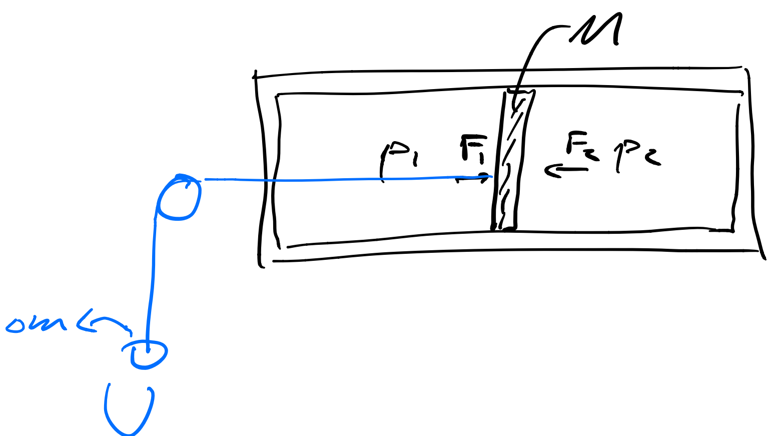
$U(S,V,N)$

$$G(T,p,N) = U - TS - (-p)V$$

$$dG = \cancel{-TdS} - SdT + \cancel{pdV} + Vdp$$

insert $\boxed{dU = \cancel{TdS} - \cancel{pdV} + \mu dN}$

$$dG = -SdT + Vdp + \mu dN$$



$p_1 > p_2$

$\Rightarrow$ THE INTERNAL ENERGY MEASURES THE AMOUNT OF WORK A SYSTEM IS ABLE TO DO IN A REVERSIBLE ADIABATIC PROCESS. IT GIVES AN UPPER-BOUND FOR THE AMOUNT OF WORK DONE IN IRREVERSIBLE PROCESSES.

$\Rightarrow$ THE INTERNAL ENERGY OF A CLOSED SYSTEM IS A MINIMUM AS A FUNCTION OF ALL PARAMETERS WHICH

ARE NOT FIXED BY EXTERNAL CONSTRAINTS.

NOW: HELMHOLTZ FREE ENERGY

$$dF = dU - d(TS)$$

$$= đW + \underbrace{đQ - TdS}_{=0 \text{ for REVERSIBLE PROCESSES}} - SdT$$

T - const. $\Rightarrow$ $-SdT = 0$

$dF = đW$ REVERSIBLE

DO WORK ON SYSTEM $dF < đW$

NO WORK $\rightarrow$ $\delta F < 0$

SPONTANEOUS PROCESS AT T = const

$\Rightarrow$ THE HELMHOLTZ FREE ENERGY MEASURES THE AMOUNT OF WORK A SYSTEM IS ABLE TO DO IN AN REVERSIBLE ISOTHERMAL PROCESS.
IT GIVES AN UPPER-BOUND FOR THE AMOUNT OF WORK DONE IN IRREVERSIBLE PROCESSES.

⇒ THE HELMHOLTZ FREE ENERGY OF SYSTEM AT CONSTANT T IS A MINIMUM AS A FUNCTION OF ALL PARAMETERS WHICH ARE NOT FIXED BY EXTERNAL CONSTRAINTS.

NOW: GIBBS FREE ENERGY

$$dG = dU + p\,dV + V\,dp - T\,dS - S\,dT$$

$$= \underbrace{đW_{pV} + p\,dV}_{=0\ \text{REV}} + dW_{\text{OTHER}} + \underbrace{đQ - T\,dS}_{=0\ \text{REV}} - S\,dT + V\,dp$$

$$dG_{\text{REV}} = đW_{\text{OTHER}} - S\,dT + V\,dp$$

$T = \text{const}$ $p = \text{const}$

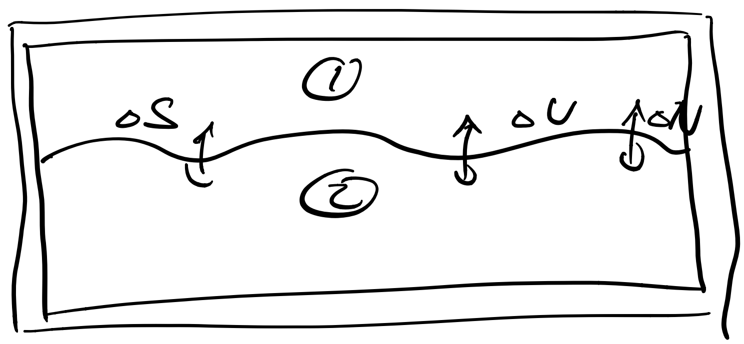
$$dG_{\text{RES}} = đW_{\text{OTHER}}$$

for example: chemical $\sum_i \mu_i\, dN_i$

$$dG_{irr} < đW_{\text{OTHER}}$$

SPONTANEOUS PROCESS: $\delta G < 0$

CONSEQUENCES OF MINIMUM PRINCIPLES FOR 2nd ORDER DERIVATIVES.



$$\Delta U = U_1(S_1+\Delta S, V_1+\Delta V, N_1+\Delta N) + U_2(S_2-\Delta S, V_2-\Delta V, N_2-\Delta N) - U_1(S_1, V_1, N_1) - U_2(S_2, V_2, N_2) > 0$$

$\overset{U_1}{1} = \overset{U_2}{2} = \overset{U}{1}$

$$\Delta U = U(S+\Delta S, V+\Delta V, N+\Delta N) + U(S-\Delta S, V-\Delta V, N-\Delta N) - 2U(S,V,N) > 0$$

GENERAL, ΔS, ΔV, ΔN ARE NOT NECESSARILY SMALL.

CHOOSE: $\Delta N = 0$, $\Delta V = 0$, $\Delta S \xrightarrow{dS} 0$

$$\lim_{\Delta S \to 0}\left[\frac{U(S+\Delta S, V, N) + U(S-\Delta S, V, N) - 2U(S,V,N)}{\Delta S^2}\right]$$

$$= \left.\frac{\partial^2 U}{\partial S^2}\right|_{V,N} > 0$$

Use $\left.\frac{\partial U}{\partial S}\right|_{V,N} = T$

$$\left.\frac{\partial T}{\partial S}\right|_{V,N} > 0$$

$$\rightarrow \quad \left.\frac{\partial S}{\partial T}\right|_{V,N} = \frac{T}{C_V} > 0$$

$$\Rightarrow C_V > 0 \qquad T > 0$$

SIMILARLY:

$$\left.\frac{\partial^2 U}{\partial V^2}\right|_{S,N,X} > 0 \qquad \left.\frac{\partial^2 U}{\partial N^2}\right|_{S,N,\alpha} > 0$$

↳ OTHER EXT. VAR

$$\downarrow \qquad\qquad \downarrow$$

$$K_S > 0 \qquad\qquad \left.\frac{\partial \mu}{\partial N}\right|_{S,N,x} > 0$$

More constraints:

$N = \text{const}, \quad \Delta S, \Delta V$

$$\Delta U = \frac{\partial^2 U}{\partial S^2}\bigg|_{V,N,X} (\Delta S)^2 + 2 \frac{\partial^2 U}{\partial S \partial V}\bigg|_{N,X} \Delta S \Delta V + \frac{\partial^2 U}{\partial V^2}\bigg|_{S,N,X} (\Delta V)^2 > 0$$

$$\frac{1}{(\Delta V)^2} \cdot \bigg| \Longrightarrow$$

$$\frac{\Delta U}{(\Delta V)^2} = a \underset{\frac{\Delta S}{\Delta V}}{\underset{\uparrow}{x}}^2 + bx + c > 0$$

We know $a >$, $c > 0$

$ax^2 + bx + c$ has 2 solutions