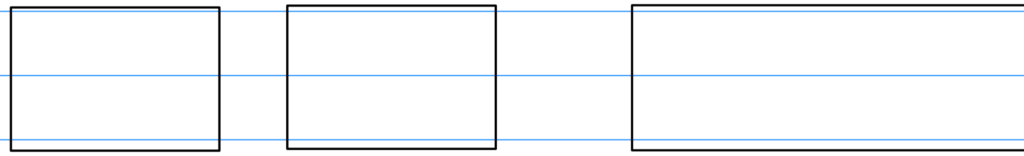
Thermodynamics

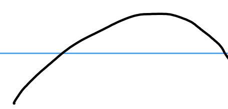


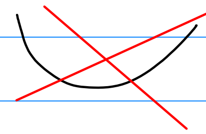
$N \; V \; E \qquad N \; V \; E \qquad 2N \; 2V \; 2E$

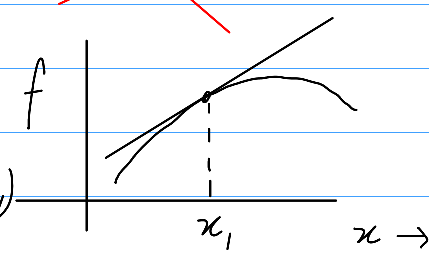
Extensive variables. Scale with system size

Entropy: There exists a quantity, called entropy which is
1) Extensive
2) Concave

$S(E, N, V)$
$\uparrow$







f concave:

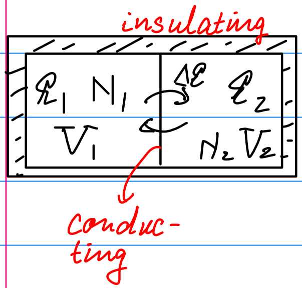
$$f(x_2) - f(x_1) \leq \frac{\partial f}{\partial x}(x_1)(x_2 - x_1)$$

3) $$\left.\frac{\partial S}{\partial E}\right)_{N,V} \geqslant 0 \quad ; \quad \left.\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}$$ temperature.

4) In a closed system, left on its own, the entropy can only increase

S maximum $\leftrightarrow$ equilibrium

Thermally conducting, fixed wall



$$\mathcal{E}_1 + \mathcal{E}_2 = \mathcal{E} = \text{fixed}.$$

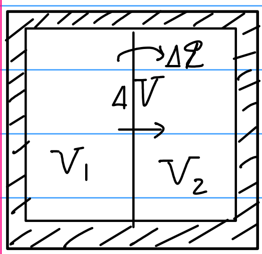
$$\frac{\partial}{\partial \mathcal{E}_1} = -\frac{\partial}{\partial \mathcal{E}_2}.$$

$$\frac{\partial S}{\partial \mathcal{E}_1} = 0 = \frac{\partial (S_1 + S_2)}{\partial \mathcal{E}_1} = \frac{\partial S_1}{\partial \mathcal{E}_1} + \frac{\partial S_2}{\partial \mathcal{E}_1} = \frac{\partial S_1}{\partial \mathcal{E}_1} - \frac{\partial S_2}{\partial \mathcal{E}_2} = 0$$

$$\left.\frac{\partial S_1}{\partial \mathcal{E}_1}\right)_{N_1, V_1} = \left.\frac{\partial S_2}{\partial \mathcal{E}_2}\right)_{N_2, V_2}$$

$$\frac{1}{T_1} = \frac{1}{T_2} \quad \rightarrow \quad T_1 = T_2$$

Thermally conducting, moving wall

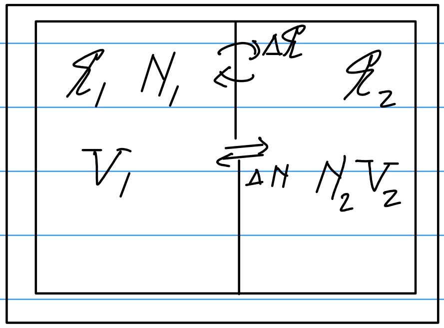


$$S \text{ max}, \quad V = V_1 + V_2 \rightarrow \frac{\partial}{\partial V_1} = -\frac{\partial}{\partial V_2}$$

$$\frac{\partial S_1}{\partial V_1} + \frac{\partial S_2}{\partial V_1} = 0 = \underbrace{\frac{\partial S_1}{\partial V_1}}_{P_1/\cancel{T_1}} - \underbrace{\frac{\partial S_2}{\partial V_2}}_{P_2/\cancel{T_2}}$$

$$\left.\frac{\partial S}{\partial \mathcal{E}}\right)_{N, V} = \frac{1}{T} \qquad \text{dim } \frac{1}{T} \times \underbrace{\frac{\mathcal{E}}{V}}_{\text{dim } P.} \qquad \left.\frac{\partial S}{\partial V}\right)_{N, \mathcal{E}} = \frac{P}{T}$$

Conducting, fixed, permeable wall



$$\frac{\partial S_1}{\partial N_1} = \frac{\partial S_2}{\partial N_2} = -\frac{\mu}{T}$$

$$T_1 = T_2$$

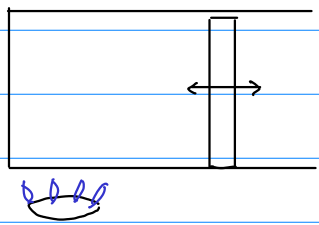
$E \quad V \quad N$ extensive

$T \quad P \quad \mu$ intensive. do not scale with system size.

$\frac{\partial S}{\partial E} \quad T\frac{\partial S}{\partial V} \quad T\frac{\partial S}{\partial N}$

1st law of thermodynamics:

$$\underset{\text{exact.}}{dE} = \underbrace{\overset{\text{heat}}{đQ} - \overset{\text{work.}}{đW}}_{\text{non exact}}$$



$$đW = PdV$$

$$dV = A\,dx$$

$$F = PA$$

$đQ$ heat flow into the system

$đW$ Work done by the system

Generally: $đW = PdV - \mu\, dN$.

$\neq$

Processes

* Quasi-static: slowly moving piston, slow escape of particles. Always (close to) equilibrium

* Reversible: $dQ = TdS$

* Spontaneous: $dQ < TdS$

* Adiabatic: $đQ = 0$

Quasi-static process with $đW = 0$

$$dS = S(E + dE) - S(E) = dQ \left.\frac{\partial S}{\partial E}\right)_{N,V} = \frac{dQ}{T}$$

$\rightarrow dQ = TdS$ reversible. In general $TdS \geq dQ$

2nd law

Reversible process with $dE = 0$

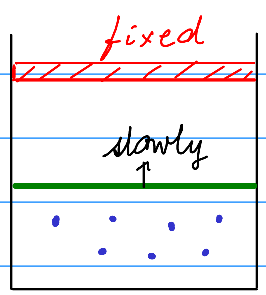
$$dE = dQ - dW = 0 = TdS - PdV = 0$$

$$\left.\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T}$$

In general, reversible process

$$dE = TdS - PdV + \mu dN \quad \text{(1st law).}$$

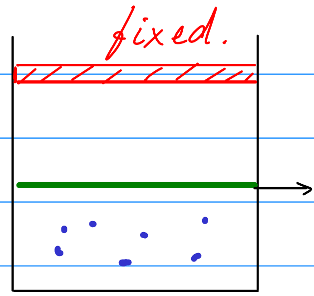
quasi-static.



T decreases due to work done by piston.

$dQ = 0.$

sudden process



T remains constant.

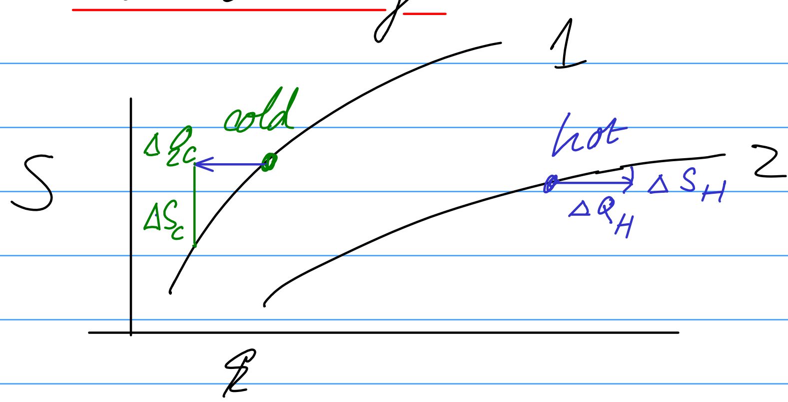
Work done $= 0$

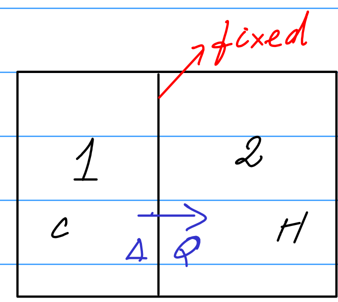
$\Delta S \geqslant 0$

$\Delta Q = 0$

$\Delta S \geqslant \dfrac{\Delta Q}{T}.$

Heat exchange





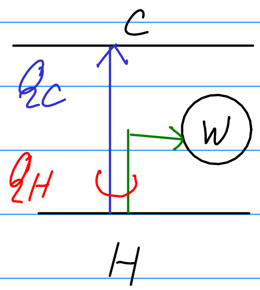
$\Delta S = \Delta S_c + \Delta S_H < 0$ Not allowed.

Heat flows from hot to cold

2nd law.

Reversible process: Carnot engine

$\Delta S = 0$ $\qquad$ $Q_H = Q_C + W.$ $\qquad$ $\eta = \dfrac{W}{Q_H}$ efficiency.



$$\Delta Q_H = -T_H \Delta S_H \qquad \Delta Q_C = T_C \Delta S_C.$$

$$\Delta S = \Delta S_H + \Delta S_C = 0 = \frac{-Q_H}{T_H} + \frac{Q_C}{T_C} = 0$$

$$\rightarrow \frac{Q_H}{T_H} = \frac{Q_C}{T_C}$$

$$\eta_C = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{T_C}{T_C}$$ carnot efficiency.

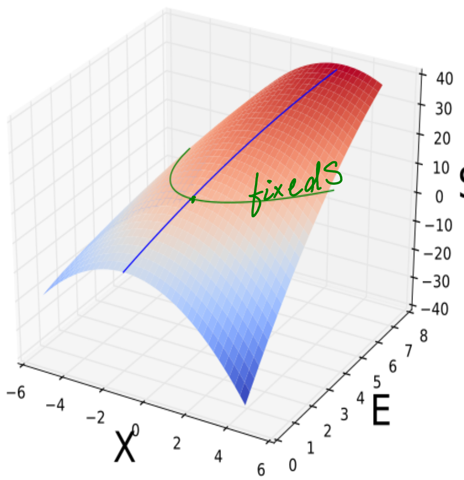
$$\eta_C = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$ Carnot efficiency.

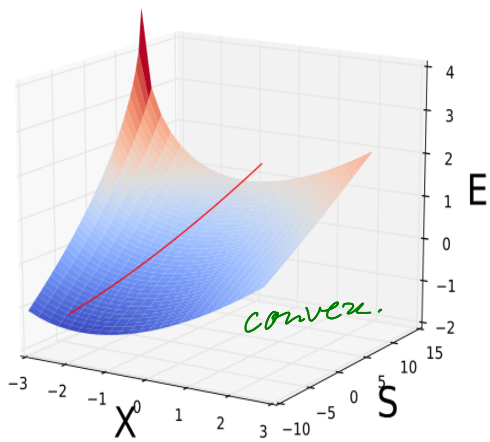
For $\Delta S > 0$ $\quad \Delta S = -\dfrac{Q_H}{T_H} + \dfrac{Q_C}{T_C} > 0 \rightarrow \dfrac{Q_C}{T_C} > \dfrac{Q_H}{T_H} \rightarrow \dfrac{Q_C}{Q_H} > \dfrac{T_C}{T_H}$

$$\eta = 1 - \frac{Q_C}{Q_H} < 1 - \frac{T_C}{T_H} = \eta_C$$

From entropy to energy

$S(\mathcal{E}, \overset{X}{\cancel{V, N}})$ $\qquad\qquad$ $\mathcal{E}(S, \overset{X}{\cancel{V, N}})$.





$$\frac{\partial S}{\partial \mathcal{E}} = \frac{1}{T} > 0$$

$\mathcal{E}(S, X)$ has a minimum as a function of X
equilibrium.

$\mathcal{E}(S, X_j)$ is convex

$\neq$

Legendre transformation

$f(x,\xi)$. f is a convex function of x and ξ

$$y = \frac{\partial f(x,\xi)}{\partial x} \quad \text{is a `useful' variable / quantity.}$$

eg. $f \to S \qquad x \to E \qquad \frac{\partial S}{\partial E} = \frac{1}{T}$

Search for a function $g(y,\xi)$ such that

$$x = -\frac{\partial g(y,\xi)}{\partial y}$$

Solution: $\quad y = \frac{\partial f(x,\xi)}{\partial x} \longrightarrow x(y,\xi)$

$$g(y,\xi) = f(x(y,\xi),\xi) - x(y,\xi)\,y.$$

$$\frac{\partial g}{\partial y} = \cancel{\underbrace{\frac{\partial f}{\partial x}}_{y} \frac{\partial x}{\partial y}} - \cancel{\frac{\partial x}{\partial y} y} - x = -x$$

$$\frac{\partial g}{\partial \xi} = \frac{\partial f}{\partial \xi} + \cancel{\underbrace{\frac{\partial f}{\partial x}}_{y} \cdot \frac{\partial x}{\partial \xi}} - \cancel{\frac{\partial x}{\partial \xi} \cdot y}. = \frac{\partial f}{\partial \xi}$$

What about convex / concave?

Suppose f is convex as a function of x and ξ.

Then g is convex as a function of ξ

concave " " " " y.

Legendre transformation of the energy

$$S(\mathcal{E},V,N) \xrightarrow{\text{invert}} \underbrace{\mathcal{E}(S,V,N)}_{\text{convex.}}$$

$$f(x,\xi)\,,\quad y=\frac{\partial f}{\partial x} \;\to\; g(y,\xi)= f(x,\xi)-x\,y.$$

$$\mathcal{E}(S,V,N)\,,\quad T=\frac{\partial \mathcal{E}}{\partial S}\Big)_{N,V} \;\to\; F(T,N,V)=\mathcal{E}-TS$$

↳ Helmholtz free energy.

$$d\mathcal{E} = TdS - PdV + \mu dN \to$$

$$\frac{\partial \mathcal{E}}{\partial V}\Big)_{S,N} = -P\,;\quad \frac{\partial \mathcal{E}}{\partial N}\Big)_{S,V} = \mu\,;\quad \frac{\partial \mathcal{E}}{\partial S}\Big)_{N,V} = T$$

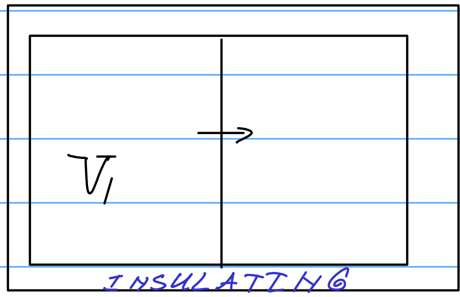
$$dF = d\mathcal{E} - d(TS) = \cancel{TdS} - PdV + \mu dN - \cancel{TdS} - SdT$$

$$-PdV + \mu dN - SdT$$

$$\frac{\partial F}{\partial T}\Big)_{N,V} = -S\,;\quad \frac{\partial F}{\partial V}\Big)_{N,T} = -P\,;\quad \frac{\partial F}{\partial N}\Big)_{T,V} = \mu.$$

Legendre transformation, the physics.

movable wall



$\mathcal{E}$ fixed.

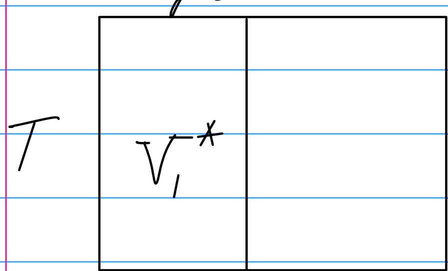
System relaxes → $\mathcal{E}$

$V_1 \to V_1^*$ (V_1^*: equilibrium)

$$\frac{\partial \mathcal{E}(S, V_1^*, N)}{\partial V_1} = 0.$$

At this equilibrium: $T = \left.\frac{\partial \mathcal{E}}{\partial S}\right)_{V_1^*}$ Equil.: $\mathcal{E}, T, V_1^*, S$

Now make the insulating wall conducting, and place the system in an environment at temp. T.



Nothing will change.
So, for a system at temperature T, V_1^* is the equil. volume.

Legendre transf.: $\left.\frac{\partial F}{\partial V_1}\right|_T (T, V_1^*) = 0$

$$F(T, V_1, V) = \mathcal{E}(S(\mathcal{E}, V_1), V_1) - T\, S(\mathcal{E}, V_1)$$

$$\left.\frac{\partial F}{\partial V_1}\right)_T = \left.\frac{\partial \mathcal{E}}{\partial V_1}\right)_S + \underbrace{\left.\frac{\partial \mathcal{E}}{\partial S}\right)_{V_1}}_{\shortparallel \; T} \cancel{\left.\frac{\partial S}{\partial V_1}\right)_{\mathcal{E}}} - \cancel{T \left.\frac{\partial S}{\partial V_1}\right)_{\mathcal{E}}} = \left.\frac{\partial \mathcal{E}}{\partial V_1}\right)_S = 0. \text{ at equil.}$$

So far: $\mathcal{E}(S,V,N)$, $d\mathcal{E} = TdS - PdV + \mu dN$

$$F(\overset{i}{T}, \overset{e}{V}, \overset{e}{N}) = \mathcal{E} - TS \quad \text{Helmholtz}$$

$$dF = d\mathcal{E} - d(TS) = \cancel{TdS} - PdV + \mu dN - \cancel{TdS} - SdT = -PdV - SdT + \mu dN$$

$$\left.\frac{\partial F}{\partial V}\right)_{N,T} = \underset{i}{-P} \; ; \quad \left.\frac{\partial F}{\partial T}\right)_{N,V} = \underset{e}{-S} \; ; \quad \left.\frac{\partial F}{\partial N}\right)_{T,V} = \underset{i}{\mu}.$$

Leg. transf. of F with respect to V

Gibbs
$$G = F - V \left.\frac{\partial F}{\partial V}\right)_{T,N} = F + PV = \mathcal{E} - TS + PV = G(T,P,N)$$

$$dG = -SdT + VdP + \mu dN \rightarrow \left.\frac{\partial G}{\partial T}\right)_{P,N} = -S \text{ etc.}$$

Leg. transf of F w.r.t N

Grand pot.
$$\Omega = F - \left.\frac{\partial F}{\partial N}\right)_{S,V} N = F - \mu N = \mathcal{E} - TS - \mu N = \Omega(T,V,\mu)$$

$$\rightarrow \quad d\Omega = -SdT - PdV - Nd\mu \rightarrow -S = \left.\frac{\partial \Omega}{\partial T}\right)_{V,\mu} \text{ etc.}$$

Legendre transf of energy w.r.t V $\quad \mathcal{E}(S,V,N)$

Enthalpy
$$H = \mathcal{E} - \underbrace{\left.\frac{\partial \mathcal{E}}{\partial V}\right)_{S,N}}_{-P} V = \mathcal{E} + PV = H(S,P,N)$$

$$dH = TdS + VdP + \mu dN$$

Summary

Extensive: scale with system: $\mathcal{E}, N, V \ldots$

Intensive: do not scale with system P, T, μ

First law $\qquad d\mathcal{E} = đQ - đW$

For a closed system: $S(\mathcal{E}, X_j)$ $\quad$ entropy

$\qquad\qquad\qquad\qquad\qquad\quad \uparrow$ extensive

S is extensive

S is convexe

$$\left.\frac{\partial S}{\partial \mathcal{E}}\right)_{X_j} = \frac{1}{T} \geq 0$$

S increases until maximum.

Second law $\qquad T\Delta S \geq \Delta Q$

Processes
- For $T\Delta S = \Delta Q$: reversible
- For $T\Delta S > \Delta Q$: spontaneous
- For $\Delta Q = 0$ $\qquad$ adiabatic
- System always close to equilibrium: quasi-static.

Reversible implies quasi static.

2nd Law: heat flows from hot to cold.

Carnot engine reaches its maximum efficiency when it is reversible: $\eta_c = 1 - \frac{T_c}{T_H}$

Legendre transformation

$f(x,\xi)$ convex, $y = \dfrac{\partial f}{\partial x}$

$$g(y,\xi) = f(x,\xi) - xy \Rightarrow x = -\frac{\partial g}{\partial y}$$

Examples $\mathcal{E} = \mathcal{E}(S,V,N)$ Leg. transf. w.r.t S:

$$T = \left.\frac{\partial \mathcal{E}}{\partial S}\right)_{N,V} \rightarrow F(T,V,N) = \mathcal{E} - TS$$

Helmholtz

$$dF = -SdT - PdV + \mu dN$$

Leg. transform of F w.r.t. V:

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

Gibbs

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

Leg. transf of F wrt N:

$$\Omega = F - \mu N = \mathcal{E} - TS - \mu N$$

Grand potential

$$d\Omega = -SdT - VdP - Nd\mu.$$

Leg. transf of $\mathcal{E}$ w.r.t. V

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

Enthalpy

$$dH = SdT + VdP + \mu dN$$