Multi-phase equilibrium

Consider a macroscopic system with r chemical species; the system is in ν co-existing phases. Then

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

↑ total en., fixed

en. in phase (α)

Surface en. neglected: $\dfrac{E(\text{surf.})}{E(\text{bulk})} \sim \dfrac{N^{2/3}}{N} = N^{-\frac{1}{3}} \to 0$ as $N \to \infty$.

Similarly,

$$S = \sum_{\alpha=1}^{\nu} S^{(\alpha)} \quad [\text{bulk terms only}]$$

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

$$n_i = \sum_{\alpha=1}^{\nu} n_i^{(\alpha)} \qquad i = 1, \ldots, r$$

Now, consider

$$\delta E = \sum_{\alpha=1}^{\nu} \left[T^{(\alpha)} \delta S^{(\alpha)} - p^{(\alpha)} dV^{(\alpha)} + \sum_{i=1}^{r} \mu_i^{(\alpha)} \delta n_i^{(\alpha)} \right.$$
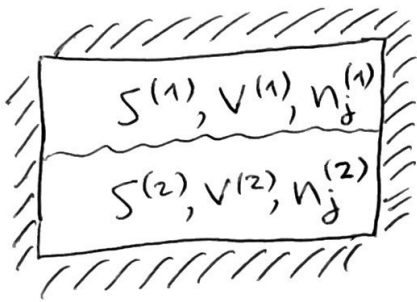
small displacement from equil.

Min E principle: $(\delta E)_{S, V, n_1, \ldots, n_r} \geq 0$

However, total S, V, n_i = const :
$$i = 1, ..., r$$

$$\sum_\alpha \delta S^{(\alpha)} = 0, \quad \sum_\alpha \delta V^{(\alpha)} = 0,$$

$$\sum_\alpha \delta n_i^{(\alpha)} = 0$$

Two-phase system $(\nu = 2)$:

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

Thus,

$$0 \leq (\delta E)_{S,V,n} = (T^{(1)} - T^{(2)}) \delta S^{(1)} -$$

$$- (p^{(1)} - p^{(2)}) \delta V^{(1)} + \sum_{i=1}^{r} (\mu_i^{(1)} - \mu_i^{(2)}) \delta n_i^{(1)}.$$

Since $\delta S^{(1)}, \delta V^{(1)}, \delta n_i^{(1)}$ can be ≤ 0
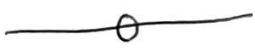
and are uncorrelated, we have:

$$\left[T^{(1)} = T^{(2)}, \quad p^{(1)} = p^{(2)}, \quad \mu_i^{(1)} = \mu_i^{(2)} \right]$$

$$i = 1, ..., r$$
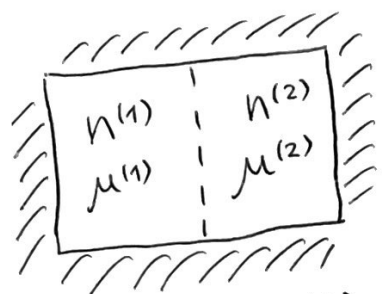
This gives $(\delta E)_{S,V,n} = 0$

With multiple phases,

$$\begin{cases} T^{(1)} = T^{(2)} = T^{(3)} = \dots & \text{thermal equil.} \\ p^{(1)} = p^{(2)} = p^{(3)} = \dots & \text{mechanical} \quad -\text{''}- \\ \mu_i^{(1)} = \mu_i^{(2)} = \mu_i^{(3)} = \dots & \text{mass} \quad -\text{''}- \end{cases}$$

This also means that $T, p, \mu_i = \text{const}$ in a single homogeneous phase.

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Consider a composite system:

$r = 1$, (single-species)

$$\mu^{(1)} > \mu^{(2)} \quad @ \; t = 0$$
$$\mu_f^{(1)} = \mu_f^{(2)} \quad @ \; t = \infty$$

$$T^{(1)} = T^{(2)} = T \qquad \left[\Delta n^{(1)} = - \Delta n^{(2)} \right]$$

$$\Delta E = \underbrace{T \Delta S}_{} + \mu^{(1)} \Delta n^{(1)} + \mu^{(2)} \Delta n^{(2)}, \quad \text{or}$$

$$\overset{\parallel}{E_f - E_i} = \underbrace{\Delta S^{(1)} + \Delta S^{(2)} =}_{= S_f - S_i}$$

$= 0$ by construction

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

$\Delta S > 0$

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

Thus, if $\begin{cases} \mu^{(1)} > \mu^{(2)} \\ \Delta S > 0 \end{cases} \Rightarrow \underline{\underline{\Delta n^{(1)} < 0}}$

matter flows from high μ to low μ

In other words, $-\nabla\left(\frac{\mu}{T}\right)$ is a generalized force for mass flow

Likewise, we had with heat exchange:

$$\Delta S > 0 \implies \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right) \Delta E^{(1)} > 0$$

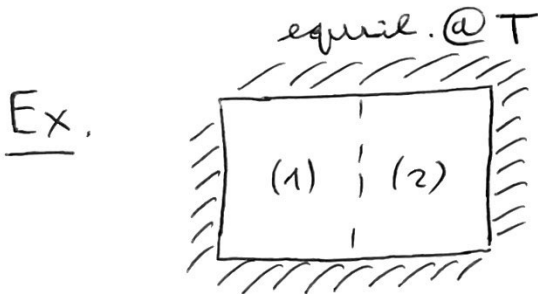heat flows from ~~cold~~ hot to cold

Thus $-\nabla\left(\frac{1}{T}\right)$ is the generalized force for heat flow

Thermodynamic stability

$$\underbrace{(\Delta E)_{S,V,n}}_{>0} = \underbrace{(\delta E)_{S,V,n}}_{=0 \text{ @ equil.}} + (\delta^2 E)_{S,V,n} + (\delta^3 E)_{S,V,n} + \ldots$$

for unconstrained systems

If $(\delta^2 E)_{S,V,n} = \begin{cases} > 0 & \text{system is stable} \\ = 0 & \text{undetermined, examine} \\ & \qquad (\delta^3 E)_{S,V,n} \\ < 0 & \text{system is unstable} \end{cases}$

Ex.

equil. @ T

$$\begin{cases} \delta S^{(1)} + \delta S^{(2)} = \delta S = 0 \\ \delta V^{(1)} = \delta V^{(2)} = 0 \\ \delta n^{(1)} = \delta n^{(2)} = 0 \end{cases}$$

Then

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

$-4-$

Recall that

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

$$\textcircled{=} \quad \frac{1}{2}(\delta S^{(1)})^2 \left[\frac{T}{C_V^{(1)}} + \frac{T}{C_V^{(2)}}\right] \geqslant 0 \quad, \quad \text{yielding} \\ (T \geqslant 0)$$

$$\frac{1}{C_V^{(1)}} + \frac{1}{C_V^{(2)}} \geqslant 0 \quad .$$

Since the division into (1) & (2) is arbitrary, we have $\frac{1}{C_V} \geqslant 0 \implies \boxed{C_V \geqslant 0}$

Stable system $\implies$ $\underline{C_V > 0}$,
needed to equilibrate
2 systems with $T^{(1)} \neq T^{(2)}$

Now, consider a fluctuation in V @ $T =$ const:

$$\begin{cases} \delta V = \delta V^{(1)} + \delta V^{(2)} = 0, \\ \delta n^{(1)} = \delta n^{(2)} = 0 \end{cases}$$

$$(\delta^2 A)_{T,V,n} = \frac{1}{2}(\delta V^{(1)})^2 \left[\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,n}^{(1)} + \left(\frac{\partial^2 A}{\partial V^2}\right)_{T,n}^{(2)}\right] \geqslant 0$$

Since $\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,n} = -\left(\frac{\partial P}{\partial V}\right)_{T,n}$, we obtain:

$$-\left[\left(\frac{\partial P}{\partial V}\right)_{T,n}^{(1)} + \left(\frac{\partial P_-}{\partial V}\right)_{T,n}^{(2)}\right] \geqslant 0 \quad .$$

This implies $-\left(\dfrac{\partial p}{\partial V}\right)_{T,n} \geqslant 0$, or

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

If the equil. is stable $\Rightarrow K_T > 0$,
as $p \nearrow$ @ $T = const$, $V \searrow$.

Many other results like that can be derived.

Phase equilibria

Suppose J phases are @ equil. at $T = const$, $p = const$. Then

$$\left[\begin{array}{l} \mu_i^{(\alpha)}(p, T, x_1^{(\alpha)}, \ldots, x_{r-1}^{(\alpha)}) = \\ = \mu_i^{(\gamma)}(p, T, x_1^{(\gamma)}, \ldots, x_{r-1}^{(\gamma)}) \end{array}\right] \quad (*)$$

$$1 \leqslant \alpha < \gamma \leqslant J$$
$$1 \leqslant i \leqslant r$$

note that
$$\sum_{i=1}^{r} x_i^{(\alpha)} = 1 \quad , \forall \alpha$$
$\underbrace{\qquad}$ mole fraction
of species i in
phase α

Eq. $(*)$ is a system of $r(J-1)$ indep. equations for $\underbrace{2}_{T,p} + \underbrace{J(r-1)}_{\substack{mole \\ fractions}}$ variables.

Hence, the # DoF is

$$f = \underbrace{2 + \nu(r-1)}_{\# \text{vars}} - \underbrace{r(\nu-1)}_{\# \text{eqs}} = 2 + r - \nu.$$

$$\underline{\underline{\text{gibbs phase rule}}}$$

Ex. $r = 1$ system: ↙ single-component

Single phase: $f = 2 + \overset{=r}{1} - \overset{=r}{\nu} = 2$
$\qquad\qquad\qquad\qquad\qquad \underset{\text{use } p, T}{}$
           can
System ✓ exists anywhere in the p-T plane.

Two phases:

$$f = 2 + 1 - 2 = 1 \Leftarrow \text{single-prm line in the p-T plane}$$
$$\quad\;\; \overset{\prime\prime}{r} \;\; \overset{\prime\prime}{\nu}$$

Three phases:

$$f = 0 \Leftarrow 3 \text{ phases can only co-exist at a point}$$

Cannot have > 3 phases in a single-
-component ($r=1$) system.

Phase diagram

critical point

$\alpha \& \beta$ coexist: $\mu^{(\alpha)}(p,T) = \mu^{(\beta)}(p,T)$

$\gamma \& \beta$ coexist: $\mu^{(\beta)}(p,T) = \mu^{(\gamma)}(p,T)$

$\mu^{(\alpha)}(p,T) = = \mu^{(\gamma)}(p,T)$

$\alpha \& \gamma$ coexist

triple points: $\alpha \& \beta \& \gamma$ coexist
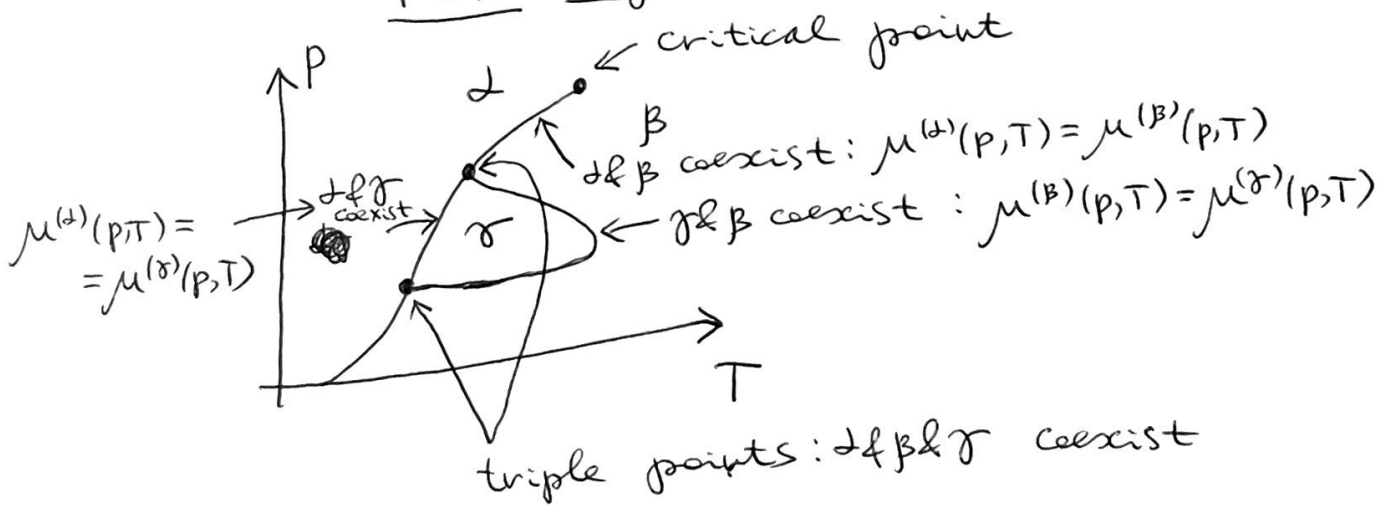
For (T, p, n) variables, the relevant thermodynamic potential is gibbs free en. G. Recall that $G = n\mu$ if $r = 1$. For phases α and β with the α-β co-existence line, the phase with the lower G (& thus μ) will be stable.

$\mu^{(\alpha)}(p, T)$ and $\mu^{\beta}(p, T)$ define Gibbs surfaces; the intersection of Gibbs surfaces is where a *phase transition* occurs.

α-β coexistence line in p-T plane
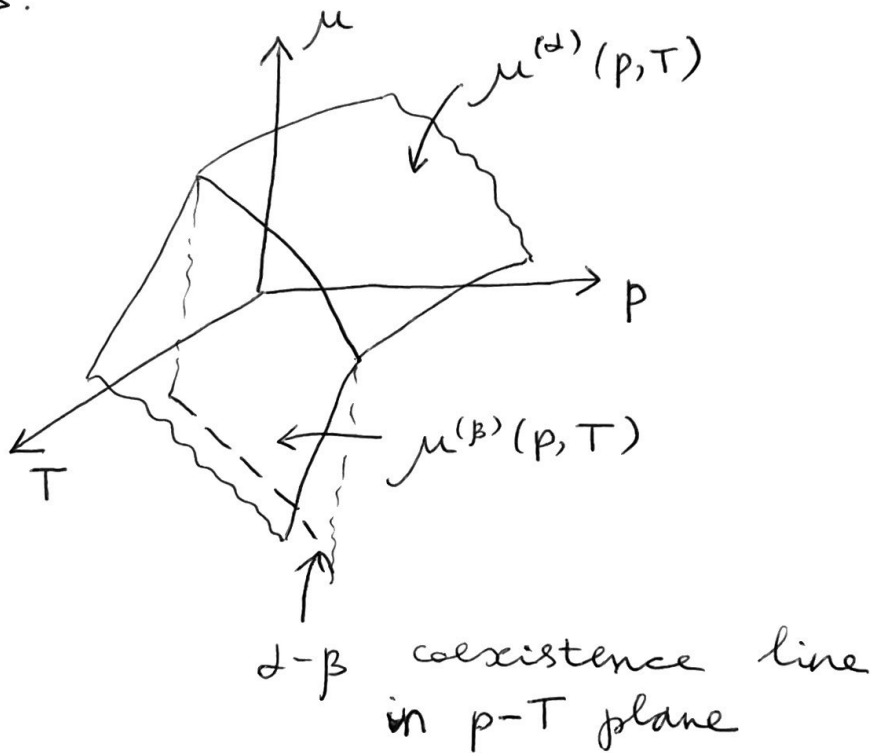
Now, consider the Gibbs-Duhem eq'n: (GD)

$$S dT - V dp + n d\mu = 0, \text{ or}$$
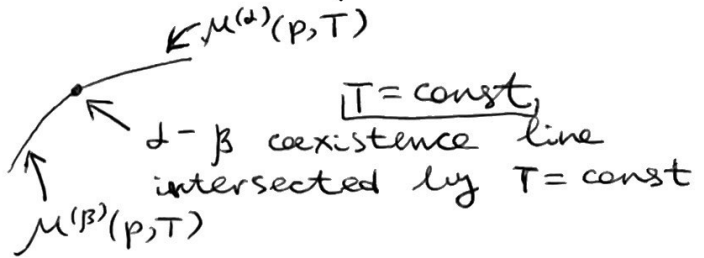
$$d\mu = \frac{V}{n} dp - \frac{S}{n} dT$$

v, volume per mole

s, entropy per mole

Then $\begin{cases} \left(\dfrac{\partial \mu}{\partial p}\right)_T = v, & \leftarrow \text{change in } v \text{ @ } T = \text{const} \\ & \text{is given by a change} \\ & \text{in } \left(\dfrac{\partial \mu}{\partial p}\right)_T \\ \left(\dfrac{\partial \mu}{\partial T}\right)_p = -s & \nwarrow \text{change in } S \text{ @ } p = \text{const} \\ & \text{is given by a change} \\ & \text{in } \left(\dfrac{\partial \mu}{\partial T}\right)_p \end{cases}$

<u>Two</u> <u>situations</u>:

(i) no kink,

no jump in $\left(\dfrac{\partial \mu}{\partial p}\right)_T = v(p,T)$

$\leftarrow \mu^{(\alpha)}(p,T)$

$T = \text{const},$
$\alpha - \beta$ coexistence line
intersected by $T = \text{const}$

$\mu^{(\beta)}(p,T)$

<u>Second-order</u>, or <u>continuous</u>

phase transition

(ii) $\exists$ kink where
the surfaces join:

$v(p,T)$ undergoes a
jump (i.e., $v(p,T)$ is a discontinuous
function)

$\mu^{(\alpha)}(p,T)$

$T = \text{const},$

$\mu^{(\beta)}(p,T)$
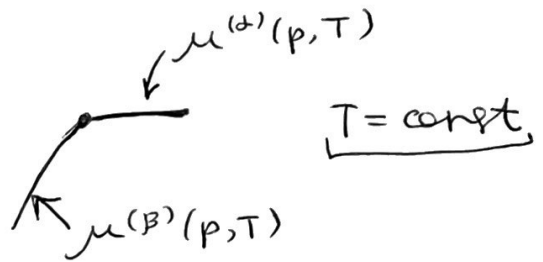
<u>First-order</u> phase transition

Finally, consider
$\mu^{(\alpha)}(p,T) = \mu^{(\beta)}(p,T)$ again

$\Downarrow$

$d\mu^{(\alpha)}(p,T) = d\mu^{(\beta)}(p,T)$ for a
small displacement along
the coexistence line

Then by GD eq'n:

$$-S^{(\alpha)} dT + v^{(\alpha)} dp = -S^{(\beta)} dT + v^{(\beta)} dp, \text{ or}$$

$$(**) \qquad \frac{dp}{dT} = \underbrace{\frac{S^{(\alpha)} - S^{(\beta)}}{v^{(\alpha)} - v^{(\beta)}}}_{} \equiv \frac{\Delta S}{\Delta v} \quad \left.\right] \begin{array}{l} \text{Clausius-} \\ \text{-Clapeyron eq'n} \end{array}$$

values for the two phases @ equil. on the co-existence line, with (p, T)

Note that Eq. (**) is useful only for 1$\underline{st}$ order phase transitions $\Rightarrow$ $\Rightarrow$ RHS is ill-defined in a 2$\underline{nd}$ order phase transition.