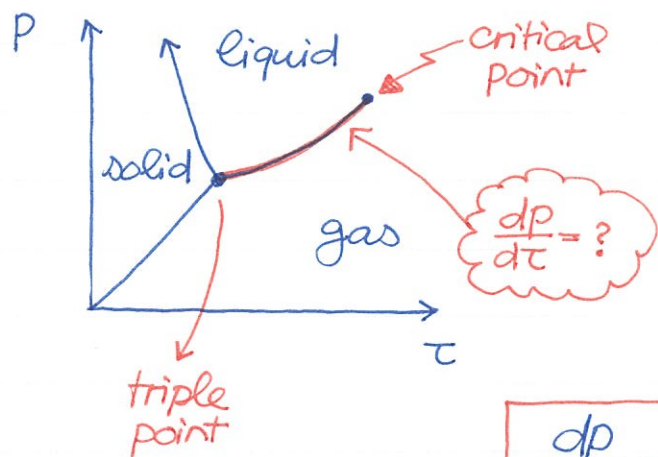


HH0029 Clausius-Clapeyron Equation

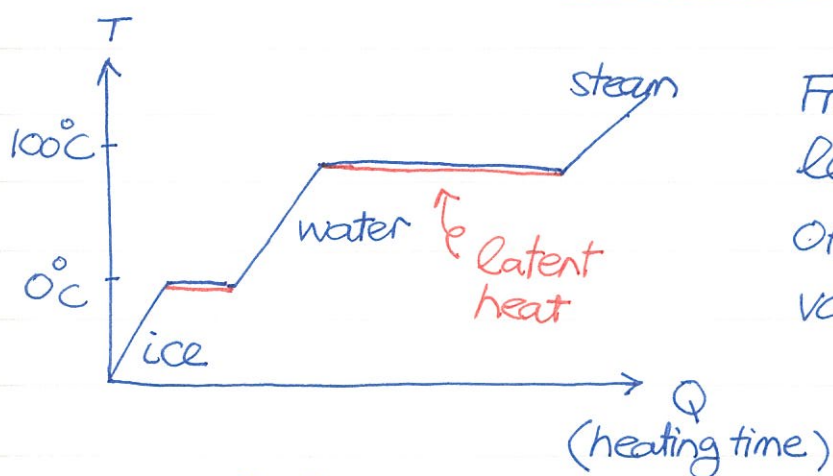
It's helpful to review the phase diagram of water at different pressure and temperature.



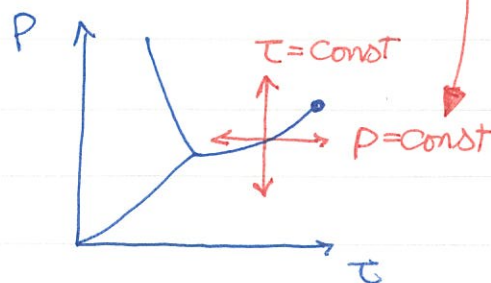
On the boundary between liquid and gas, both phases coexist. Between the critical and the triple points, the slope $dp/d\tau$ satisfies the Clausius-Clapeyron equation:

$$\frac{dp}{d\tau} = \frac{L}{\tau \Delta v}$$

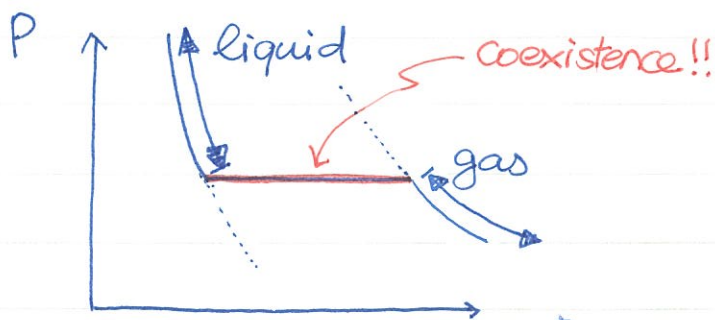
\rightarrow latent heat
 \rightarrow $\Delta v = v_g - v_l$ volume change.



From high-school physics, we learn that certain amount of latent heat is required to vaporize water

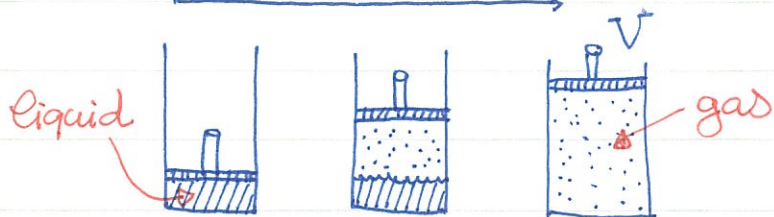


Now let's try to cross the phase boundary vertically ($\tau = \text{const}$)!



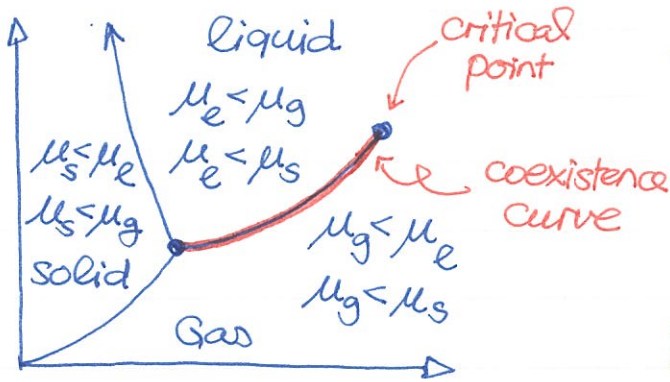
When liquid and gas coexist,

$$\tau_l = \tau_g, P_l = P_g, \mu_l = \mu_g$$



At const τ and p , the right free energy to use is Gibbs free energy G

In the p - τ phase diagram, $G = N\mu$ should be a minimum, implying the minimal chemical potential reigns.



The chemical potentials equal on the coexistence curve:

$$\mu_e(p, \tau) = \mu_g(p, \tau)$$

From this equality, it's straightforward to derive $dp/d\tau$.

review box:

$$f(x, y) = 0 \rightarrow \frac{dy}{dx} = - \frac{\partial f / \partial x}{\partial f / \partial y}$$

$$\begin{aligned} f &\rightarrow \mu_g - \mu_e \\ x &\rightarrow \tau \\ y &\rightarrow p \end{aligned} \quad \frac{dp}{d\tau} = - \frac{\frac{\partial f}{\partial \tau}}{\frac{\partial f}{\partial p}}$$

Written down the explicit partial derivatives,

$$\frac{dp}{d\tau} = - \frac{\left(\frac{\partial \mu_g}{\partial \tau}\right)_p - \left(\frac{\partial \mu_e}{\partial \tau}\right)_p}{\left(\frac{\partial \mu_g}{\partial p}\right)_\tau - \left(\frac{\partial \mu_e}{\partial p}\right)_\tau}$$

$G = N\mu(p, \tau)$ will help here $\ddot{\circ}$

$$\left(\frac{\partial G}{\partial p}\right)_{N, \tau} = V \rightarrow \left(\frac{\partial \mu}{\partial p}\right)_\tau = \frac{V}{N} = v$$

Similarly, one can work out the other partial derivative,

$$\left(\frac{\partial G}{\partial \tau}\right)_{N, p} = -\sigma \rightarrow \left(\frac{\partial \mu}{\partial \tau}\right)_p = -\frac{\sigma}{N} = -s$$

Volume and entropy associated with one molecule.

Substitute into the expression for the slope $dp/d\tau$

$$\frac{dp}{d\tau} = \frac{s_g - s_e}{v_g - v_e}$$

Heat to convert $e \rightarrow g$: $L = \tau (s_g - s_e)$

Volume change $\Delta U = v_g - v_e$.

$$\frac{dp}{d\tau} = \frac{L}{\tau \Delta U}$$

Clausius-Clapeyron equation $\ddot{\circ}$

It's also referred as the vapor pressure equation.

Two approximations make the coexistence curve easy to

(1) $v_g \gg v_e$ so that $\Delta v \approx v_g$

(2) ideal gas law: $pV_g = N_g \tau \rightarrow \Delta v \approx v_g = \tau/p$

The Clausius - Clapeyron equation takes the approximate form

$$\frac{dp}{d\tau} = \frac{L}{\tau \Delta v} \approx \frac{Lp}{\tau^2}$$

Suppose the latent heat $L \approx L_0$ remains constant over the interested τ range,

$$\int \frac{dp}{p} \approx L_0 \int \frac{d\tau}{\tau^2} \rightarrow \log p = -\frac{L_0}{\tau} + \text{const.} \quad p(\tau) = p_0 e^{-L_0/\tau}$$

Latent heat and enthalpy $H = U + pV$

The total differential for H is $dH = dU + pdV + Vdp$. Making use of the thermodynamic identity $dU = \tau d\sigma - pdV + \mu_e dN_e + \mu_g dN_g$

$$dH = \tau d\sigma + Vdp + (\mu_g - \mu_e) dN$$



Across the coexistence curve at constant p, $dp=0$ and $\mu_g = \mu_e$

$$-dN_e = dN_g = dN$$

$$\Delta H = \tau \Delta \sigma = L$$

The change of enthalpy is just the latent heat. The value of H can be related to C_p :

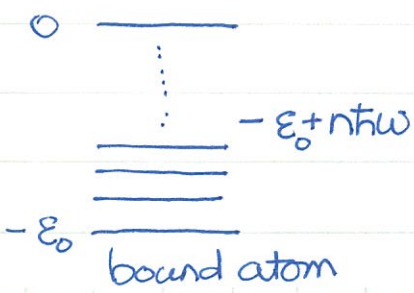
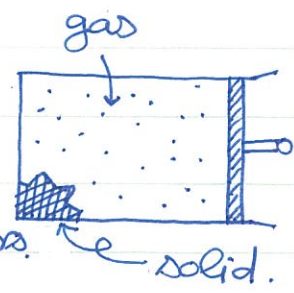
$$C_p = \tau \left(\frac{\partial \sigma}{\partial \tau} \right)_p = \left(\frac{\partial U}{\partial \tau} \right)_p + p \left(\frac{\partial V}{\partial \tau} \right)_p = \left(\frac{\partial H}{\partial \tau} \right)_p$$

no particle change $dN=0$
OR, $\mu_g = \mu_e$ on the coexistence curve.

$$H = \int C_p d\tau$$

Simple model for gas-solid equilibrium

Suppose the solid is captured by the simple harmonic oscillators.



$$Z_s = \left[e^{\epsilon_0/\tau} + e^{(\epsilon_0 + hw)/\tau} + \dots \right]$$

0-phonon
1-phonon
many phonons ...

Sum up the partition function to get Helmholtz free energy.

$$Z_s = \frac{e^{\epsilon_0/\tau}}{1 - e^{-\hbar\omega/\tau}} \rightarrow F_s = -\tau \log Z_s = -\epsilon_0 + \tau \log(1 - e^{-\hbar\omega/\tau})$$

Because $v_s \ll v_g$, $G_s = F_s + p v_s \approx F_s$. The chemical potential is just the Gibbs free energy per atom,

$$\mu_s = G_s \approx F_s = -\epsilon_0 + \tau \log(1 - e^{-\hbar\omega/\tau})$$

← chemical potential for solid.

Assuming the gas phase is ideal

$$\mu_g = \tau \log\left(\frac{n}{n_\phi}\right) = \tau \log\left(\frac{p}{n_\phi \tau}\right)$$

At the coexistence curve, $\mu_s = \mu_g$

$$e^{-\epsilon_0/\tau} (1 - e^{-\hbar\omega/\tau}) = \frac{p}{n_\phi \tau} \rightarrow p = n_\phi \tau e^{-\epsilon_0/\tau} (1 - e^{-\hbar\omega/\tau})$$

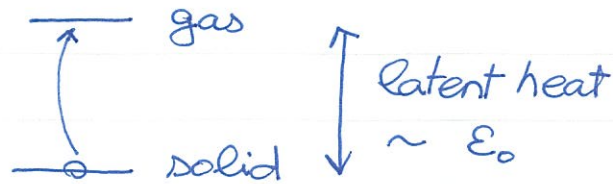
Note that $n_\phi \tau \sim \tau^{5/2}$ gives a smooth temperature dependence.

↑ $\tau^{5/2}$ dependence ↑ phonon correction

The presence of phonons deliver a correction factor $(1 - e^{-\hbar\omega/\tau})$.

The most important dependence is exponential due to ϵ_0 :

$$p(\tau) \sim e^{-\epsilon_0/\tau}$$



The latent heat

is roughly ϵ_0 , i.e. the energy to transform a molecule in solid into gas ☺



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