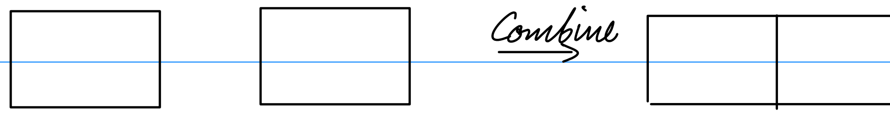
Thermodynamics

Extrinsic variables — Scale with system size

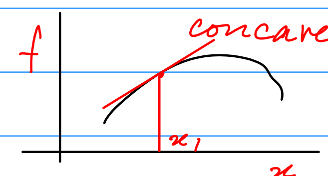


N, V, E $\quad$ N, V, E $\quad\quad$ $2N, 2V, 2E$

S $\quad$ S $\quad\quad$ $2S$

Entropy: There exists a quantity S, called the entropy

Properties 1) extrinsic
2) concave.



Concave: $S(X^2) - S(X^1) \leq \left.\frac{\partial S}{\partial X}\right)_{X^1} (X^2 - X^1)$

$X = N, V, E.$

$X^1 = (N^1, V^1, E^1) = X_j^1 \quad j = 1, 2, 3$ (N, V, E)

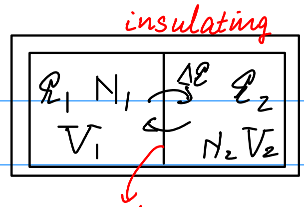
$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right)_{X_j \neq E} \geq 0$$

temperature

$\Rightarrow$ S always strives towards a maximum (isolated system).

This maximum is reached at equilibrium

Thermally conducting, fixed wall



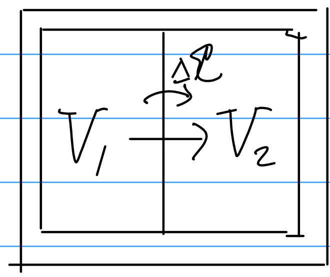
$$\mathcal{E}_1 + \mathcal{E}_2 = \text{const.} = \mathcal{E}$$

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

because we search for maximum of S!

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

Thermally conducting, moving wall



2 parameters $\mathcal{E}_1$ and V_1

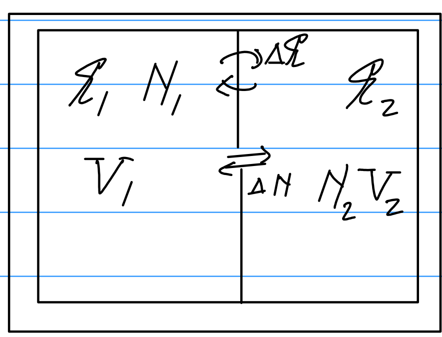
$$V_1 + V_2 = V = \text{fixed};$$

$$\frac{\partial S_1}{\partial \mathcal{E}_1} = \frac{\partial S_2}{\partial \mathcal{E}_2} \rightarrow \frac{1}{T_1} = \frac{1}{T_2} = \frac{1}{T}$$

$$\frac{\partial S_1}{\partial V_1} = \frac{\partial S_2}{\partial V_2} = \frac{P_1}{T_{\cancel{1}}} = \frac{P_2}{T_{\cancel{2}}}$$

P: pressure

Conducting, fixed, permeable wall



2 parameters: $\mathcal{E}_1$ and N_1

$$N_1 + N_2 = N = \text{fixed}$$

N_1

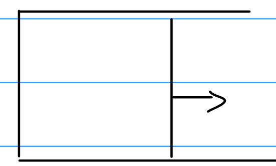
$$\frac{\partial S_1}{\partial N_1} = \frac{\partial S_2}{\partial N_2} = -\frac{\mu_2}{T_{\cancel{2}}} = -\frac{\mu_1}{T_{\cancel{1}}}$$

$\mu_1 = \mu_2$ chemical potential.

1st law of thermodynamics:

$$\underset{\text{exact}}{d\mathcal{E}} = \underbrace{\overset{\text{heat}}{\bar{d}Q} - \overset{\text{work}}{\bar{d}W}}_{\text{non-exact.}}$$

$$\bar{d}W = P\,dV$$



$\bar{d}Q$: heat flow into system

$\bar{d}W$: work done by the system

If we change N: $\bar{d}W = P\,dV - \mu\,dN$

Processes
* quasi-static : always in equil.
* reversible : $\Delta S = 0$
* adiabatic : $\bar{d}Q = 0$

Example quasi static process with $\bar{d}W = 0$

$$dS = S(\mathcal{E} + dQ) - S(\mathcal{E}) = dQ \cdot \frac{\partial S}{\partial \mathcal{E}} = dQ\,\frac{1}{T}$$

$\rightarrow dQ = T\,dS$. In general $dQ \leq T\,dS$ 2nd law

Example quasi-static, $\mathcal{E} = \text{const} \Rightarrow d\mathcal{E} = 0$
$N = \text{const.}$

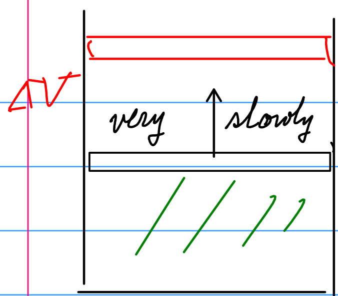
$$d\mathcal{E} = \bar{d}Q - \bar{d}W = 0$$

$$T\,dS - P\,dV = 0 \qquad P\text{: mechanical pressure}$$

$$\rightarrow \frac{\partial S}{\partial V} = \frac{P}{T}$$

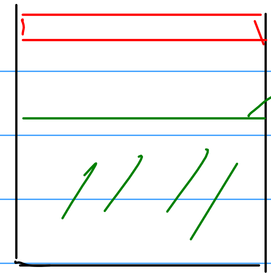
So the mechanical pressure is the one we have met before: movable, conducting wall.

quasi-static



If insulating, $dQ = 0$
T decreases due to work done by piston.

Sudden



wall, suddenly pulled away.

For ideal gas T remains constant.

adiabatic $\Delta Q = 0$

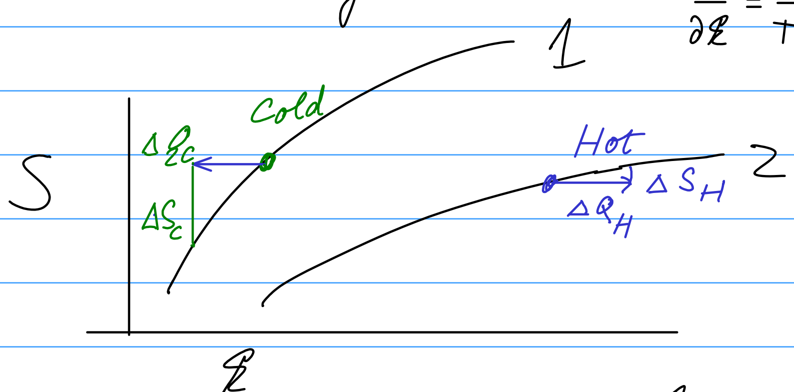
No work $\Delta W = 0$

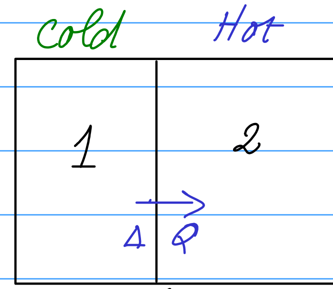
$\Delta S \geqslant 0$

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

Heat exchange

$\dfrac{\partial S}{\partial Q} = \dfrac{1}{T}$



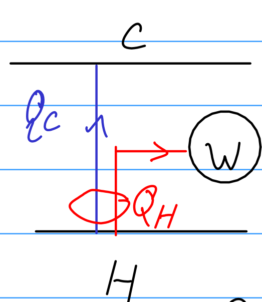


Heat flow from cold to hot?

$\Delta S = \Delta S_c + \Delta S_H < 0$ Impossible, should be $\geqslant 0$!

So: heat flow only from hot to cold.

$\Delta S = 0$ Reversible Carnot engine.



$$Q_H = \underline{Q_C} + \underline{W}$$

$$\Delta S_H = - Q_H / T_H \leq 0$$

$$\Delta S_c = Q_c / T_c \geqslant 0$$

$$\Delta S = \Delta S_H + \Delta S_c = 0 \rightarrow \frac{Q_H}{T_H} = \frac{Q_c}{T_c}$$

Efficiency: $\eta = \dfrac{W}{Q_H} = 1 - \dfrac{Q_c}{Q_H} = 1 - \dfrac{T_c}{T_H}$ Carnot eff. $= \eta_c$

Now, relax the condition $\Delta S = 0$ allow $\Delta S > 0$.

$$W = -\Delta \mathcal{E}^H - \Delta \mathcal{E}^C \qquad \Delta \mathcal{E} = \mathcal{E}^f - \mathcal{E}^i.$$

$$= -T^H \Delta S^H - T^C \Delta S^C$$

$$Q_H = -\Delta \mathcal{E}^H = -T^H \Delta S^H$$

$$\eta = \frac{W}{Q_H} = 1 + \frac{T_C \Delta S^C}{T^H \Delta S^H} \leq 1 - \frac{T_C}{T_H} = \eta_C$$

$$\Delta S^C + \Delta S^H \geqslant 0 \Rightarrow + \frac{\Delta S^C}{\Delta S^H} \leq -1$$

So $\eta \leq \eta_C$

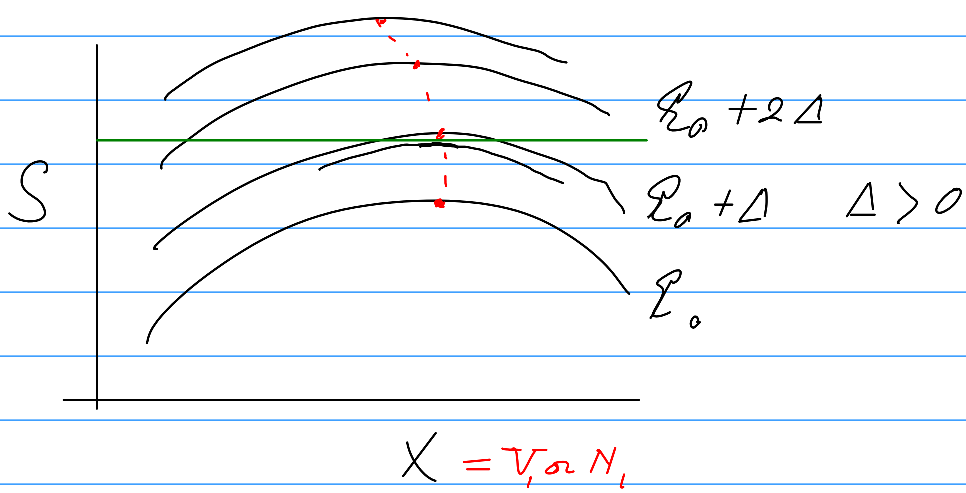
Carnot engine with $\Delta S = 0$ is the best we can do.

$\neq$

Legendre transformation.

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

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



$S \rightarrow \max$ $\qquad$ $\mathcal{E} \rightarrow \min.$

Mathematical Intermezzo Legendre transf.

$$f(x,\xi) \rightarrow \xi^*: \frac{\partial f}{\partial \xi}(x,\xi^*) = 0 \quad \text{min.}$$

$$y = \frac{\partial f(x,\xi)}{\partial x} \longrightarrow x = x(y,\xi).$$ possible provided f is convex

Legendre transf: $g(y,\xi) = f(x,\xi) - xy.$

$$\left.\frac{\partial g}{\partial \xi}\right|_y = \frac{\partial f}{\partial \xi} + \underbrace{\frac{\partial f}{\partial x}}_{y}\frac{\partial x}{\partial \xi} - \frac{\partial x}{\partial \xi}\cdot y = \frac{\partial f}{\partial \xi}$$ IF: $=0$ Max!

$$\left(L = \frac{m}{2}\dot{x}^2 - V(x) \qquad p = \frac{\partial L}{\partial \dot{x}} = m\dot{x} \qquad \dot{x} = p/m \right)$$

$E(S,V,N)$ strives towards minimum.

$$\left.\frac{\partial E}{\partial S}\right|_{V,N} = T \;(=y)$$

$F = E - TS =$ Helmholz free energy.

F strives towards minimum.

$F(T,V,N)$

Keep T const $\Delta F = \Delta E - T\Delta S$

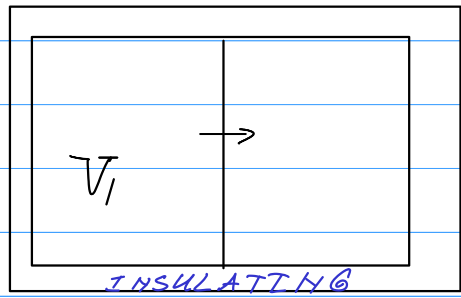
use $T\Delta S \geq \Delta Q$

$$= \Delta Q - \Delta W - T\Delta S \leq -\Delta W$$ work done by system

or: $\Delta W \leq -\Delta F$, hence $-\Delta F$ is the max. amount done by the system.

Legendre transformation revisited.

movable wall



$\mathcal{E}$ fixed.

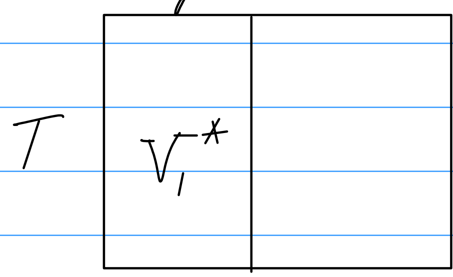
System relaxes →

$V_1 \to V_1^*$
↳ equilibrium value

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

also at equil: $\frac{\partial \mathcal{E}(S, V_1^*, N)}{\partial V_1} = 0$ $\frac{1}{T} = \frac{\partial S}{\partial \mathcal{E}}\Big)_{N,V}$

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.

So we should have $\frac{\partial F}{\partial V_1}\Big|_T (T, V_1^*) = 0$

That works for $F = \mathcal{E} - TS$ (Note $T = \frac{\partial \mathcal{E}}{\partial S}\Big)_V$)
because that is a Legendre transf.

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

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

So far: $\mathcal{E}(S, V, N)$ P. 2.9, 2.11, 2.14

$$F(T, V, N) = \mathcal{E} - TS$$

Helmholz

$$dF = d\mathcal{E} - TdS - SdT = \underbrace{TdS - PdV + \mu dN}_{\text{1st law}} - TdS - SdT$$

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

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

eq of state

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.

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

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

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

Enthalpy

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

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

Maxwell relations (P2.10)

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

$$\frac{\partial^2 F}{\partial V \partial T} = -\left.\frac{\partial P}{\partial T}\right)_{V,N} = -\left.\frac{\partial S}{\partial V}\right)_{T,N}$$

and many other relations.

$\neq$

Euler relation (P2.15).

* S is a function of the extensive variables:

$$S = S(E, V, N)$$

* S itself is an extensive variable.

So: $\quad S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N)$

Take the derivative w.r.t. λ on left & right hand side and set $\lambda = 1$

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

$$\rightarrow \quad E \cdot \frac{1}{T} + V \frac{P}{T} - N \frac{\mu}{T} = S, \quad \text{or}$$

$$\underline{E = TS - PV + \mu N} \quad \text{(Euler eqn).}$$

Consequence:

$$dE = \underline{TdS} + SdT - \underline{PdV} - VdP + \underline{\mu dN} + N d\mu$$

Using $dE = TdS - PdV + \mu dN$, we obtain

$$SdT - VdP + Nd\mu = 0 \quad \text{(Gibbs-Duhem)}$$

Gibbs free energy:

$$\mathcal{G} = \mathcal{E} - TS + PV = \underbrace{TS - PV + \mu N}_{\mathcal{E}} - TS + PV$$
$$= \mu N$$

Generalizations, magnetic systems. (P2.16)

$S = S(\mathcal{E}, X_1, \ldots, X_r)$ $\quad X_i$: extensive variables.

and $\mathcal{E} = \mathcal{E}(S, X_1, \ldots, X_r)$. $\quad \left.\frac{\partial S}{\partial \mathcal{E}}\right)_{X_j} = \frac{1}{T} > 0$

Generalized forces: $f_i = \left.\frac{\partial \mathcal{E}}{\partial X_i}\right)_{X_{j\neq i}}$

intrinsic

$$-d\mathcal{E} = đW = -\sum_i f_i \, dX_i$$

Example $X_i = V$, then $f_i = \frac{\partial \mathcal{E}}{\partial V} = -P$

So $đW \overset{-}{=} P dV$.

And $\mu = \left.\frac{\partial \mathcal{E}}{\partial N}\right)_{S,V}$ so this gives $đW \overset{-}{=} -\mu \, dN$.

For a magnet, the external field H is the generalised force

The magnetisation M is the extrinsic variable

$$\left.\frac{\partial \mathcal{E}}{\partial M}\right|_{S,N} = +\mu_0 H, \quad \text{so } đW = -\mu_0 H \, dM$$

So $d\mathcal{E} = TdS + \mu_0 H \, dM + \mu \, dN$

Legendre transf. with respect to M

$$E(S, H, N) = \mathcal{E} - \mu_0 HM$$

'enthalpy'

Leg. transf w.r.t. S:

$$\mathcal{G}(T, H, N) = \mathcal{E} - TS - \mu_0 HM$$

and $d\mathcal{G} = -S\,dT - \mu_0 M\,dH + \mu\,dN.$

$\#$

Specific heats.

Q: How much heat do I have to put into a system to change its temperature by an amount dT?

Quasistatic: $dQ = T\,dS = c_V\,dT$ $\quad V$ const
$\quad\quad = c_p\,dT$ $\quad P$ const.

Keep V const, N const: $d\mathcal{E} = dQ$ $\quad$ ($dW = 0$ since V const).

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

c_p? $\quad V = V(T,P,N)$ (eqn of state, derived from $P = -\left.\frac{\partial F}{\partial V}\right)_{T,N}$)

Suppose we have $S(T,V,N)$. $\quad$ (N const)

Then $c_p = T\left.\frac{\partial S}{\partial T}\right)_P = T\left.\frac{\partial S}{\partial T}\right)_V + T\left.\frac{\partial S}{\partial V}\right)_T \left.\frac{\partial V}{\partial T}\right)_P$

$$= \underbrace{T\left.\frac{\partial S}{\partial T}\right)_V}_{c_V} + T\underbrace{\left.\frac{\partial P}{\partial T}\right)_V}_{\text{Maxwell relation.}}\left.\frac{\partial V}{\partial T}\right)_P$$

Math intermezzo

$f(x,y) \rightarrow df = \left.\frac{\partial f}{\partial x}\right)_y dx + \left.\frac{\partial f}{\partial y}\right)_x dy$

$\rightarrow \left.\frac{\partial x}{\partial y}\right)_f = -\left.\frac{\partial f}{\partial y}\right)_x \Big/ \left.\frac{\partial f}{\partial x}\right)_y = -\left.\frac{\partial f}{\partial y}\right)_x \left.\frac{\partial x}{\partial f}\right)_y$

Hence: $\left.\frac{\partial \overset{x}{V}}{\partial \underset{y}{T}}\right)_{\underset{f}{P}} = -\left.\frac{\partial P}{\partial T}\right)_V \left.\frac{\partial V}{\partial P}\right)_T$

$\rightarrow c_p = T\left.\frac{\partial S}{\partial T}\right)_P = c_V - T\left[\left.\frac{\partial P}{\partial T}\right)_V\right]^2 \left.\frac{\partial V}{\partial P}\right)_T = c_V + TV\,\alpha^2/\kappa$

where $\kappa = \frac{-1}{V}\left.\frac{\partial V}{\partial P}\right)_T$; $\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right)_P$; $\rightarrow \alpha = \kappa\left.\frac{\partial P}{\partial T}\right)_V.$

compressibility

Ideal gases: $\frac{c_p}{c_v} = \gamma$

Chemical equilibrium (P 2.19)

$$\nu_1 A_1 + \nu_2 A_2 + \dots + \nu_r A_r \rightleftarrows \nu_{r+1} A_{r+1} + \dots + \nu_K A_K$$

Example: $2H_2 + O_2 \rightleftarrows 2H_2O$

$\nu_{r+1} \dots \nu_K$ negative

For a reaction: $\frac{\delta N_1}{\nu_1} = \frac{\delta N_2}{\nu_2} = \dots = \frac{\delta N_K}{\nu_K}$

Fix P and T: Gibbs free energy.

$$G = \sum_{i=1}^{K} \mu_i N_i$$

$$dG = 0 = \sum_i \mu_i \, dN_i \propto \sum_i \mu_i \nu_i$$

$$\rightarrow \sum_i \mu_i \nu_i = 0$$

$\neq$

Phase coexistence

Gas and liquid. $\underset{\nu_g = -\nu_l}{\mu_g = \mu_l} \equiv \mu$

$N_g + N_l = N = \text{const.}$

$\rightarrow \Delta N_g = -\Delta N_l$

and $\Delta G = \Delta N_g \mu + \Delta N_l \mu = 0$

So the Gibbs free energy is independent of N_g (N_l).

The two phases l and g occupy different volumes

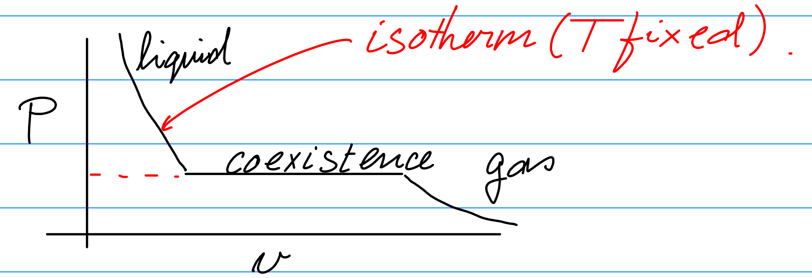
v_l : volume per liquid particle

v_g : " " gas "

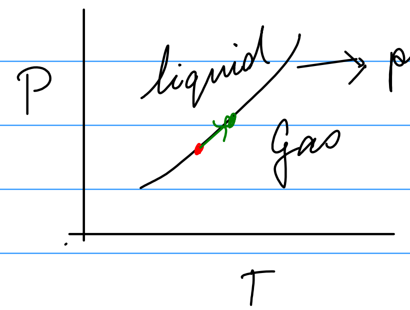
Total volume $V = N_l v_l + N_g v_g$.

$v = V/N$

P-v curve:



Clausius-Clapeyron equation (P 2.21).



The phase transition is defined by

$$\mu_{liq}(P,T) = \mu_{gas}(P,T)$$

Consider

$$\mu_{liq}(P+\Delta P, T+\Delta T) = \mu_{gas}(P+\Delta P, T+\Delta T)$$

obviously $\Delta\mu_{liq} = \Delta\mu_{gas}$ → similar.

$\mu_{liq}(P+\Delta P, T+\Delta T) - \mu_{liq}(P,T)$

So we have

$$\left.\frac{\partial \mu_{liq}}{\partial P}\right|_T \Delta P + \left.\frac{\partial \mu_{liq}}{\partial T}\right)_P \Delta T = \left.\frac{\partial \mu_{gas}}{\partial P}\right)_T \Delta P + \left.\frac{\partial \mu_{gas}}{\partial T}\right)_P \Delta T$$

Divide by ΔT:

$$\left.\frac{\partial \mu_{liq}}{\partial P}\right)_T \frac{\partial P_l}{\partial T} + \left.\frac{\partial \mu_{liq}}{\partial T}\right)_P = \left.\frac{\partial \mu_{liq}}{\partial P}\right)_T \frac{\partial P_g}{\partial T} + \left.\frac{\partial \mu_{gas}}{\partial T}\right)_P$$

Now realise that $G = \mu N$ and

$$dG = -S\,dT + V\,dP + \mu\,dN$$

So $\left.\dfrac{\partial \mu_{liq}}{\partial P}\right)_T = v_{liq}$ and $\left.\dfrac{\partial \mu_{liq}}{\partial T}\right)_P = -s_{liq}$

$\downarrow$ entropy per particle.

similar for μ_{gas}

$$\Rightarrow \quad (v_{liq} - v_{gas})\frac{dP}{dT} = -s_{gas} + s_{liq}$$

So $\dfrac{dP}{dT} = \dfrac{s_{gas} - s_{liq}}{v_{gas} - v_{liq}} \geqslant 0$ except eg for water between 0 and 4°C.

$\Delta Q/T$

$\hookrightarrow$ Latent heat.

Clausius Clapeyron.