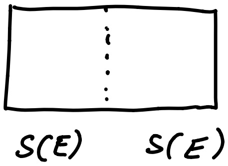


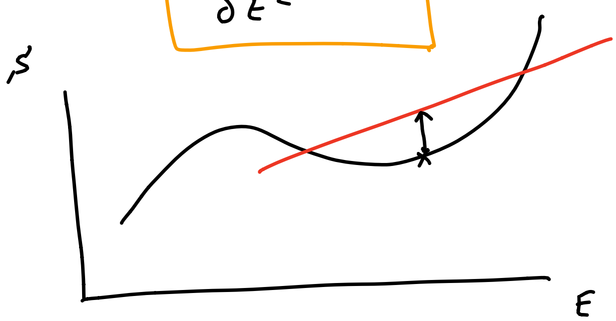
$\Delta S \geq 0$

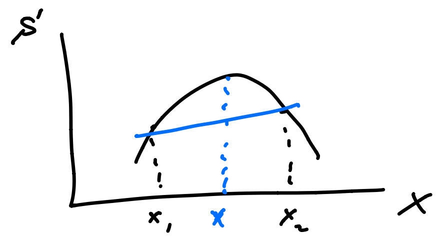
Stability of equilibrium

$$S(E+\Delta E) + S(E-\Delta E) \leq 2S(E)$$

Entropy is concave function of E, V, N

$$\boxed{\frac{\partial^2 S}{\partial E^2} \leq 0}$$





$$\left(\frac{\partial^2 S}{\partial E^2}\right)_{V,N} = \frac{\partial}{\partial E}\left(\frac{1}{T}\right) = -\frac{1}{T^2}\left(\frac{\partial T}{\partial E}\right)_{V,N} = -\frac{1}{T^2 C_V} \leq 0$$

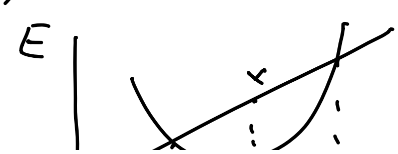
$C_V(T) \geq 0$ stable states

$$S_2'(E_2) - S_1(E_1) \geq 0 \qquad \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right) > 0$$

$$S_2(E_2) - S_1(E_1'') = 0$$

$\max S(E) \Leftrightarrow \min E(S)$ isolated system

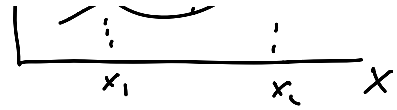
$E(S,V,N)$



$\partial^2 E \quad > 0$

$$\partial V^2$$

$$\frac{\partial^2 E}{\partial S^2} \geq 0$$



Energy is a convex function

$$E \to E - TS \to E - TS + PV$$

$$E(N,V,S) \to A(N,V,T) \longrightarrow G(N,p,T)$$

$$X \leftrightarrow p$$

$$p = \frac{\partial E}{\partial X}, \quad X = -\frac{\partial E}{\partial p}$$

$$\frac{\partial X}{\partial p} = -\frac{\partial^2 V}{\partial p^2} = \frac{1}{\frac{\partial^2 V}{\partial X^2}}$$

$$\left(\frac{\partial^2 F}{\partial V^2}\right) \geq 0 \qquad \left(\frac{\partial^2 F}{\partial T^2}\right) \leq 0$$

$$\left(\frac{\partial^2 G}{\partial N^2}\right) \geq 0 \qquad \left(\frac{\partial^2 G}{\partial p^2}\right) \leq 0$$

convex over extensive variables | concave over intensive variables

$$\left(\frac{\partial^2 F}{\partial V^2}\right) = -\left(\frac{\partial P}{\partial V}\right) = \frac{1}{V K_T} \geq 0$$

$$K_T \geq 0 \qquad C_v \geq 0$$

$$\boxed{\begin{gathered} C_p \geq C_v \geq 0 \\ K_T \geq K_S \geq 0 \end{gathered}}$$

Phase-stability

α - # phases

$i = 1, 2, \ldots c$ components

$$S = \sum_{\alpha=1} S^\alpha \qquad V = \sum_\alpha V^\alpha \qquad n_i = \sum_\alpha n_i^\alpha$$

$$\delta E = \sum_{\alpha=1} \left(T^\alpha \delta S^\alpha - p^\alpha \delta V^\alpha + \sum_i \mu_i^\alpha d n_i^\alpha \right)$$

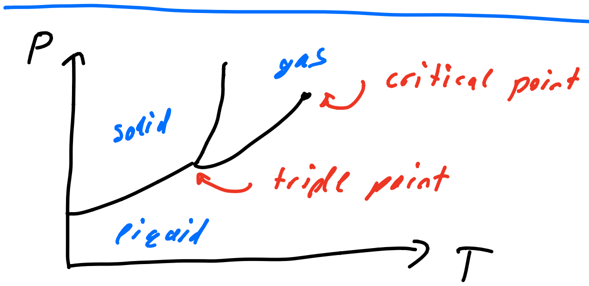
$\delta E = 0$

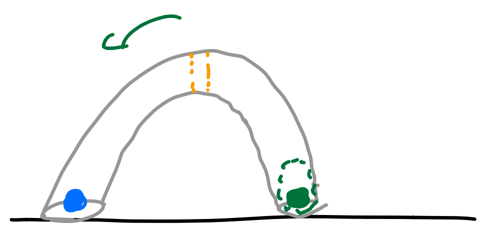
Two-phase example

$$\delta S^{(1)} = -\delta S^{(2)}$$
$$\delta V^{(1)} = -\delta V^{(2)}$$
$$\delta n^{(1)} = -\delta n^{(2)}$$

$$(T^1 - T^2)\,\delta S^{(1)} - (p^{(1)} - p^{(2)})\,\delta V^{(1)} + (\mu^{(1)} - \mu^{(2)})\,\delta N^{(1)} = 0$$

$$T^{(1)} = T^{(2)}$$
$$p^{(1)} = p^{(2)}$$
$$\mu_i^{(1)} = \mu_i^{(2)}$$





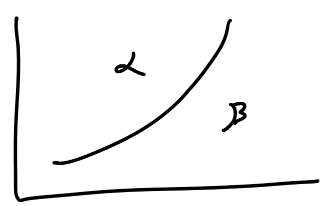
T_f

First order phase transition

abrupt changes in ext var

Second order phase transitions

gradual changes in ext var



$$\mu_\alpha = \mu_\beta$$
$$+ d\mu_\alpha \qquad + d\mu_\beta$$

$$d\mu^\alpha = -s^\alpha dT + v^\alpha dp$$

1-substance

Gibbs-Duhem equation

$$-S^{(\alpha)} dT + V^{(\alpha)} dp = -S^{(\beta)} dT + V^{(\beta)} dp$$

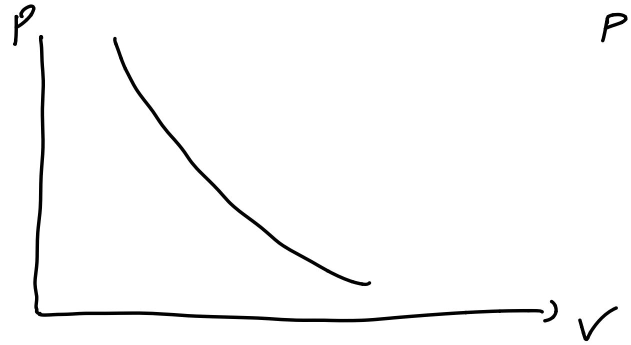
$$\frac{dp}{dT} = \frac{\Delta S'(T)}{\Delta V(T)}$$

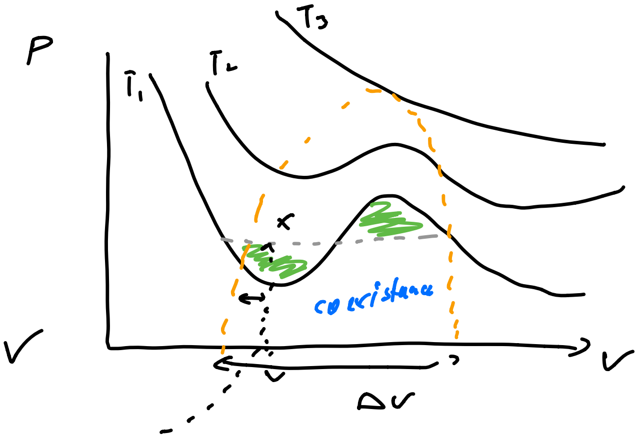
mol entropy dif between phases

mol vol diff between

phases

Clausius-Klapeyron





$\frac{v}{\Delta v}$ liquid

$\frac{\Delta v - v}{\Delta v}$ gas