Consider 3 variables \( x, y, z \). There is an "equation of state" \( f(x, y, z) = 0 \) relating these so that they are not independent. Then we introduce the function \( w(x, y, z) \) which depends on these - but only on 2 independently, i.e. we have \( x(y, z), y(x, z), z(x, y) \)

\[ d\omega = \left( \frac{\partial w}{\partial x} \right)_z dy + \left( \frac{\partial w}{\partial y} \right)_z dz \]

(a) \( \omega = \omega(x, y) \)

\[ d\omega = \left( \frac{\partial \omega}{\partial x} \right)_y dx + \left( \frac{\partial \omega}{\partial y} \right)_x dy \]

\[ \Rightarrow \left( \frac{\partial \omega}{\partial x} \right)_y = \left( \frac{\partial \omega}{\partial y} \right)_x + \left( \frac{\partial \omega}{\partial x} \right)_y \frac{dx}{dy} \frac{dy}{dz} \]

(b) \( \frac{dx}{dy} \frac{dy}{dz} = \frac{\partial x}{\partial y} \frac{\partial y}{\partial z} + e = \frac{1}{\left( \frac{\partial y}{\partial x} \right)_y} \]

(c) \( z(x, y) \)

\[ dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy \]

\[ \Rightarrow \frac{dy}{dx} = \left( \frac{\partial z}{\partial y} \right)_x + \left( \frac{\partial z}{\partial x} \right)_y \frac{dx}{dy} \]

\[ dy = \left( \frac{\partial y}{\partial x} \right)_y dx + \left( \frac{\partial y}{\partial y} \right)_x dy \]

\[ = \frac{1}{3} \left( \frac{\partial y}{\partial x} \right)_y \frac{dx}{dy} + \left( \frac{\partial y}{\partial y} \right)_x dy \]

The coeff \( \frac{\partial y}{\partial x} \frac{dx}{dy} = 0 \) because \( dy \) must = \( dx \)

\[ \Rightarrow (\frac{\partial y}{\partial y})_x \frac{dx}{dy} = \frac{1}{(\frac{\partial y}{\partial x})_y} = \frac{1}{\frac{dy}{dz}} \]

and

\[ \frac{\partial y}{\partial z} \frac{dx}{dy} \frac{dy}{dz} + (\frac{\partial y}{\partial z})_x \left( \frac{\partial z}{\partial y} \right)_y \frac{dy}{dz} = -1 \]

(d) \( \left( \frac{\partial x}{\partial y} \right)_z = \left( \frac{\partial x}{\partial w} \right)_z \left( \frac{\partial w}{\partial y} \right)_z - \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial y} \right)_y \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial y} \right)_y \]

\[ = \left( \frac{\partial x}{\partial w} \right)_z \frac{\partial w}{\partial y} - \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial y} \right)_y \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial y} \right)_y \]

\[ = \left( \frac{\partial x}{\partial w} \right)_z \frac{\partial w}{\partial y} - \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial y} \right)_y \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial y} \right)_y \]
Definitions:

$$v = \left( \frac{B}{\rho} \right)^{1/2}$$  \hspace{1cm} B \text{ = Bulk modulus} \hspace{1cm} \rho = \frac{M}{V} \text{ = density}

B is either

$$B_s = -v \left( \frac{\partial P}{\partial V} \right)_s$$ \hspace{1cm} \text{constant entropy} \hspace{1cm} "\text{adiabatic}"

$$B_T = -v \left( \frac{\partial P}{\partial V} \right)_T$$ \hspace{1cm} \text{constant } T \hspace{1cm} "\text{isothermal}"

$$K_T = \frac{1}{B_T} = -\frac{1}{v} \left( \frac{\partial V}{\partial P} \right)_T$$ \hspace{1cm} \text{isothermal compressible}

$$K_s = \frac{1}{B_s} = -\frac{1}{v} \left( \frac{\partial V}{\partial P} \right)_s$$ \hspace{1cm} \text{adiabatic}"

$$v_s = \left( -\frac{1}{\rho} \left( \frac{\partial P}{\partial V} \right)_s \right)^{1/2}$$

If V constant:

$$\frac{\partial V}{\partial P} = -\frac{\partial P}{\partial V} \frac{\partial V}{\partial P} = -\frac{N m}{\gamma V} \frac{\partial P}{\partial V} = -\frac{P}{\gamma V} \frac{\partial P}{\partial V}$$

$$v_s = \left( \frac{\partial P}{\partial V} \right)_s$$ \hspace{1cm} $$v_s = \left( \frac{1}{K_s P} \right)^{1/2}$$

Want to show:

$$v_s = \left( \frac{c_P}{k_s c_v} \right)^{1/2} = \left( \frac{1}{k_s P} \right)^{1/2}$$

Basically, need to show that

$$K_s = \frac{c_v}{c_p} K_T$$

Have

$$K_s = -\frac{1}{v} \left( \frac{\partial V}{\partial P} \right)_s = -\frac{1}{v} \left( \frac{\partial S}{\partial P} \right)_V \frac{1}{v} \left( \frac{\partial V}{\partial S} \right)_P$$

$$\left( \frac{\partial S}{\partial P} \right)_V = \left( \frac{\partial S}{\partial T} \right)_V \left( \frac{\partial T}{\partial P} \right)_V = \frac{c_v}{\gamma} \left( \frac{\partial T}{\partial P} \right)_V$$

$$\left( \frac{\partial S}{\partial V} \right)_P = \frac{c_p}{\gamma} \left( \frac{\partial T}{\partial V} \right)_P$$
\[ K_S = - \frac{1}{V} \frac{c_v}{c_p} \left( \frac{\partial T}{\partial p} \right)_V \frac{1}{(\frac{\partial T}{\partial V})_p} \]

Using \( \left( \frac{\partial p}{\partial V} \right)_T \), \( \left( \frac{\partial T}{\partial V} \right)_p = -1 \)

\[ K_S = - \frac{1}{V} \left( \frac{c_v}{c_p} \right)_T = \frac{c_v}{c_p} \frac{c_p}{c_v} \frac{V^2}{mRT} \]

\[ V_S = \left( \frac{RT}{m \frac{c_p}{c_v}} \right)^{\frac{1}{2}} = \left( \frac{1}{K_T \frac{c_p}{c_v}} \right)^{\frac{1}{2}} \]

\[ P V = nRT \]

\[ \frac{\partial p}{\partial V} = -nRT \frac{1}{V^2} \]

\[ K_T = - \frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \]

\[ = + \frac{1}{V} \frac{V^2}{mRT} = \frac{V}{mRT} = \frac{m}{c_p} \]

\[ V_S = \left( \frac{RT}{m \frac{c_p}{c_v}} \right)^{\frac{1}{2}} \]

\[ dF = -SdT - pdV = -SdT - dW \]

\[ F(T, V) = - \int_{V_0}^{V} \frac{T}{T_0} dT - \int_{V_0}^{V} \frac{V}{V_0} \]

\[ = -RT \frac{V}{V_0} \left( \frac{T}{T_0} \right) - \int_{V_0}^{V} \frac{V}{V_0} \]

\[ F(T, V) = -RT \frac{V}{V_0} \left( \frac{T}{T_0} \right) - \int_{V_0}^{V} \frac{V}{V_0} \]

\[ P = -\frac{\partial F}{\partial V} \bigg|_{T} = -\frac{RT_0 V_0}{V^2 (c_{OH})} \left[ \frac{T}{T_0} \right] - \int_{V_0}^{V} \frac{V}{V_0} \]

Work done

\[ W = \int_{V_0}^{V} P dV \]

\[ W = \frac{RT_0}{c_{OH}} \left[ \frac{V_0}{V} - 1 \right] \left[ \frac{V}{V_0} \right] - \int_{V_0}^{V} \frac{V}{V_0} \]

\[ \text{Work done} \]

\[ = \frac{RT_0}{c_{OH}} \left[ \frac{V_0}{V} - 1 \right] \left[ \frac{V}{V_0} \right] - \int_{V_0}^{V} \frac{V}{V_0} \]

\[ = \frac{RT_0}{c_{OH}} \left[ \frac{V_0}{V} - 1 \right] \left[ \frac{V}{V_0} \right] + \int_{V_0}^{V} \frac{V}{V_0} \]
4. Show \( F = F(T, V, N) \), \( \Delta = \Delta(T, V, N) \)

Using the second law, \( Tds = du + pdV - u\,dn \), and the definition of \( F \), \( F = u - TS \), we have
\[
dF = du + ds = s\,dT \\
= du - (du + pdV - u\,dn) = s\,dT \\
= -pdV = s\,dT + u\,dn
\]

Thus, \( F = F(T, V, N) \).

From the definition, \( \Delta = F - u\,N \), we have
\[
d\Delta = dF - u\,dn = -u\,dn \\
= -pdV = s\,dT - u\,dn
\]

Thus, \( \Delta = \Delta(T, V, N) \).

5. (a) \( F = u - TS \)
\[
\frac{\partial}{\partial p} (pF) = F + p \frac{\partial F}{\partial p} = F + p \left( -kT \right) \frac{2F}{\partial V} \\
= F - T(\Delta) = F + TS = u
\]

(b) \( \frac{\partial}{\partial p} (p\Delta) = \Delta + p \frac{\partial \Delta}{\partial p} = \Delta + p \left( -kT \right) \frac{\partial \Delta}{\partial T} \)

From \( \partial^2 \epsilon / \partial T = -\Delta \), so that
\[
\frac{\partial p\Delta}{\partial p} = \Delta + TS = F - u\,N + TS = u - u\,N
\]

Using statistical mechanics, we have

(a) Canonical ensemble,
\[
U = \frac{1}{Z} \sum E_i e^{-pE_i S} \\
Z = \sum e^{-pE_i S} \\
\frac{\partial}{\partial p} (\log Z) = \frac{\partial}{\partial p} (pF)
\]

(b) Grand ensemble,
\[
U = \frac{1}{N} \sum E_i e^{-p(E_i - uN)}
\]
\[
Z = \frac{\sum e^{-B(\theta - \mu N)}}{n} \sum e^{-B(\theta - \mu N)}
\]

\[
-\frac{\partial}{\partial \theta} \log Z = \frac{1}{n} \sum e^{-B(\theta - \mu N)} Z(T, \theta, N, S)
\]

\[
= u - \frac{1}{n} \sum e^{-B(\theta - \mu N)} Z(T, \theta, N, S)
\]

\[
= u - \mu \bar{N}
\]

\[
u - \mu \bar{N} = -\frac{\partial}{\partial \theta} \log Z = \frac{3}{\partial \theta} (\theta^2)
\]
6. Clapeyron Equation

1. Start with a "Maxwell's Rule",
\[ \frac{dF}{dV} = \left( \frac{\partial F}{\partial T} \right)_V dT + \left( \frac{\partial F}{\partial V} \right)_T dV = -SdT - p dV \]
\[ \left( \frac{\partial F}{\partial T} \right)_V = -S \]
\[ \left[ \frac{\partial}{\partial V} \left( \frac{\partial F}{\partial T} \right)_V \right]_T = \left( \frac{\partial S}{\partial V} \right)_T \]
\[ \left[ \frac{\partial}{\partial T} \left( \frac{\partial F}{\partial V} \right)_T \right]_V = \left( \frac{\partial P}{\partial V} \right)_T \]
\[ \left( \frac{\partial P}{\partial T} \right)_V = \left( \frac{\partial S}{\partial V} \right)_T \]

Integrating the \( \left( \frac{\partial P}{\partial T} \right)_V \) as change of \( P \) with \( T \) or
we move along a co-existence line between at vapor (\( V \)) and liquid (\( L \)) phase,
\[ \left( \frac{\partial P}{\partial T} \right)_V = \frac{\Delta S}{\Delta V} = \frac{\Delta S}{\Delta V} \]
with \( \Delta S \) and \( \Delta V \) the change in entropy and volume between the two phases.
With \( \Delta Q = T \Delta S \) and \( \Delta Q = L \), the latent heat of vaporization, have
\[ \left( \frac{\partial P}{\partial T} \right)_V = \frac{L}{T \Delta V} \quad \text{Clapeyron Equation} \]

2. Consider two points \( P \) and \( P' \)
at coordinates \( p, T \) and \( p', T' \) on the co-existence line between the \( L \) and \( V \) phases. The change in Gibbs free energy is
\[ G(q + dp, T + dT) = G(q, T) + \left( \frac{\partial G}{\partial q} \right)_T dp + \left( \frac{\partial G}{\partial T} \right)_q dT \]
\[ dq = v dp = s dT \]

We do this just inside each phase \( \Phi \) above and take the difference to obtain
\[ d(\mathcal{G}_2 - \mathcal{G}_1) = (v_2 - v_1) dp - (s_2 - s_1) dT \]

where \( \mathcal{G} = G/V \) in the Gibbs free energy per particle (or per mole). Since \( s_2 - s_1 \) - the phases are in equilibrium - we have
\[ \frac{dp}{dT} = \left( \frac{s_2 - s_1}{v_2 - v_1} \right) = \frac{\Delta s}{\Delta v} \]

where \( \Delta s \) and \( \Delta v \) are the entropy and volume changes across the phases.

With \( T \Delta s = \Delta \mathcal{G} = 1 \)

where \( h \) is the latent heat per mole
\[ \left( \frac{dp}{dT} \right) = \frac{1}{T \Delta s} \]

This is the Clapeyron Eq. - sometimes called the Clausius-Clapeyron Eq.