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Then: $dU = Tds - pdV + \sum_{j=1}^{m} \mu_j dN_j$ ... ①

divide both sides by T, rearrange:

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \sum_{j=1}^{m} \frac{\mu_j}{T} dN_j$$

$$\Rightarrow \left(\frac{\partial S}{\partial U}\right)_{N.V} = \frac{1}{T} \; ; \; \left(\frac{\partial S}{\partial V}\right)_{N.U} = \frac{P}{T} \; ; \; \left(\frac{\partial S}{\partial N_j}\right)_{U.V.N_{i \neq j}} = -\frac{\mu_j}{T}$$

First order homogeneous functions.

If $f = f(X_1, X_2 \cdots)$ is homogeneous of 1st order,

then: $f(\lambda X_1, \lambda X_2, \cdots) = \lambda f(X_1, X_2 \cdots)$

an important property: $f(X_1, X_2 \cdots) = \sum_{i=1}^{m} X_i \frac{\partial f}{\partial X_i}$

If $U(N.V.S)$ is a homogeneous 1st order fn.

then: T. P. μ are intensive variables.

$$T = \left(\frac{\partial U}{\partial S}\right)_{N.V} = \left(\frac{\partial(\lambda U)}{\partial(\lambda S)}\right)_{N.V} = \left(\frac{\partial U(\lambda S.\lambda V.\lambda N)}{\partial(\lambda S)}\right)_{N.V}$$

$$dU(\lambda S.\lambda V.\lambda N) = T\, d(\lambda S) - p\, d(\lambda V) + \sum_{j=1}^{m} \mu_j d(\lambda N_j)$$

$$= \lambda T dS - \lambda p dV + \lambda \sum_{j=1}^{m} \mu_j dN_j$$

$$\lambda dU(N.V.S)$$

leave the same form as eq ①.

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T expresses the tendency of a system to vary its U in response to "S" change.

$\boxed{A}$ $\boxed{B}$ two subsystems, both in thermal contact, but isolated from surr.
no V and N exchange.

A. $\frac{1}{T_A} = \left(\frac{\partial S_A}{\partial U_A}\right)_{N_A, V_A}$

$S = S_A + S_B$

$U = U_A + U_B$

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at equilibrium. S is maximized. so. $dS = 0$.

$$dS = \left(\frac{\partial S_A}{\partial U_A}\right)_{N_A, V_A} dU_A + \left(\frac{\partial S_B}{\partial U_B}\right)_{N_B, V_B} dU_B$$

$$= 1/T_A \, dU_A + 1/T_B \, dU_B$$

$$= \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU_A \qquad (dU_B = -dU_A)$$

$$\therefore \quad \frac{1}{T_A} = \frac{1}{T_B} \qquad \text{(subject to any value of } dU_A\text{)}$$

moving towards eq.: $dS > 0 \Rightarrow \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU_A > 0$

energy flow from high T to low T.

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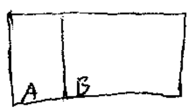
ex: P describes the tendency to change V

$$P = -\left(\frac{\partial U}{\partial V}\right)_{N,S}$$



piston

$$V_{tot} = V_A + V_B = \text{Constant.}$$

$$\therefore \quad dV_A = -dV_B$$

$$U_{tot} = U_A + U_B = \text{constant} \Rightarrow dU_A = -dU_B$$

at eq. $\quad dS = 0$

$$= \left(\frac{\partial S_A}{\partial U_A}\right) dU_A + \left(\frac{\partial S_A}{\partial V_A}\right) dV_A + \left(\frac{\partial S_B}{\partial U_B}\right) dU_B + \left(\frac{\partial S_B}{\partial V_B}\right) dV_B$$

$$= \frac{1}{T_A} dU_A + \frac{1}{T_B} dU_B + \frac{P_A}{T_A} dV_A + \frac{P_B}{T_B} dV_B$$

$$= \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right) dV_A = 0$$

$$\therefore \quad T_A = T_B, \quad P_A = P_B.$$

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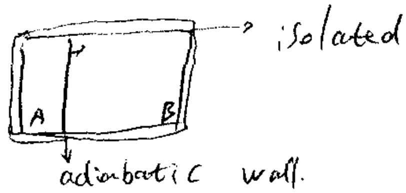
Towards equilibrium.

if $T_A = T_B$. $\quad dS_{TOT} = \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right) dV_A > 0$.

then, we know: when $dV_A > 0$, $P_A > P_B$.

for the case.

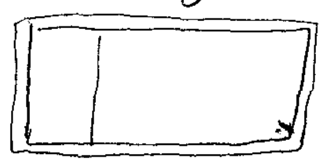


If $T_A = T_B$. then $\Rightarrow$ previous case.

If $T_A \neq T_B$: $\quad \frac{P_A}{T_A} - \frac{P_B}{T_B} = 0$ but $T_A \neq T_B$. ?

ex. μ express the tendency for particles exchange.

$$\mu_j = \left(\frac{\partial U}{\partial N_j}\right)_{S.V.N_{i\neq j}}$$



$N_{TOT} = N_A + N_B = const.$

$dN_A + dN_B = 0$

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$U_{TOT} = U_A + U_B = \text{const.} \Rightarrow dU_A + dU_B = 0$

Impose this constraint: $T_A = T_B$. ?

at equilibrium: $dS_{TOT} = \left(\frac{\partial S_A}{\partial U_A}\right) dU_A + \left(\frac{\partial S_B}{\partial U_B}\right) dU_B + \left(\frac{\partial S_A}{\partial N_A}\right) dN_A + \left(\frac{\partial S_A}{\partial N_B}\right) dN_B$

$$dS_{TOT} = \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU_A + \left(\frac{\mu_B}{T_B} - \frac{\mu_A}{T_A}\right) dN_A = 0$$

$\therefore \quad T_A = T_B, \quad \mu_A = \mu_B.$

Towards equilibrium: $\left(\frac{\mu_B}{T_B} - \frac{\mu_A}{T_A}\right) dN_A > 0$

so as $dN_A < 0$, $\mu_B < \mu_A$

"μ" as particle escaping tendency.

measurable quantity: P. V. T. N. q. W

quantities that are difficult to measure: U. μ. S.