Multiphase Equilibrium:

Since E is extensive:

total energy: $$E = \sum_{\alpha=1}^{\nu} E^{(\alpha)}$$

where α labels the phase and ν is the total number of phase

Similarly: $$S = \sum_{\alpha=1}^{\nu} S^{(\alpha)}$$

$$V = \sum_{\alpha=1}^{\nu} V^{(\alpha)}$$

$$n_i = \sum_{\alpha=1}^{\nu} n_i^{(\alpha)}$$

then δE as the first variational displacement of E:

$$\delta E = \sum_{\alpha=1}^{\nu} \left[T^{(\alpha)} \delta S^{(\alpha)} - p^{(\alpha)} \delta V^{(\alpha)} + \sum_{i=1}^{r} \mu_i^{(\alpha)} dn_i^{(\alpha)} \right]$$

where condition for equilibrium is:

$$(\delta E)_{S,V,n_i} \geq 0$$

with S, V, and n_i fixed:

$$\sum_{\alpha=1}^{\nu} \delta S^{(\alpha)} = 0 \qquad \sum_{\alpha=1}^{\nu} \delta V^{(\alpha)} = 0 \qquad \sum_{\alpha=1}^{\nu} \delta n_i^{(\alpha)} = 0$$

Example:

$S^{(1)}, V^{(1)}, n_i^{(1)}$
$S^{(2)}, V^{(2)}, n_i^{(2)}$

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

Then:

$$0 \leq (\delta E)_{S,V,n_i} = \left(T^{(1)} - T^{(2)}\right)\delta S^{(1)} - \left(p^{(1)} - p^{(2)}\right)\delta V^{(1)} + \sum_{i=1}^{r}\left(\mu_i^{(1)} - \mu_i^{(2)}\right)\delta n_i^{(1)}$$

$\therefore$

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

In general:

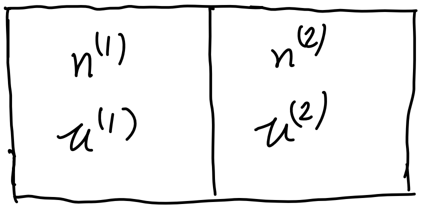
If all phases in:

Thermal Equilibrium: $T^{(1)} = T^{(2)} = T^{(3)} = \cdots$

Mechanical Equilibrium: $p^{(1)} = p^{(2)} = p^{(3)} = \cdots$

Mass Equilibrium: $\mu_i^{(1)} = \mu_i^{(2)} = \mu_i^{(3)} = \cdots$

Now since $\mu^{(1)} > \mu^{(2)}$ guarantees mass equilibrium,
what happens when there is a gradient in μ.



Initially $\mu^{(1)} > \mu^{(2)}$.

Mass flow would make $\mu^{(1)}_{final} = \mu^{(2)}_{final}$.

If no work is done on the total system, and no heat flow:

$$\Delta S > 0$$

$$dE = 0 = TdS - \cancel{pV} + \mu dn$$

$$\Delta S = -\frac{\mu^{(1)}}{T}\Delta n^{(1)} - \frac{\mu^{(2)}}{T}\Delta n^{(2)}$$

$$\overset{!}{=} -\left(\frac{\mu^{(1)}}{T} - \frac{\mu^{(2)}}{T}\right)\Delta n^{(1)} \quad \text{for } \Delta n^{(1)} = -\Delta n^{(2)}$$

Now given $\mu^{(1)} > \mu^{(2)}$

in order for ΔS to be positive

$\Delta n^{(1)}$ is negative or $\Delta n^{(2)}$ is positive.

which is when matter flows from high μ to low μ.

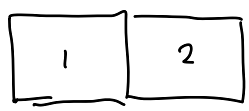
Stability:

When $(\delta^2 E)_{S,V,n} > 0$: Stability

If $(\delta^2 E)_{S,V,n} = 0$: undetermined stability,
need to examine higher order.

when $(\delta^2 E)_{S,V,n} < 0$: unstable.

Consider system:



where $\delta S = 0 = \delta S^{(1)} + \delta S^{(2)}$

and $\delta V^{(1)} = \delta V^{(2)} = \delta n^{(1)} = \delta n^{(2)} = 0$

then $\delta^2 E = \delta^2 E^{(1)} + \delta^2 E^{(2)}$

$$= \frac{1}{2}\left(\frac{\partial^2 E}{\partial S^2}\right)^{(1)}_{V,n} \left(\delta S^{(1)}\right)^2 + \frac{1}{2}\left(\frac{\partial^2 E}{\partial S^2}\right)^{(2)}_{V,n} \left(\delta S^{(2)}\right)^2$$

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

and $\left(\frac{\partial^2 E}{\partial S^2}\right)_{V,n} = \left(\frac{\partial T}{\partial S}\right)_{V,n} = \frac{T}{T\left(\frac{\partial S}{\partial T}\right)_{V,n}} = \frac{T}{C_V} > 0$

for stability.

$$\hookrightarrow \quad (\delta^2 E)_{S,V,n} = \frac{1}{2}(\delta S^{(1)})^2\left(\frac{T^{(1)}}{C_V^{(1)}} + \frac{T^{(2)}}{C_V^{(2)}}\right)$$

$$= \frac{1}{2}(\delta S^{(1)})^2\, T\left(\frac{1}{C_V^{(1)}} + \frac{1}{C_V^{(2)}}\right)$$

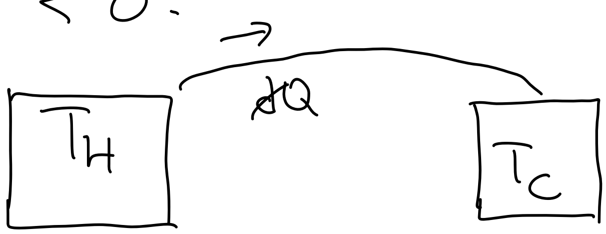
For stability $(\delta^2 E)_{S,V,n} \geq 0$

$$\hookrightarrow \quad T\left(\frac{1}{C_V^{(1)}} + \frac{1}{C_V^{(2)}}\right) \geq 0$$

$$\rightarrow \quad \boxed{C_V \geq 0}$$

Therefore, a stable system has $\underline{C_V \geq 0}$.

If $C_V < 0$:



$$đQ = C_V\, dT_C$$

if $C_V < 0$, dT_C must be < 0
for $đQ > 0$

which makes it runaway

Similarly: require $(\delta^2 A)_{T,V,n} \geq 0$ for stable.

$$\delta V = 0 = \delta V^{(1)} + \delta V^{(2)}$$

and $\delta n^{(1)} = \delta n^{(2)} = 0$

then: $$(\delta^2 A)_{T,V,n} = \frac{1}{2}(\delta V^{(1)})^2 \left[\left(\frac{\partial^2 A}{\partial V^2}\right)^{(1)}_{T,n} + \left(\frac{\partial^2 A}{\partial V^2}\right)^{(2)}_{T,n} \right]$$

since $$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,n} = -\left(\frac{\partial p}{\partial V}\right)_{T,n}$$

for $(\delta^2 A)_{T,V,n} \geq 0$

$$-\left[\left(\frac{\partial p}{\partial V}\right)^{(1)}_{T,n} + \left(\frac{\partial p}{\partial V}\right)^{(2)}_{T,n} \right] \geq 0$$

or $$\left(\frac{\partial V}{\partial p}\right)_{T,n} < 0$$

or $$K_T = \frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,n} > 0$$

$$C_p - C_V = TV\frac{\alpha^2}{K_T} > 0 \quad \text{where } \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,n}$$

Application to phase Equilibria:

Suppose ν phases are coexisting in equilibrium.

At constant T and p, the condition for equilibrium are:

$$\mu_i^{(\alpha)}(T, p, X_1^{(\alpha)}, X_2^{(\alpha)} \cdots X_{r-1}^{(\alpha)}) = \mu_i^{\gamma}(T, p, X_1^{(\gamma)}, X_2^{(\gamma)} \cdots X_{(r-1)}^{(\gamma)})$$

For $1 \le \alpha < \gamma \le \nu$ and $1 \le i \le r$

Here $X_i^{(\alpha)}$ is the mole fraction of species i in phase α.

(# of intensive variable)

Degrees of Freedom: originally $3 \xrightarrow{\text{Gibbs Duhem}} 2$

but Gibbs-Duhem allows us to eliminate one.

There are $\underbrace{\nu(r-1)}_{\text{why not } \nu r}$ more variables.

There are $\mu^{(1)} = \mu^{(2)} = \cdots \mu^{(\nu)}$

there are $\nu - 1$ constraint equations for ν-phases for r # of species.

<u>All in all:</u>

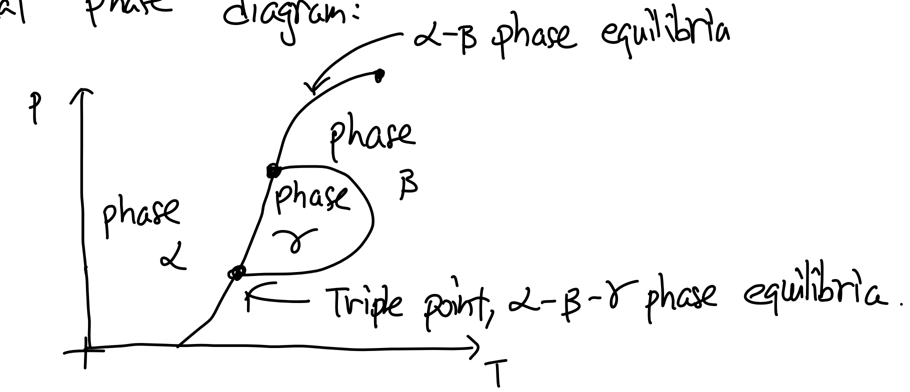
There are $r(\nu-1)$ equations and there are $2 + \nu(r-1)$ different intensive variables.

So the thermodynamic degrees of freedom:

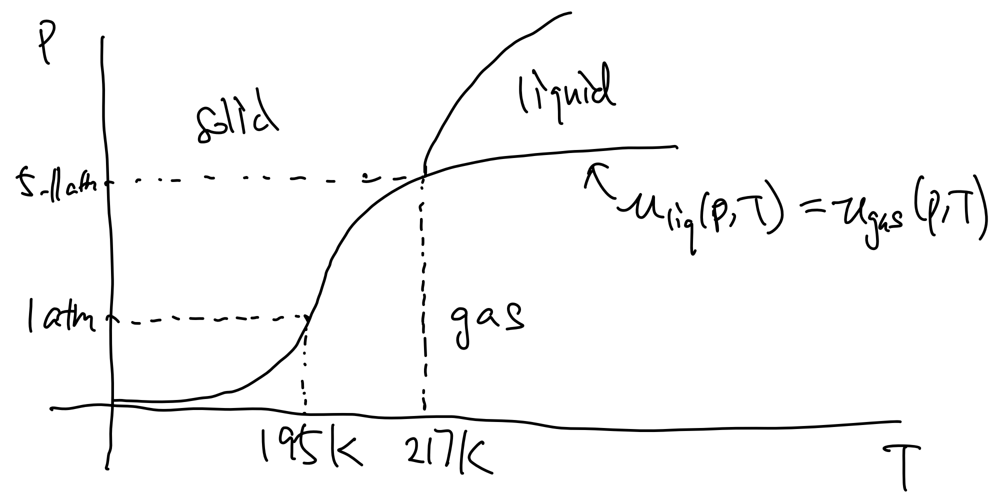
$$\boxed{\begin{aligned} DoF &= 2 + \nu(r-1) - r(\nu-1) \\ &\overset{!}{=} 2 + r - \nu \end{aligned}}$$

Gibbs-phase rule.

Hypothetical phase diagram:



Example:



Dry ice at equilibrium w/ $CO_2^{(g)}$

we have 2 coexisting phases, solid and gas.

So $DoF = 2+1-2 = 1$

If at triple point, we have 3 coexisting phases.

So $DoF = 2+1-3 = 0$

Phase Transition happens during intersection of Gibbs Surface.
characterized by u.

The change in volume in moving from one surface to another is:

$$\left(\frac{\partial u}{\partial p}\right)_T = V$$

And the change in entropy:

$$\left(\frac{\partial u}{\partial T}\right)_p = -S$$

used Gibbs-Duhem Relation:

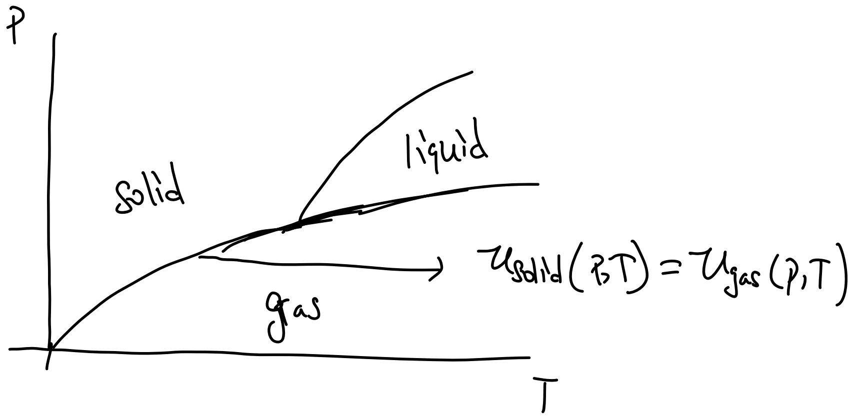
$$n\,du = -S\,dT + p\,dV$$

Second order or higher order transition:

If two surfaces join smoothly to another, v and S are continuous during phase change.

First Order:

when two surfaces join discontinuously.



along phase-transition boundary:

$$d\mu_{solid}(p,T) = d\mu_{gas}(P,T)$$

With Gibbs-Duhem relation: $SdT - Vdp + \sum n d\mu = 0$

$$d\mu = \frac{-S}{n} dT + \frac{V}{n} dp$$

changed to per mole $v = \frac{V}{n}$

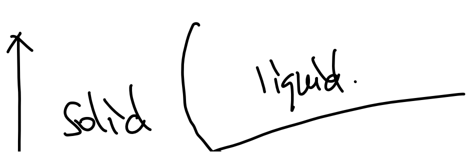
$$-s^{(\alpha)} dT + v^{(\alpha)} dp = -s^{(\beta)} dT + v^{(\beta)} dp$$

$$\boxed{\frac{dP}{dT} = \frac{s^{(\beta)} - s^{(\alpha)}}{v^{(\beta)} - v^{(\alpha)}} = \frac{\Delta S}{\Delta V}}$$

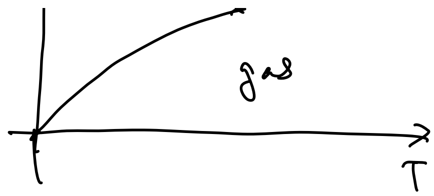
Clausius-Clapeyron Relation *

$$\boxed{\frac{dP}{dT} = \frac{\Delta H_{trans}}{T \Delta V}}$$

enthalpy of transformation

H_2O 

from ice to water. $\Delta V < 0$.



HW# 6-10:

Rewrite Gibbs - Duhem

$$d\mu = -s\,dT + v\,dp$$

$$s = \frac{S}{n} \qquad v = \frac{V}{n}$$

Since $d\mu^{(\alpha)} = d\mu^{(\beta)}$

$$-s^{(\alpha)}dT + v^{(\alpha)}dp = -s^{(\beta)}dT + v^{(\beta)}dp$$

$$\frac{dp}{dT} = \frac{s^{(\beta)} - s^{(\alpha)}}{v^{(\beta)} - v^{(\alpha)}} = \frac{\Delta H_{trans}}{T\Delta V}$$

Phase Transition takes extra energy,

ex: water takes $\Delta H_{vap} = 40.68$ kJ/mol to vaporize.

Central limit Theorem:

$g(x)$ = distribution

$g(x)dx$ = probability on any particular trial to get x between x and $x+dx$.

$$\langle x \rangle_N = \frac{1}{N}\sum_{i=1}^{N} x_i$$ with

$$p(\langle x \rangle_N) = \frac{1}{\sqrt{\sigma_1^2/N}\sqrt{2\pi}} \exp\left\{ \frac{-(\langle x \rangle_N^2 - \bar{x}^2)}{2\sigma_1^2/N} \right\}$$ for $N \to \infty$

where $$\bar{x} = \int dx\, g(x)\, x$$

$$\sigma_1^2 = \int dx\, (x-\bar{x})^2 g(x)$$

Consider an ensemble of systems in different microstates corresponding to the same macro (i.e. thermo) variables, i.e. (N, V, E)

$\boxed{N, V, E}$ . . . . $\boxed{N, V, E}$

State 1 . . . . State Ω

there are Ω # of systems.

$$\langle G \rangle = \frac{1}{\Omega} \sum_i G_i$$

some observable

Ergodic Hypothesis:

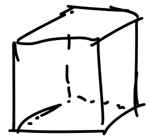
$$\langle G \rangle = \langle G \rangle_t$$

ensemble

time average of 1 system

$$\langle G \rangle_t = \frac{1}{\Omega} \sum_i G_i$$

1 particle in a box:



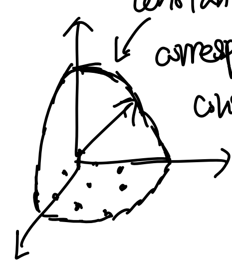
$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) = \varepsilon\psi(\vec{r})$$

$$\psi(x,y,z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x\pi}{L}x\right)\sin\left(\frac{n_y\pi}{L}y\right)\sin\left(\frac{n_z\pi}{L}z\right)$$

$$\varepsilon = \frac{\hbar^2|\vec{k}|^2}{2m}$$

$$\vec{k} = \frac{n_x\pi}{L}\hat{e}_x + \frac{n_y\pi}{L}\hat{e}_y + \frac{n_z\pi}{L}\hat{e}_z$$

$$\varepsilon = \frac{\hbar^2\pi^2}{2mL^2}\left(n_x^2+n_y^2+n_z^2\right)$$



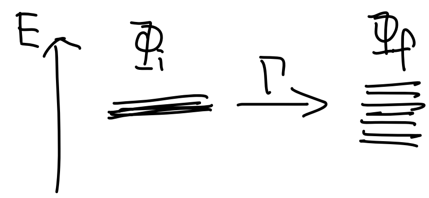
$$g(\varepsilon)d\varepsilon = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon^{1/2}d\varepsilon$$

For N particles in box:

$$E = \varepsilon_1 + \cdots + \varepsilon_N$$
$$= \frac{\hbar^2}{2mV^{2/3}}\left(n_{1x}^2 + n_{1y}^2 + n_{1z}^2 + \cdots n_{Nx}^2 + n_{Ny}^2 + n_{Nz}^2\right)$$

total DoS $= \bar{\Omega}(E) = \left(\frac{V}{h^3}\right)^N \left(\frac{2\pi m}{\Gamma\left(\frac{3N}{2}\right)}\right)^{3N/2} E^{\left(\frac{3N}{2}-1\right)}$

Fermi's Golden Rule:



$$W_{f\leftarrow i} = \frac{2\pi}{\hbar} \Big|\underbrace{\langle \Phi_f | \hat{H} | \Phi_i \rangle}_{\text{perturbation Matrix Element.}}\Big|^2 \underbrace{\bar{\Omega}(E)}_{\text{DoF}}$$

For 1000 atoms in box

to stay Φ_i for 1 second (coherent)

$$|\langle \Phi_f | \hat{H} | \Phi_i \rangle|^2 \leq \frac{\hbar}{2\pi} \frac{1}{\Omega} \Gamma \approx 10^{-27,316} \text{ eV}$$

but $V_{grav} \cong 10^{-22}$ eV for two argon atoms far away.

Which is greater than $|\langle \Phi_f | \hat{H} | \Phi_i \rangle|^2$. So it's impossible to stay in 1 state.