A particle moving freely in an external potential $U(x)$ dissipates energy and settles to equilibrium at minimum value of $U$. $\left( \frac{d^2U}{dx^2} > 0 \right)$

Minimize enthalpy : $H = U - Jx$ $\quad \frac{d^2H}{dx^2} = \frac{d^2U}{dx^2} > 0 \Rightarrow$ new equilibrium point $x_{eq}(J) \rightarrow$ convex of $U(x)$ is accessible

More than one mechanical coordinates $\rightarrow$ any $\delta x_i$ results in an increase of energy

$$\sum_{i,j} \frac{\partial^2 U}{\partial x_i \partial x_j} \delta x_i \delta x_j > 0 \quad \text{or} \quad \sum_{i,j} \frac{\partial^2 H}{\partial x_i \partial x_j} \delta x_i \delta x_j > 0$$

$\Rightarrow$ more symmetric

$|||$

Equivalent eqn.

$$\delta J_i = \delta\left(\frac{\partial U}{\partial x_i}\right) = \sum_j \frac{\partial^2 U}{\partial x_i \partial x_j} \delta x_i \qquad (\delta : \text{change in non-equilibrium})$$

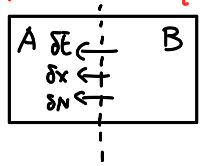
$$\sum_i \delta J_i \delta x_i > 0$$

↳ generalized in chemistry

$$\delta T \delta S + \sum_i \delta J_i \delta x_i + \sum_\alpha \delta \mu_\alpha \delta N_\alpha > 0 \quad \text{(thermal \& chemical inputs)}$$

uniformity of an extended thermodynamic body

A and B are equal




(stable to unstable)

$E(T)$, $x(J)$, $\mu(N)$ // at fixed $E, x, N$

$\rightarrow$ first-order relation:

$$\delta T_A = -\delta T_B = \delta T, \quad \delta J_A = -\delta J_B = \delta J; \quad \delta \mu_A = -\delta \mu_B = \delta \mu$$

$$S = S_A + S_B = \left( \frac{E_A}{T_A} - \frac{J_A}{T_A} x_A - \frac{\mu_A}{T_A} N_A \right) + \left( \frac{E_B}{T_B} - \frac{J_B}{T_B} x_B - \frac{\mu_B}{T_B} N_B \right)$$

first order change $\frac{1}{T_A}\delta E_A$ & $\frac{1}{T_B}\delta E_B$ $\quad E_A \delta\left(\frac{1}{T_A}\right)$ & $E_B \delta\left(\frac{1}{T_B}\right)$ ……

are all eliminated

second order are the same

intensive $\quad$ intensive

$$\delta S = \delta S_A + \delta S_B = 2 \left[ \delta E_A \, \delta\left(\frac{1}{T_A}\right) - \delta\left(\frac{J_A}{T_A}\right) \delta x_A - \delta\left(\frac{\mu_A}{T_A}\right) \delta N_A \right]$$

$$= 2 \left[ -\frac{\delta E_A \delta T_A}{T_A^2} - \frac{T_A \delta J_A - J_A}{T_A^2} \delta x_A - \frac{T_A \delta \mu_A - \mu_A}{T_A^2} \delta N_A \right]$$

$$= -\frac{2}{T_A} \left[ \delta T_A \left( \frac{\delta E_A - J_A \delta x_A - \mu_A \delta N_A}{T_A} \right) + \delta J_A \delta x_A + \delta \mu_A \delta N_A \right]$$

$$= -\frac{2}{T_A} \left[ \delta T_A \delta S_A + \delta J_A \delta x_A + \delta \mu_A \delta N_A \right]$$

stable equilibrium: any change leads to a decrease of entropy

$$\delta T \, \delta S + \delta J \, \delta x + \delta \mu \, \delta N \geq 0$$

Example: $\delta T$ and $\delta x$ with $\delta N = 0$

same result for any constraint

$$\begin{cases} \delta S = \frac{\partial S}{\partial T}\Big|_x \delta T + \frac{\partial S}{\partial x_i}\Big|_T \delta x_i \\ \delta J_i = \frac{\partial J_i}{\partial T}\Big|_x \delta T + \frac{\partial J_i}{\partial x_j}\Big|_T \delta x_j \end{cases} \quad \& \quad \delta T\,\delta S + \delta J\,\delta x + \delta\mu\,\delta N \geq 0$$

$$\frac{\partial S}{\partial T}\Big|_x (\delta T)^2 + \frac{\partial J_i}{\partial x_j}\Big|_T \delta x_j \delta x_i + \cancelto{0}{\frac{\partial S}{\partial x_i}\Big|_T \delta x_i \delta T + \frac{\partial J_i}{\partial T}\Big|_x \delta T \delta x_i} \geq 0$$

as $dF = d(E - TS) = -SdT + Jdx$

Maxwell Relation: $-\left(\frac{\partial S}{\partial x}\right)_T = \left(\frac{\partial J}{\partial T}\right)_x$

$\frac{\partial S}{\partial T}\Big|_x > 0$

$\Rightarrow$ quadratic form, so it is positive for any $\delta T$ or $\delta x_i$

Example: $\delta T$ with $\delta x, \delta N = 0$ $\quad C_x = \frac{đQ}{dT}\Big|_x = T\left(\frac{\partial S}{\partial T}\right)_x \geq 0$

$\delta x_i$ with $\delta T, \delta x_{i\neq j}, \delta N = 0$ $\quad$ Matrix of coefficients $\frac{\partial J_i}{\partial x_j}\Big|_T$ must be positive definite

positive definite matrix: all eigenvalues are positive

so trace and determinant are positive as well.

pressure (mechanical) & Chemical work for gas

$$\begin{bmatrix} -\frac{\partial P}{\partial V}\Big|_{T,N} & -\frac{\partial P}{\partial N}\Big|_{T,V} \\ \frac{\partial \mu}{\partial V}\Big|_{T,N} & \frac{\partial \mu}{\partial N}\Big|_{T,V} \end{bmatrix}$$

diagonals are all inverse response funcs.

$K_{T,N} = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_{T,N}$ & $\frac{\partial N}{\partial \mu}\Big|_{T,V}$

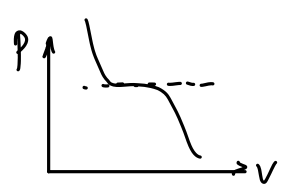
diagonals are positive.

$$-\frac{\partial P}{\partial V}\Big|_{T,N}\frac{\partial \mu}{\partial N}\Big|_{T,V} + \frac{\partial P}{\partial N}\Big|_{T,V}\frac{\partial \mu}{\partial V}\Big|_{T,N} \geq 0$$

critical point of gas $\quad \frac{\partial P}{\partial V}\Big|_{T,N} = 0$ (Not justified but works for Talyor expansion)

$$\delta P(T=T_c) = \cancelto{0}{\frac{\partial P}{\partial V}\Big|_{T,N}}\delta V + \frac{1}{2}\frac{\partial^2 P}{\partial V^2}\Big|_{T,N}\delta V^2 + \frac{1}{3!}\frac{\partial^3 P}{\partial V^3}\Big|_{T,N}\delta V^3$$

as $-\delta P\delta V \geq 0 \Rightarrow \delta P\delta V \leq 0 \Rightarrow \frac{1}{2}\frac{\partial^2 P}{\partial V^2}\Big|_{T,N}\delta V^3 + \frac{1}{3!}\frac{\partial^3 P}{\partial V^3}\Big|_{T,N}\delta V^4 \leq 0$




$\Rightarrow \frac{\partial^2 P}{\partial V^2} = 0$ and $\frac{\partial^3 P}{\partial V^3} < 0$ as $\delta V^4 > 0$