Concept of phase diagram (fixed $T$, $P$)

We know $G(N, P, T)$ is a minimum at fixed $P, T$.

A phase is a region in which $G(P, T)$ varies with $P, T$ smoothly.

Typical gas phase diagram:

1st order because discontinuities in 1st derivatives of $G$ across line.

- Solid line
- Liquid line

$P_m(T)$

"Two-phase coexistence" Aragon

Critical pt. 1st order phase transition

"Triple point"
Can have many phases; not just two

First-order phase transition

\[ G_1(P,T) \]
\[ G_2(P,T) \]

At boundary:

\[ G_{g_1}(P,T) = G_{g_2}(P,T) \] (suppressing \( N \)-dependence)

\[ U_1(P,T) + PV_1(P,T) - TS_1(P,T) = U_2(P,T) + PV_2(P,T) - TS_2(P,T) \]

\[ H_1 - H_2 = T(S_1 - S_2) \] at boundary

\[ \Delta H = H_1 - H_2 = N(h_1 - h_2) = N\Delta h \]

\[ \Delta S = S_1 - S_2 = N(\Delta_1 - \Delta_2) = N\Delta S \]

\[ \Delta h = T\Delta S = \Delta U + P\Delta V \]

\( \Delta U + T\Delta S = \text{"heat of transition"} \)

or \( \text{"latent heat"} \)

Why called "first-order transition"?

Because 1st derivative of \( G \), namely \( S \), is discontinuous.
Usually size $s_3$ of higher-temphase is larger, so, e.g., melting leads to absorption of heat, i.e. $u_s + P v_s < u_e + P v_e$

$\Delta H$ at high $T$

$T \Delta S = \Delta$ latent heat of melting, vaporization, sublimation

Clausius-Clapeyron equation:

$$G_{A_2} (P, T) = G_{A_2} (P, T)$$

$$G_1 (P + dP, T + dT) = G_2 (P + dP, T + dT)$$

But

$$G_1 (P + dP, T + dT) = G_1 (P, T) + dP \left( \frac{\partial G}{\partial P} \right)_{T,N} + dT \left( \frac{\partial G}{\partial T} \right)_{P,N}$$

$$= G_1 (P, T) + dP N v_1 (P, T) - dT N \Delta_1 (P, T)$$

using

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

(and $dN = 0$)
Also,
\[
G_2(P, T, +dP, T +dT) = G_2(P, T) + dP Nv_2(P, T) + dT N\Delta_2(P, T)
\]

But \( G_1(P, T) = G_2(P, T) \) so
\[
dP v_1 - dT \Delta_1 = dP v_2 - dT \Delta_2
\]

Thus
\[
\frac{dP}{dT} v_1 - \Delta_1 = \frac{dP}{dT} v_2 - \Delta_2
\]

\[
\frac{dP}{dT} (v_1 - v_2) = \Delta_1 - \Delta_2
\]

Can also write this as
\[
\frac{dP}{dT} = \frac{\Delta_1 - \Delta_2}{v_1 - v_2}
\]

**Clausius-Clapeyron equation**

\[
\frac{dP}{dT} = \frac{T(\Delta_1 - \Delta_2)}{T(v_1 - v_2)} = \frac{\text{freev}}{T \Delta v}
\]

\[
l = T(\Delta_1 - \Delta_2) = T \Delta s
\]

E.g. melting curve of ice:

\[
\text{b} < l \Rightarrow \frac{dP}{dT} < 0
\]

But \( v_l < v_s \)
Consequences: ice skate ~ high pressure ~ melts ice.

Actual slope: 

\[ V_{\text{eq}} = 18 \text{ cm}^3/\text{mole} = 18 \times 10^{-6} \text{ m}^3/\text{mole} \]

\[ V_{\text{sol}} = 22.5 \text{ cm}^3/\text{mole} = 22.5 \times 10^{-6} \text{ m}^3/\text{mole} \]

\[ \Delta V = V_e - V_s = -4.5 \times 10^{-6} \text{ m}^3/\text{mole} \]

\[ T \Delta V = -4.5 \times 10^{-6} \times 273 = 1.25 \text{ K-m}^3/\text{mole} \]

Latent heat = 80 cal/gram

\[ = 80 \times 18 \times 4.2 \text{ cal gram mole}^{-1} \text{ gram}^{-1} \text{ mole}^{-1} \]

\[ \frac{dP}{dT} = -5 \times 10^6 \text{ Pa/K} \]

Example 2: Boiling temp of \( H_2O \) at high altitudes:

\[ \frac{dP}{dT} > 0 \]

Here, so lowering \( P \) also lowers boiling temperature.
Unstable isotherms and Van der Waals equation:

Schematic Van der Waals equation of state:

\[ P = \frac{RT}{\nu - b} - \frac{a}{\nu^2} \]

If \( \left( \frac{\partial P}{\partial \nu} \right)_T < 0 \) everywhere, we have stability.

If \( \left( \frac{\partial P}{\partial \nu} \right)_T > 0 \) in some regions – unstable!

To find stable regions, common tangent construction:

We have \( P = -\left( \frac{\partial F}{\partial \nu} \right)_T = -\left( \frac{\partial (N\nu F)}{\partial (N\nu)} \right)_T \)

\[ = -\left( \frac{\partial f}{\partial \nu} \right)_T \]

Must have \( \left( \frac{\partial P}{\partial \nu} \right)_T \leq 0 \) or \( \left( \frac{\partial^2 f}{\partial \nu^2} \right)_T \geq 0 \).
Two pts shown are limits of stability.

Proof. First, suppose we start with a mole at pt. v.

Let it divide into a frac. x with molar volume $v_1$
and $1-x$ with molar volume $v_2$

Then we must have

$$xv_1 + (1-x)v_2 = v$$

or

$$x(v_1 - v) = (1-x)(v_2 - v) + (1-x)(v_2-v) = 0$$

("lever rule")

But clearly $f$ is lowered; new $f$ is

Also, both (1)

and (2) have same

pressure (since slopes are the same)

\[ f = f_1 + \frac{f_2-f_1}{v_2-v_1} (v-v_1) \]

\[ x = \frac{v_2-v}{v_2-v_1} \]
This gives:

\[ f = \frac{v_2 - v}{v_2 - v_1} f_1 + \left(1 - \frac{v_2 - v}{v_2 - v_1}\right) f_2 \]

\[ = \frac{v_2 - v_1}{v_2 - v_1} f_1 + \frac{v_1 - v}{v_2 - v_1} f_1 + \frac{v - v_1}{v_2 - v_1} f_2 \]

\[ = f_1 + \left(f_2 - f_1\right) \frac{v - v_1}{v_2 - v_1} \quad \text{q.e.d.} \]

Can also show Gibbs' free energies of two phases are equal, as follows:

\[ g_1 = f_1 + P v_1 \]
\[ g_2 = f_2 + P v_2 \]

\[ g_2 - g_1 = f_2 - f_1 + P (v_2 - v_1) \]

but \[ P = -\frac{f_2 - f_1}{v_2 - v_1} \]

\[ g_2 - g_1 = 0 \]

Maxwell construction:
Pick \( v_1, v_2 \) so that \( A_1 = A_2 \)

**Proof:** This would give

\[ + \int_{v_1}^{v_2} p(v) \, dv = P_1(v_2 - v_1) \]

We have

\[ g_2 = f_1 + P_1 v_1 \]

\[ g_2 = f_2 + P_2 v_2 \]

\[ f_2 = f_1 - \int_{v_1}^{v_2} p(v) \, dv \quad \text{since} \quad \frac{dP}{dv} = -f \]

\[ g_2 = f_1 - \int_{v_1}^{v_2} p(v) \, dv + P_2 v_2 \]

(taking \( P_1 = P_2 \))

\[ = f_1 - \int_{v_1}^{v_2} p(v, T) \, dv + P_1 v_1 + P_2 \int_{v_1}^{v_2} p(v, T) \, dT \]

\[ = g_1 + P_1(v_2 - v_1) - \int_{v_1}^{v_2} p(v, T) \, dT \]

so must have

\[ P_1(v_2 - v_1) - \int_{v_1}^{v_2} p(v, T) \, dT = 0 \]

Hence, areas must be equal as shown.
Critical pt. of Gibbs isotherm:

\[ P = \frac{RT}{v-b} - \frac{a}{v^2} \]

\[ \left( \frac{\partial P}{\partial v} \right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} < 0 \text{ for stability} \]

\[ \left( \frac{\partial^2 P}{\partial v^2} \right)_T = 0 \]

\[ T_c \text{ determined by} \]

\[ \left( \frac{\partial P}{\partial v} \right)_T = 0 \]

\[ \left( \frac{\partial^2 P}{\partial v^2} \right)_T = 0 \]
Gibbs phase rule

\[ r \text{ components} \]

\[ M \text{ phases} \]

\[ \frac{M(r-1)+2}{\# \text{ of indep } P, T} \]

mole fractions \( x_i \)

\[ \frac{r}{\text{th fraction is determined by}} \]

\[ \sum_{i=1}^{r} x_i = 1 \]

so is not independent
You would think you could have: 
\[P, T, N_1, \ldots, N_r\]
but really, it is:
\[P, T, x_1, \ldots, x_r] \quad \text{where} \quad x_k = \frac{N_k}{N} = \frac{1}{\sum_{k=1}^{r} N_k}

\# of conditions of equilibrium:
1. \[\mu_1 = \mu_1^* = \ldots = \mu_1^*(M)\]
2. \[\mu_2^* = \mu_2^* = \ldots = \mu_2^*(M)\]
3. \[\mu_r^* = \mu_r^* = \ldots = \mu_r^*(M)\]
4. \[(M-1)\] eqs.

So \# of degrees of freedom is:
\[f = M(M-1) + 2 - r(M-1)\]
\[\text{or } f = r - M + 2\] Gibbs phase rule

E.g.: \(\text{NaCl}, \ r = 1\) (one component system)
\[
\begin{align*}
M = 1 &\quad f = 2 \quad (P, T) \\
M = 2 &\quad f = 1 \quad \text{line in } PT \text{ space} \\
M = 3 &\quad f = 0 \quad \text{Pt. in } PT \text{ space} \\
M = 4 &\quad \text{doesn't happen in general}
\end{align*}
\]
Say we are at fixed $P$, $T$

$M$ phases, $n$ components

$M$th phase

\[
\begin{align*}
\mu_{1k} &= \mu_{2k} = \cdots = \mu_{rk} \\
&\quad k=1, \ldots, r
\end{align*}
\]

$r(M-1)$ equations

\[\text{# of variables is } 2 + M(n-1)\]
$r = 2$ #of phases
$M = 1$ #of degrees of freedom
$P, T, x_1$
$M = 2$ $f = 2$ Surface in $P,T,x$ space
$M = 3$ $f = 1$ line in $P,T,x$ space
$M = 4$ $f = 0$ pt. in $P,T,x$ space

Some examples of binary phase diagrams:

- Liquid
- Solid
- Liquidus
- Solidus
- Two phases coexisting

Slice at constant pressure
"Coexistence" ("hole")
"Liquidus"
"Solidus"
(e.g. CuNi)

Entire point (three phases coexist)