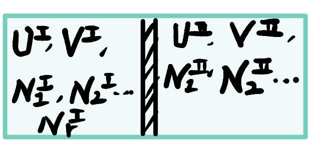
3. Basic Problem (Abstract)



isolated

*. Determine equilibrium state after removal of certain constraints in an isolated sys.

4. Postulates & Fundament Equations.

*. here formulate the solutions by a series of postulates.

t-dependent evolution in Q.M.

$$\frac{\partial}{\partial t}|\psi(t)\rangle = -\frac{i}{\hbar}\hat{H}|\psi(t)\rangle$$

For thermo.

$$\frac{d}{dt}S(t) \geq 0$$

↓ Entropy

Postulate I: There exists a function

$S = S(U, V, N_1, N_2 \cdots)$ of extensive parameters

defined for equilibrium states, $U, V, N_1, \cdots$

tend to maximize S.

Fundamental relation.

Postulate II:

S of a composite system.

*. additive $S = \sum_i S^{(i)}$

*. continuous & differentiable w/ respect to U

*. $U \uparrow \Longrightarrow S \uparrow$

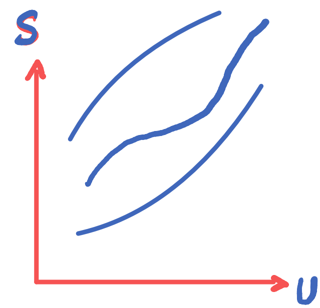
→ S is 1^{st}-order function of extensive parameters

$S = S(U, V, N_1 \cdots)$

$\lambda = $ const.

$S' = S(\lambda U, \lambda V, \lambda N_1 \cdots)$

$= \lambda S(U, V, N_1 \cdots)$



→ S(U, V, N) can be inverted w/ respect U.

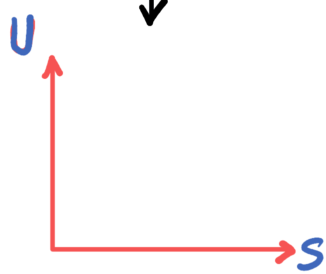
$\Downarrow$

$* \; U = U(S, V, N)$

$\left(\frac{\partial S}{\partial U}\right)_{V, N_1, N_2 \cdots} > 0$

$\Downarrow$

$1/T$



Postulate III

"S" vanish is $\left(\frac{\partial U}{\partial S}\right)_{V, N_1, \cdots} = 0$.

(3rd law of thermo. or "Nernst Postulate")

Obj. #2. Equilibrium process / conditions.

1. Intensive Parameters. ($T \to U(S, V, N)$).
2. Equation of states ($PV = NRT$)
3. The entropic intensive parameters.
4. Different types of equilibrium.
   - Thermal
   - Mechanical.
   - Matte flow
   - chemical

---

1. Intensive Parameters.

*. P.D.

Def. continuous function of multivariables.

$\psi = \psi(x, y, z)$

if. y, z = consts. $\psi = \psi(x)_{y,z}$

the derivative is so-called P.D. w/ respect to

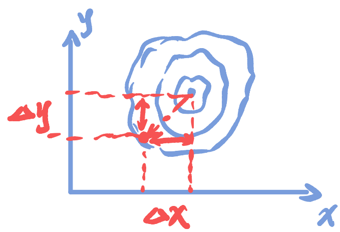
x, and denoted as $\left(\frac{\partial \psi}{\partial x}\right)_{y,z}$

* For 1^{st}-order differential. $\psi(x.y.z)$

$$d\psi_x = \left(\frac{d\psi(x, y_0, z_0)}{dx}\right) \cdot dx = \left(\frac{\partial \psi}{\partial x}\right)_{y,z} dx.$$

$$d\psi_y = \left(\frac{\partial \psi}{\partial y}\right)_{x,z} \cdot dy \qquad d\psi_z = \left(\frac{\partial \psi}{\partial z}\right)_{x,y} dz$$

$$d\psi = d\psi_x + d\psi_y + d\psi_z$$



* $U = U(S, V, N_1 \cdots N_r)$

$$dU = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,N_1\ldots}}_{T} dS + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S,N_1\ldots}}_{-P} dV + \underbrace{\left(\frac{\partial U}{\partial N_1}\right)_{S,V,N_2\ldots}}_{\mu} dN_1$$

$$dU = \underline{\text{đ}Q} + \underline{\text{đ}W}$$

$\Rightarrow \text{đ}Q = T \cdot dS$

$$dW \begin{cases} dW_M = -p\,dV \\ dW_c = \sum_i \mu_i dN_i \end{cases}$$