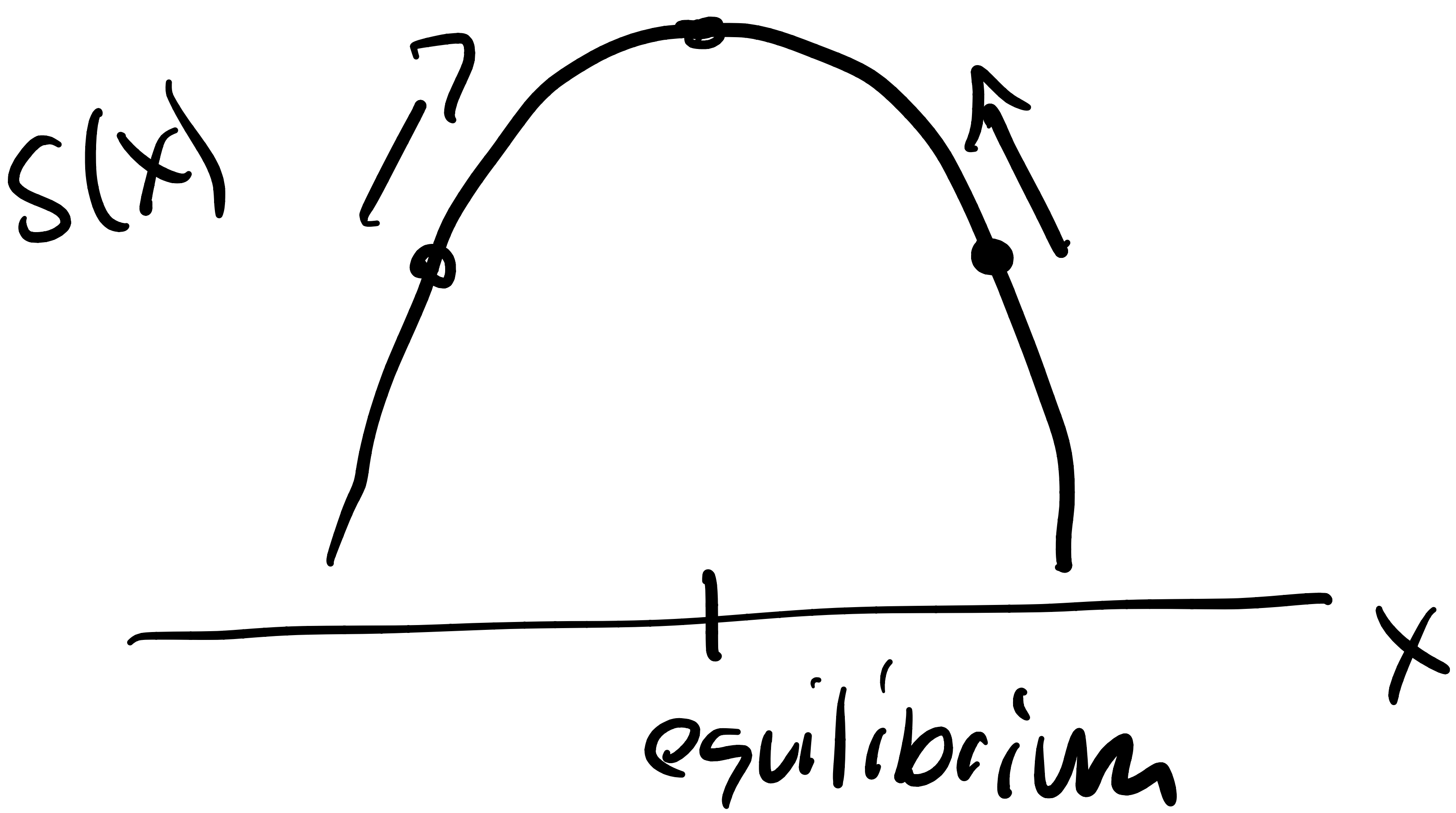
Lecture 7

Entropy ↑ spontaneous process

$dS \geq 0$ (isolated system)



$\mathcal{E}$ is const
V is const

$d\mathcal{E} = 0$
$dV = 0$

Energy as a potential

$\mathcal{E}$ always goes down for certain conditions

[non isolated system]

1st law + 2nd law:

$$d\mathcal{E} = dq + dw = dq - p\,dV \leq T\,dS - p\,dV$$

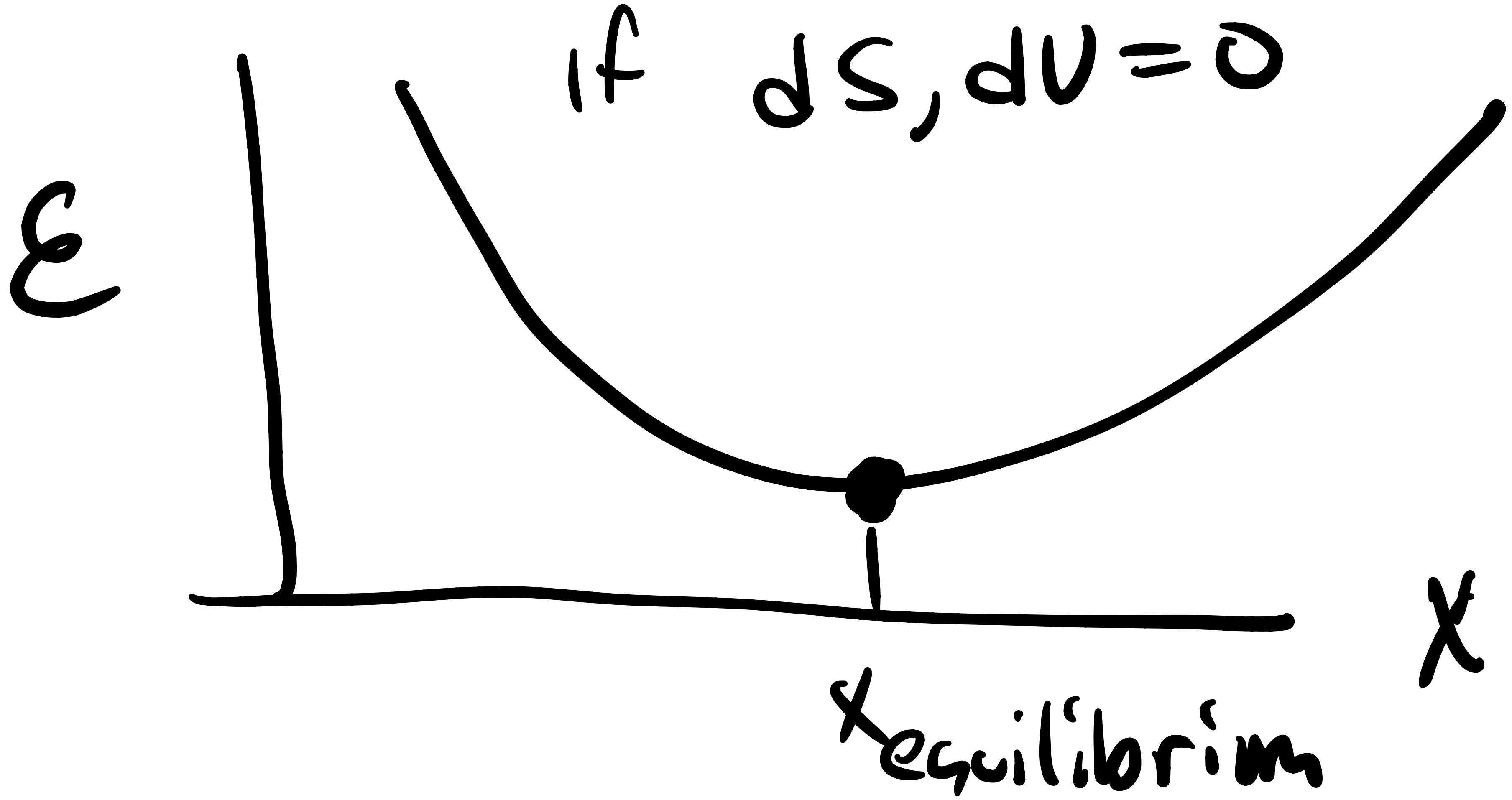
2nd law (Claussius inequality)

$$dS \geq dq/T \Leftrightarrow dq \leq T\,dS$$

$$d\mathcal{E} \leq T\,dS - p\,dV$$

what if $dS = 0$, $dV = 0$ $\Leftarrow$ make change w/ S const, V const

If S & V const, $\mathcal{E}$ can only go down or stay the same



$$T = \left(\frac{\partial \mathcal{E}}{\partial S}\right)_V$$

$$-p = \left(\frac{\partial \mathcal{E}}{\partial V}\right)_S$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial \mathcal{E}}\right)_V \leftarrow \text{kind of interesting}$$

$$\mathcal{E}(S, V) \Rightarrow d\mathcal{E} = \left(\frac{\partial \mathcal{E}}{\partial S}\right)_V dS + \left(\frac{\partial \mathcal{E}}{\partial V}\right)_S dV$$

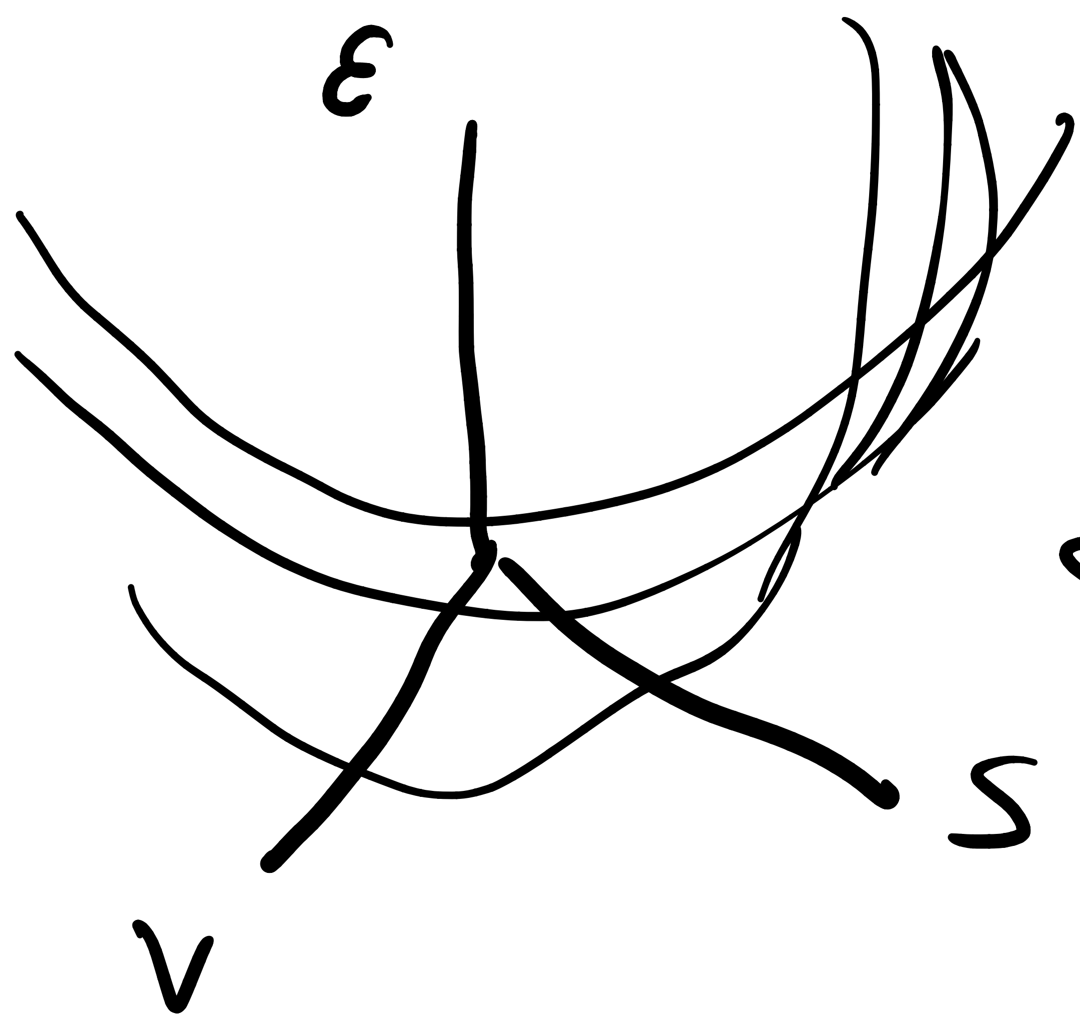
energy depends on S, V

$$d\mathcal{E} = T\,dS - p\,dV$$

1st law

For an (mono) ideal gas, formula for

$$\mathcal{E}(S,V) = \frac{3}{2} n R T_{ref} e^{(S-S_{ref})/c_V} \left(V_{ref}/V \right)^{2/3}$$



goes up fast w/ entropy

every point on this surface is an equilibrium state

Can't go below

Enthalpy

$$H = \mathcal{E} + pV$$

compare

$\mathcal{E}(S,V)$

$H(S,P)$ $+pV$

$$dH = d\mathcal{E} + p\,dV + V\,dp$$

$$d\mathcal{E} \leq T\,dS - P\,dV$$

$$\leq \underbrace{T\,dS}_{0?} + \underbrace{V\,dP}_{0?}$$

Enthalpy always goes down for const S & const P

$$H(S,P)$$

$H(S,P) - TS \equiv G$ (going to be a function of T, P)

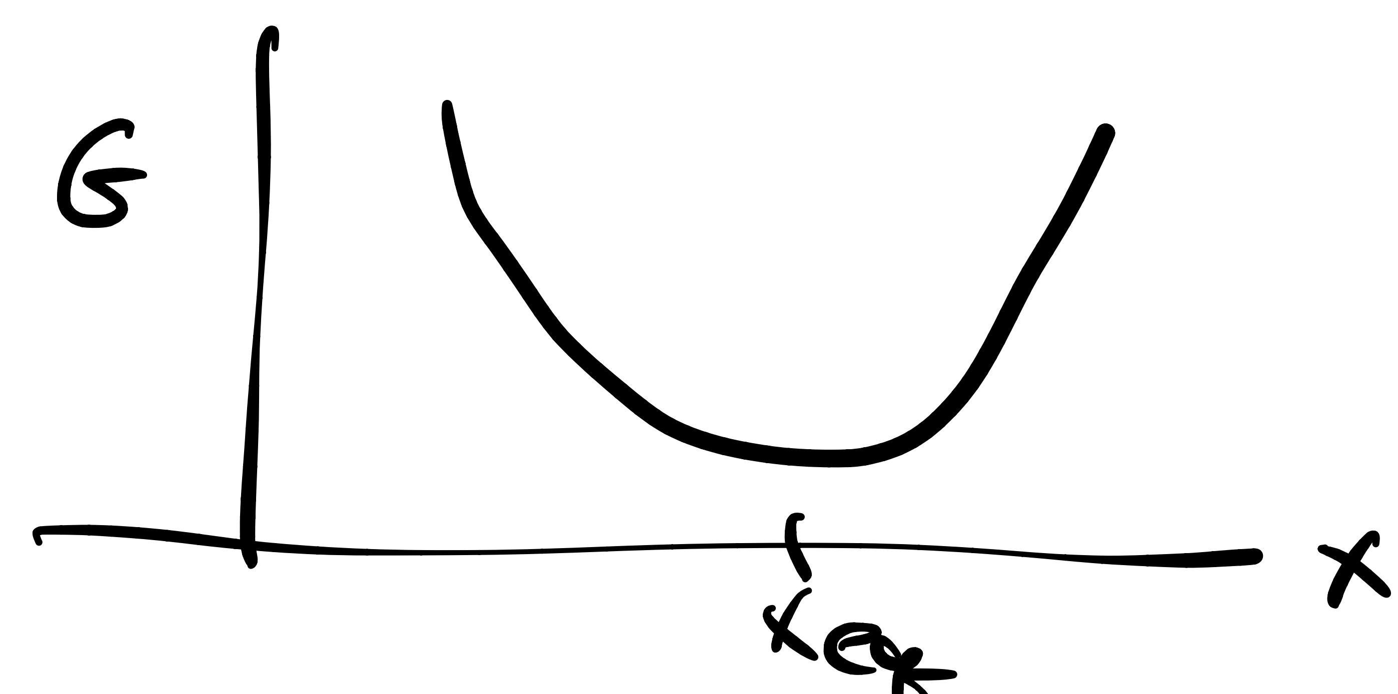
$G = H - TS$

$dG = dH - TdS - SdT$ ($dH \leq TdS + VdP$)

$\leq VdP - SdT$

zero when P, T are constant

$dG \leq 0$



For completeness

$$A = \mathcal{E} - TS \qquad \text{(Helmholz FE)}$$

$$dA = \underbrace{d\mathcal{E}} - TdS - SdT$$

$$\leq TdS - PdV$$

$$\leq -SdT - PdV$$

$A(T, V) \Leftarrow$ potential fixed volume temperature can equilibrate

$$\begin{tikzcd} E \arrow[r, "-TS"] \arrow[d, "+pV"'] & A \arrow[d, "+PV"] \\ H \arrow[r, "-TS"'] & G \end{tikzcd}$$

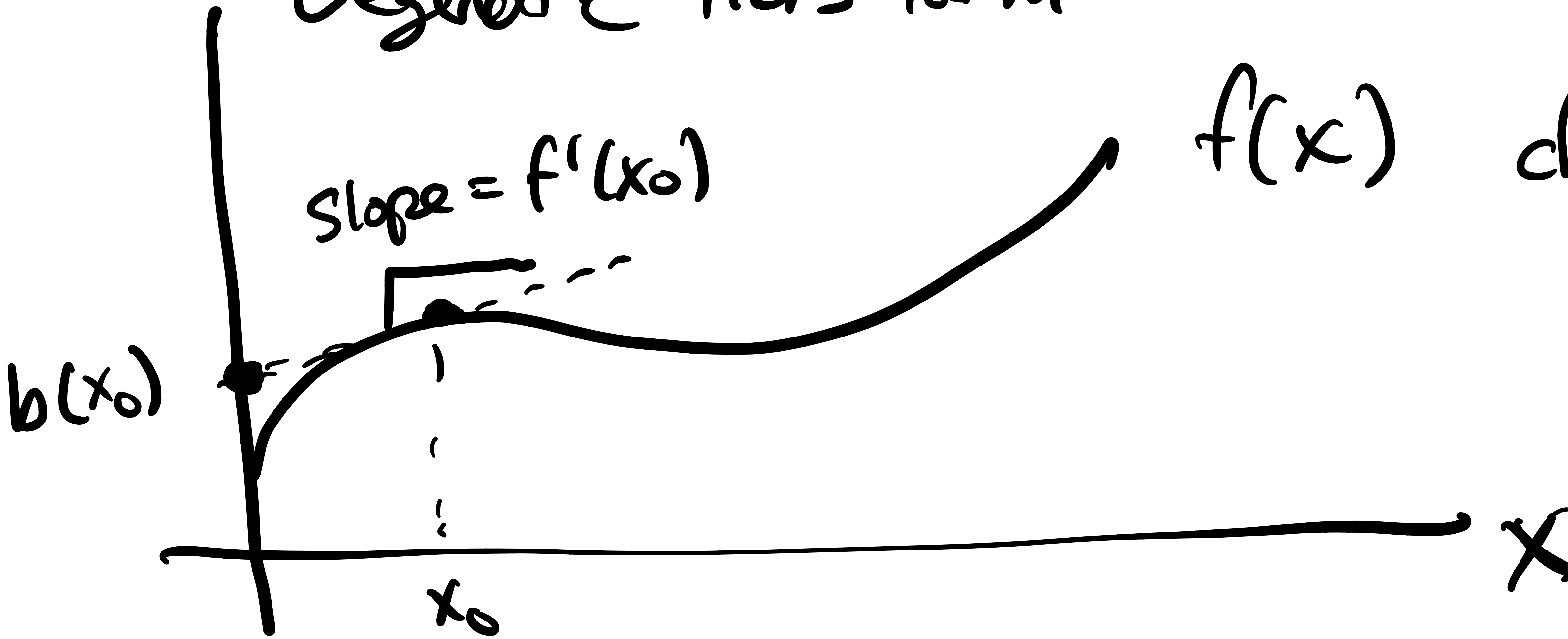
Can "exchange"

T&S

or P and $-V$

Legendre transformations

Legendre transform



differentiable function

tangent line: $y = f'(x_0)\,x + b(x_0)$

$$b(x_0) = y - f'(x_0)\,x$$

$f(x) \Longleftrightarrow \mathcal{E}(S, V)$ $\qquad A = \mathcal{E}(S, V) - S\overbrace{\left(\frac{\partial \mathcal{E}}{\partial S}\right)_V}^{T}$

$A(T, V)$

$G(p,T)$

$$\Rightarrow \; dG = \overbrace{\left(\frac{\partial G}{\partial P}\right)_T}^{?} dP + \overbrace{\left(\frac{\partial G}{\partial T}\right)_P}^{?} dT$$

$$G = \mathcal{E} - TS + PV$$

$$dG = d\mathcal{E} - TdS - SdT + PdV + VdP$$

$$= \underbrace{(d\mathcal{E} - TdS + PdV)}_{0} - SdT + VdP$$

$$= -SdT + VdP$$

comparing $\quad -S = \left(\frac{\partial G}{\partial T}\right)_P \qquad V = \left(\frac{\partial G}{\partial P}\right)_T$

2 things: $\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\partial y/\partial x\right)_z}$

$$T = \left(\frac{\partial E}{\partial S}\right)_V \iff \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V$$

<u>Maxwell Relations</u> ← equalities, come from

$$\frac{\partial}{\partial x}\left(\frac{\partial}{\partial y} G\right) = \frac{\partial}{\partial y}\left(\frac{\partial}{\partial x} G\right)$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_P \leftrightarrow V = \left(\frac{\partial G}{\partial P}\right)_T \Rightarrow -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$