Phase Transitions, Part 4

Last time

Mean-field theory

Real gases and liquids

Today

Thermodynamics of phase transitions

Chemical potential

Phase diagrams

Next time

Heat capacity

Calorimetry

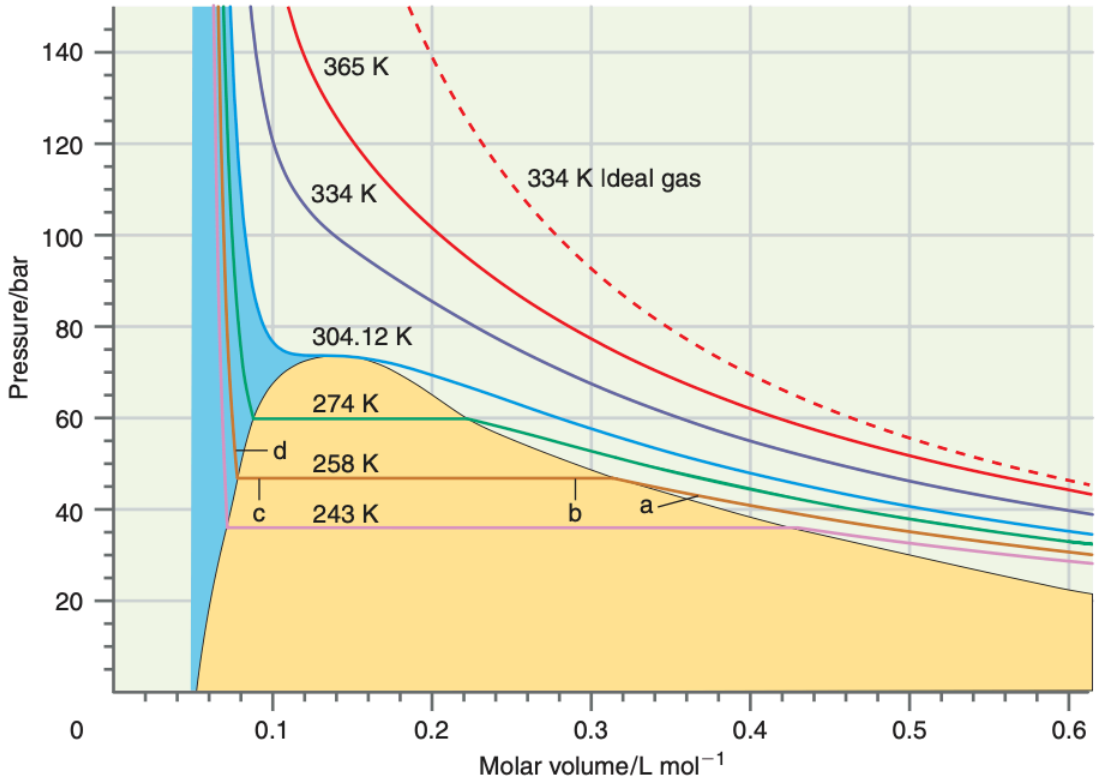
Last time

Mean-field theory:

- Approximates individual interactions with average interactions
- Predicts sharp phase transitions in Ising and van der Waals models

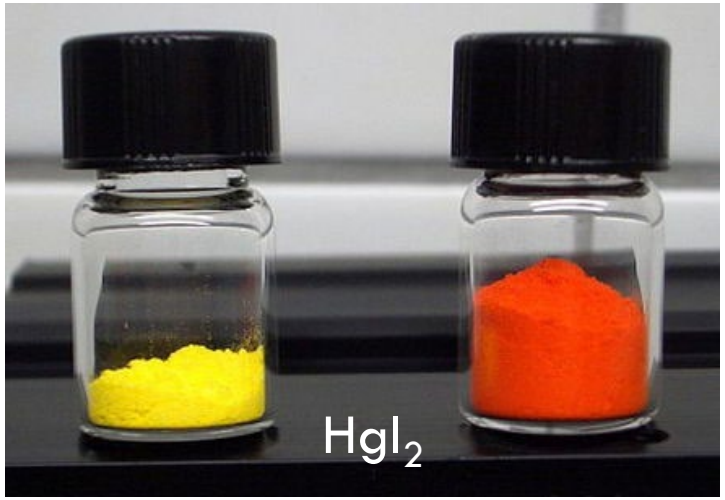
Van der Waals fluid

- Predicts gas/liquid coexistence
- Predicts supercritical fluids



Thermodynamics of phase transitions







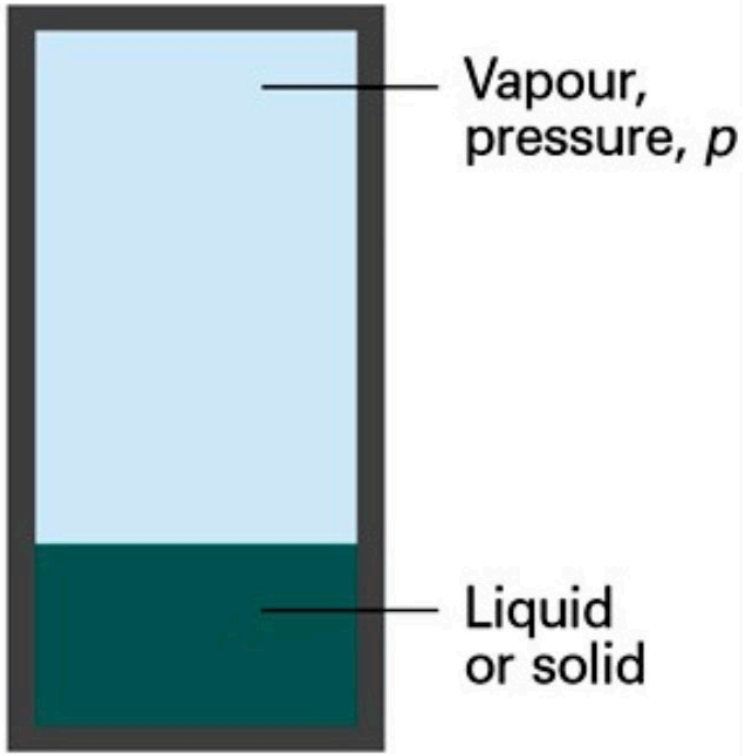




Thermodynamics of mixtures

So far, we looked at the thermodynamics of systems with fixed composition, usually with one phase.

Today, we will consider mixtures, changing compositions, and phase equilibrium



Chemical potential

We will consider processes at constant pressure, so we focus on G:

$$dG = \underbrace{\left(\frac{\partial G}{\partial T}\right)_{p,n_i}}_{-S} dT + \underbrace{\left(\frac{\partial G}{\partial p}\right)_{T,n_i}}_{V} dp + \sum_i \underbrace{\left(\frac{\partial G}{\partial n_i}\right)_{T,p}}_{\mu_i} dn_i$$

The chemical potential μ_i is the change in the Gibbs free energy per mole of substance added *i* (in the limit of small changes)

I.e., the chemical potential is the molar Gibbs free energy, $\mu_i = \Delta G_{m,i}$

Chemical potential

At constant *T* and *p*:

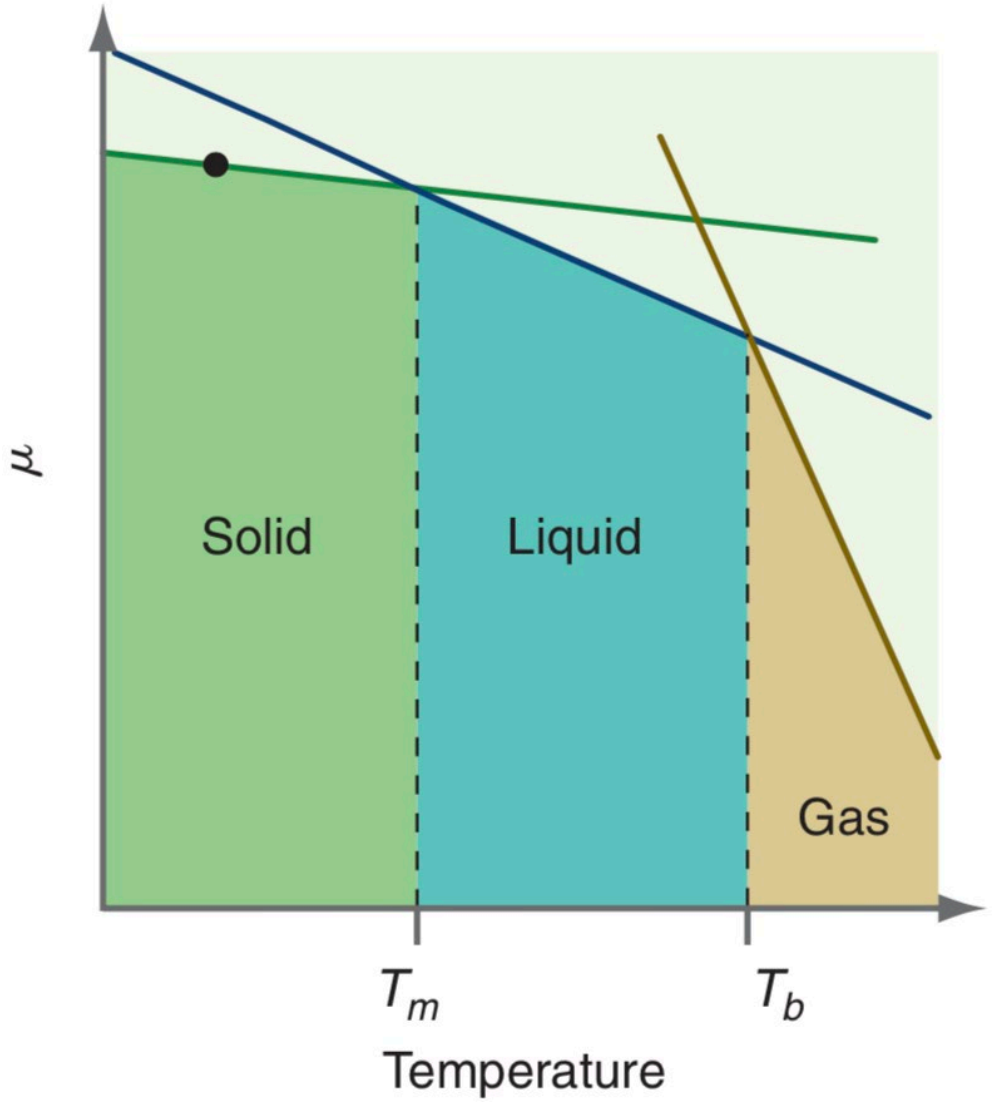
$$dG = \sum_i \mu_i \, dn_i$$

The chemical potential describes transport of substances. Species *i* will spontaneously move from region I to region II only if the chemical potential μ_i^I is higher than μ_i^{II}:

$$dG = \mu_i^I dn_i^I + \mu_i^{II} dn_i^{II} = -\mu_i^I dn_i + \mu_i^{II} dn_i = \left(\mu_i^{II} - \mu_i^I\right) dn_i < 0$$

At equilibrium, the chemical potential of all species is uniform throughout a mixture.

Phase stability



Phase stability

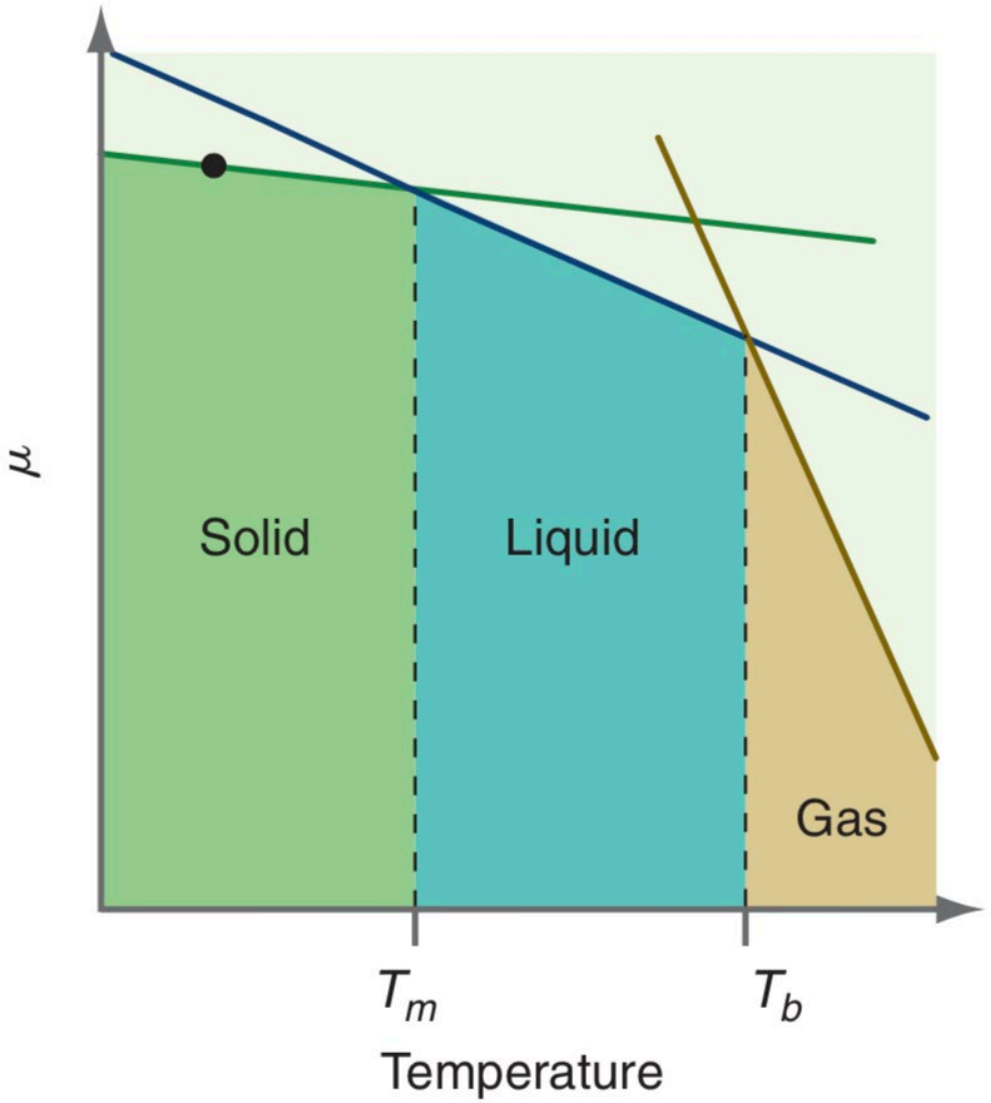
The curves always slope down

$$dG = Vdp - SdT$$

$$d\mu = V_m dp - S_m dT$$

Hence,

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m < 0$$



Phase stability

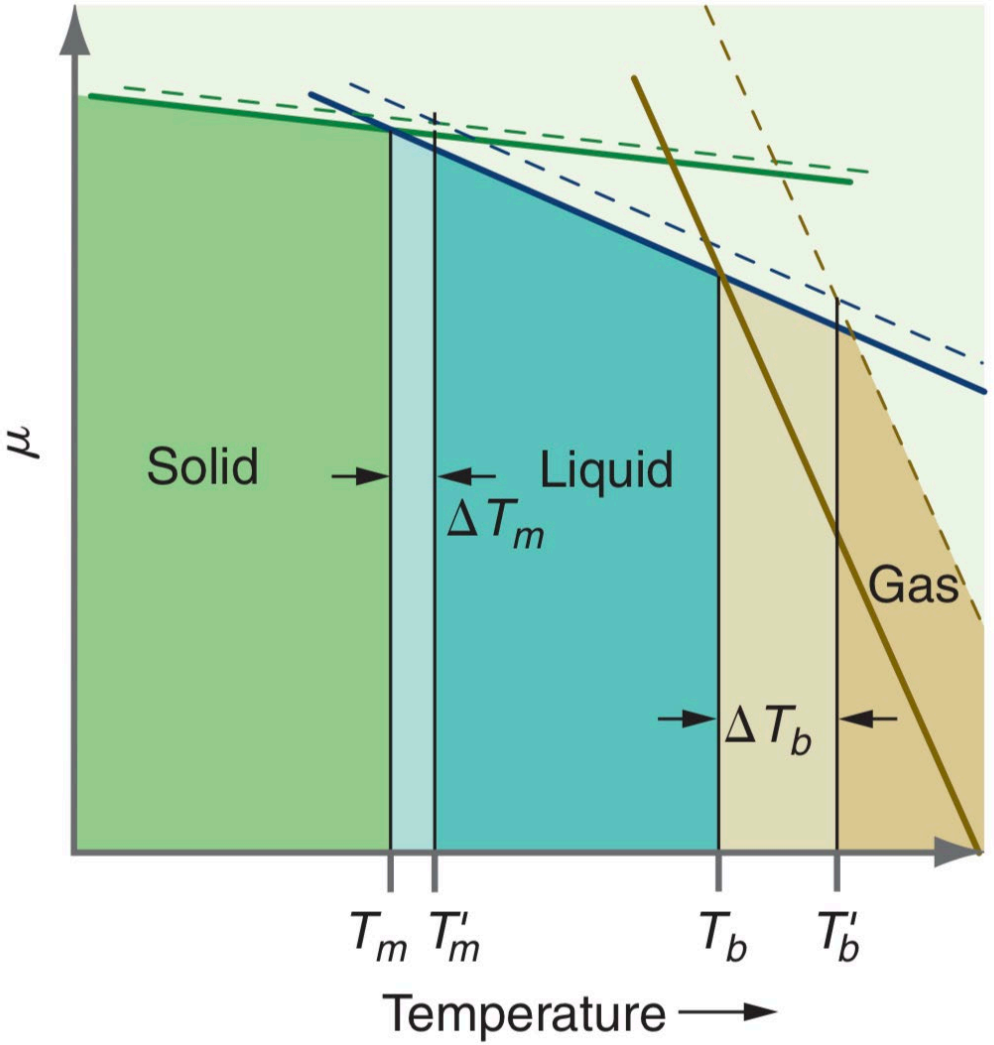
Similarly,

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m > 0$$

Therefore, the curves go up at increased pressure (denoted by dashed lines and primed temperatures).

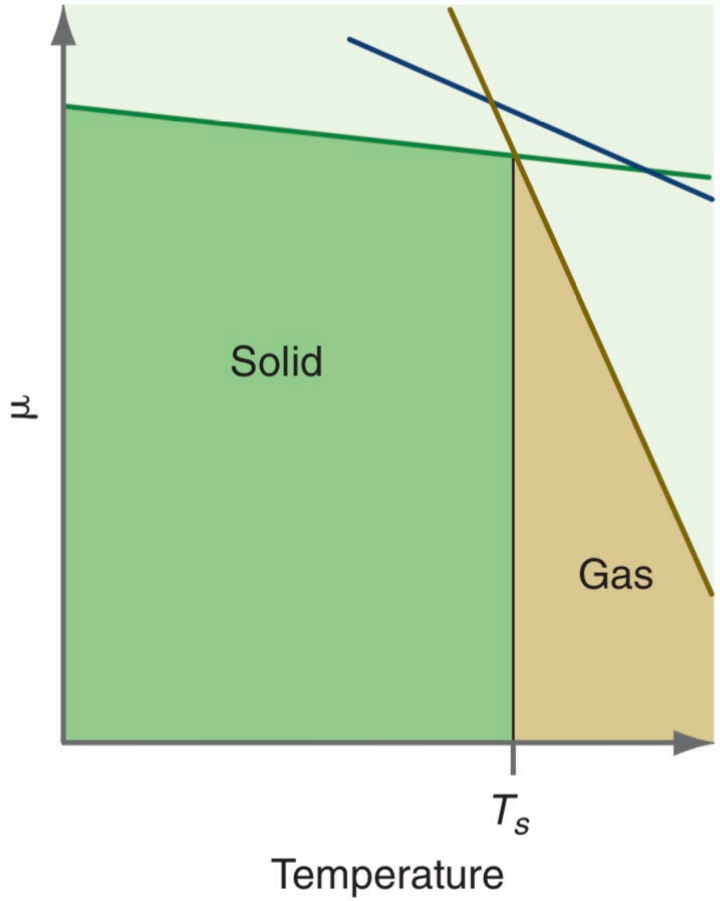
Diagram at right assumes

$$V_m^{liquid} > V_m^{solid}$$

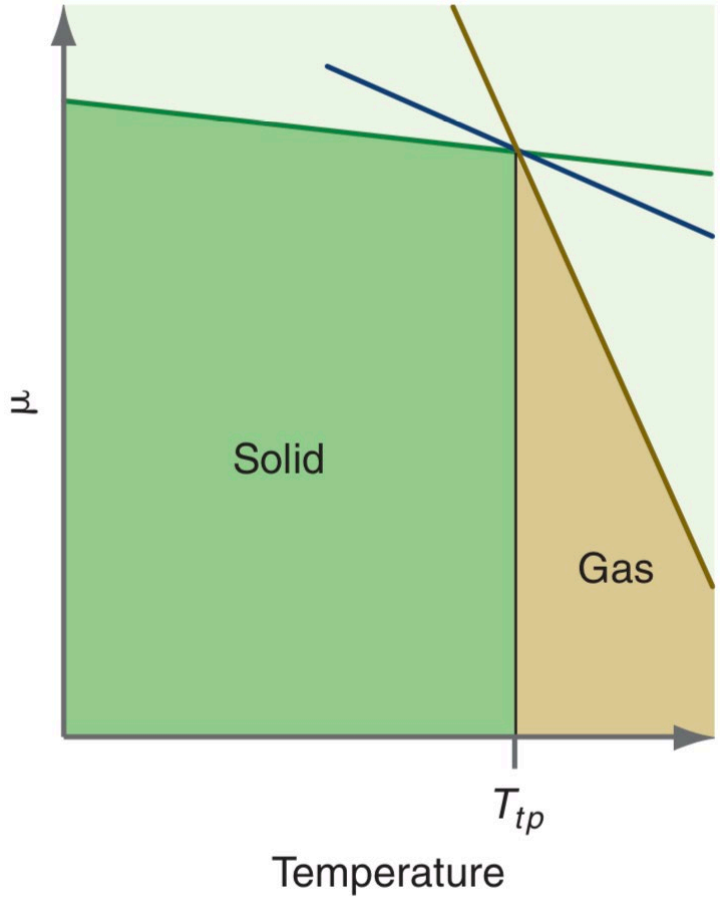


Phase stability

Sublimation



Triple point

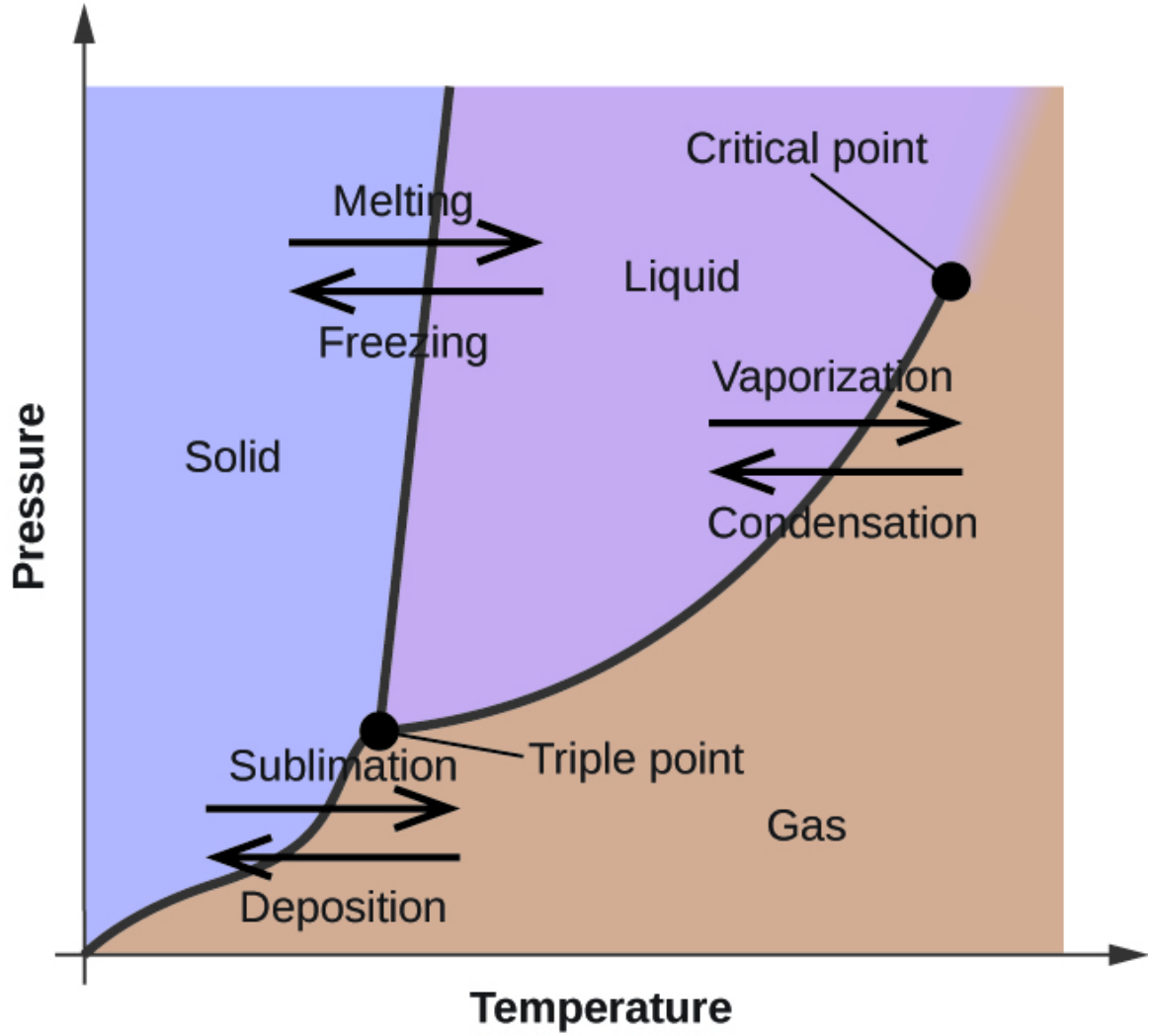


Triple point of water (0.01 °C, 612 Pa)



UCSC Physics, https://youtu.be/Juz9pVVsmQQ

Simple *pT* phase diagram

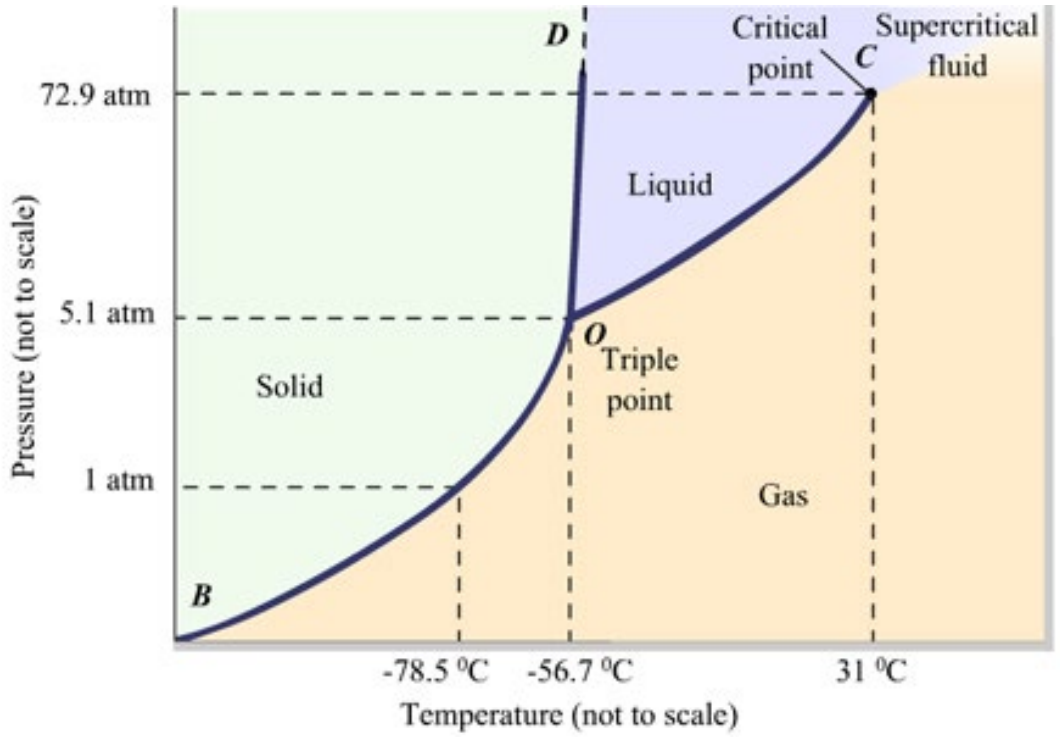


Mentimeter

Critical behaviour

Beyond the critical point, it is impossible to distinguish liquid from gas—there is only *supercritical fluid*

Supercritical CO_2 is easily achieved and is often used as a solvent (e.g. for decaffeinating coffee), because it can be completely removed by lowering the pressure.

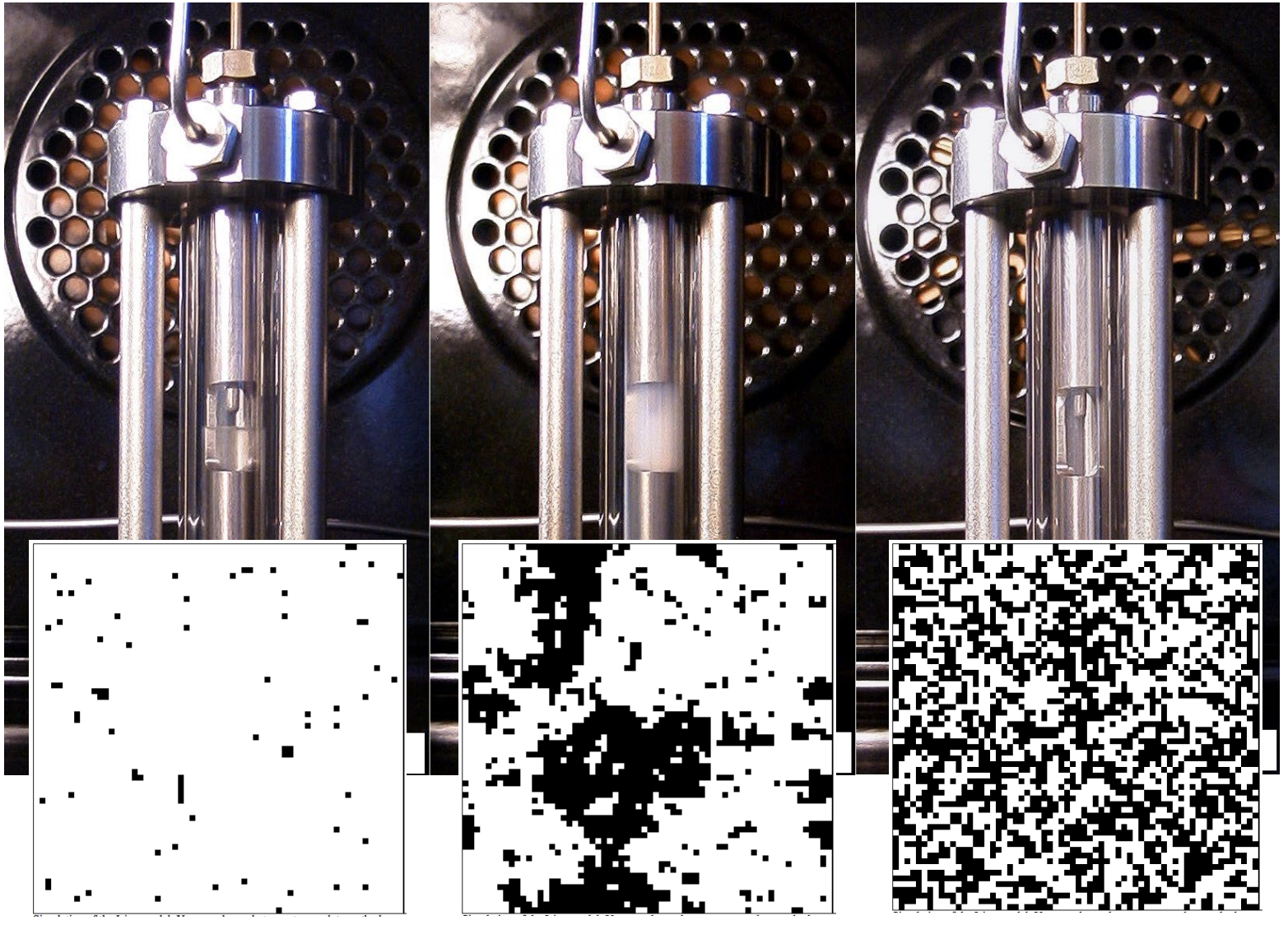


Critical behaviour

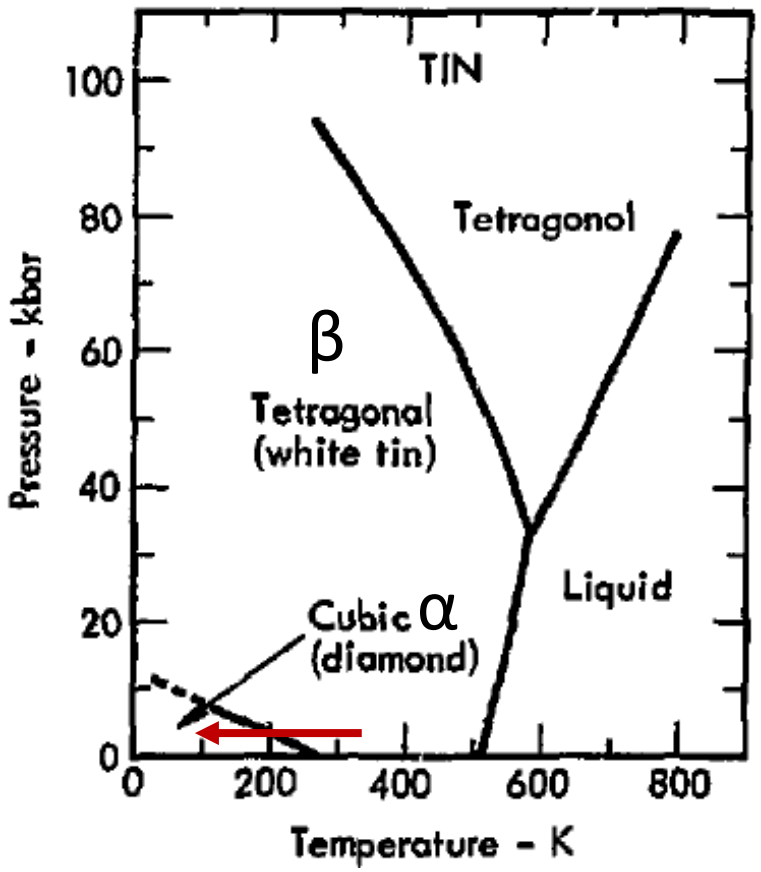
Ethane:

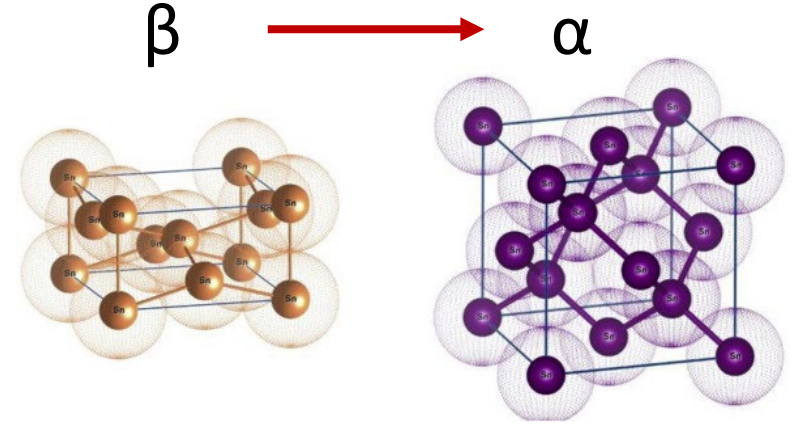
1. Subcritical
2. At critical point (note critical opalescence)
3. Supercritical fluid

Compare to the structure in the Ising model



Solid phases: Allotropy of tin





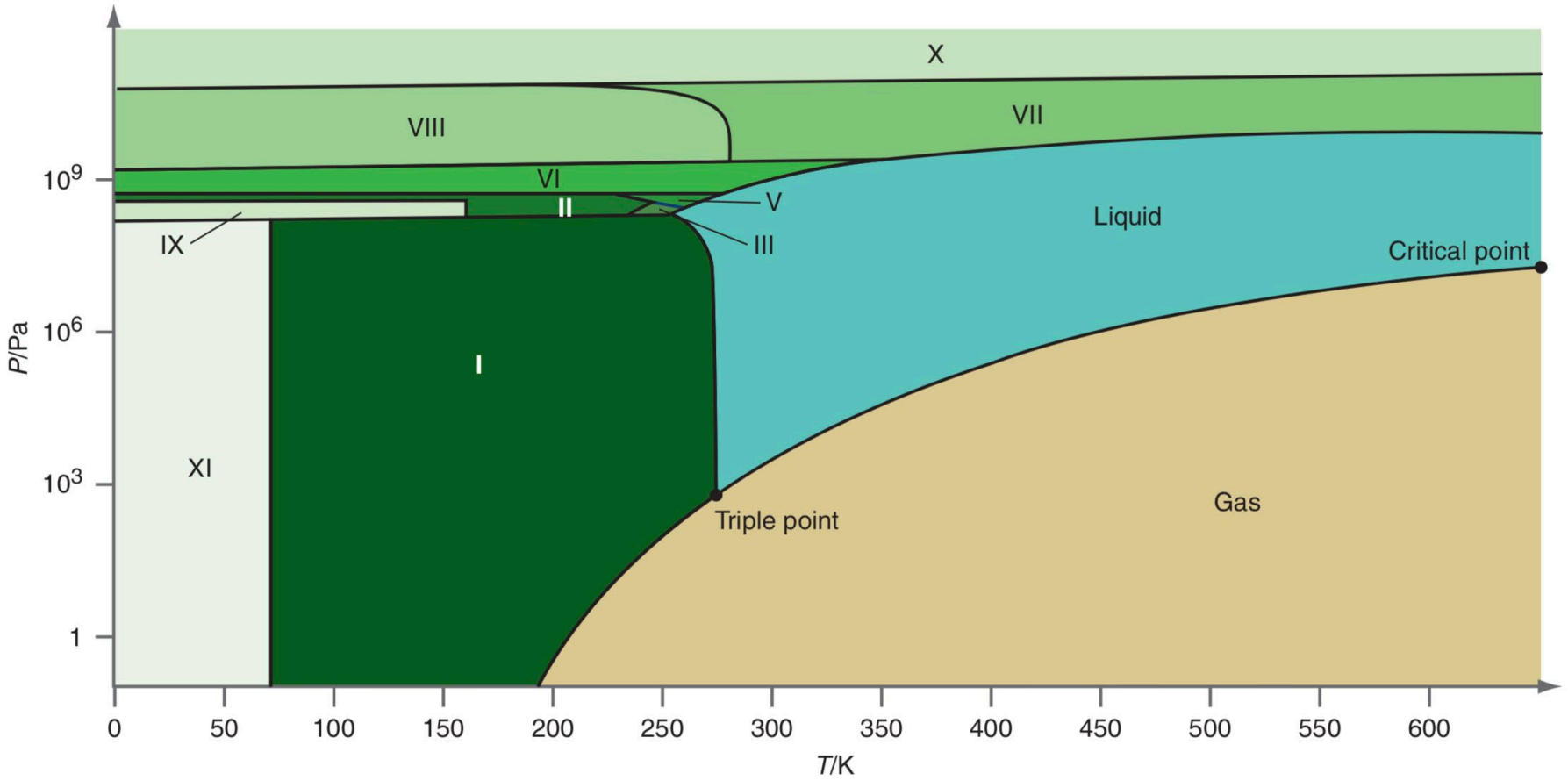


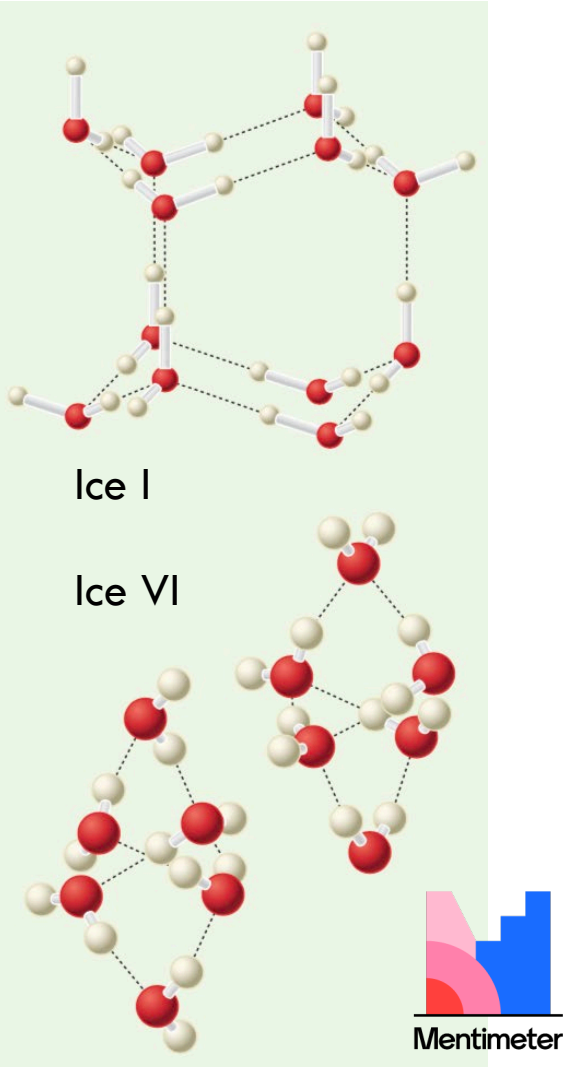


Tin pest, upon cooling below 13°C

In mediaeval times, tin organ pipes would degrade in northern Europe

Phase diagram of water





Mentimeter

Location of phase boundaries

At a coexistence curve,

$$\mu_\alpha(p,T) = \mu_\beta(p,T)$$

Along a coexistence curve,

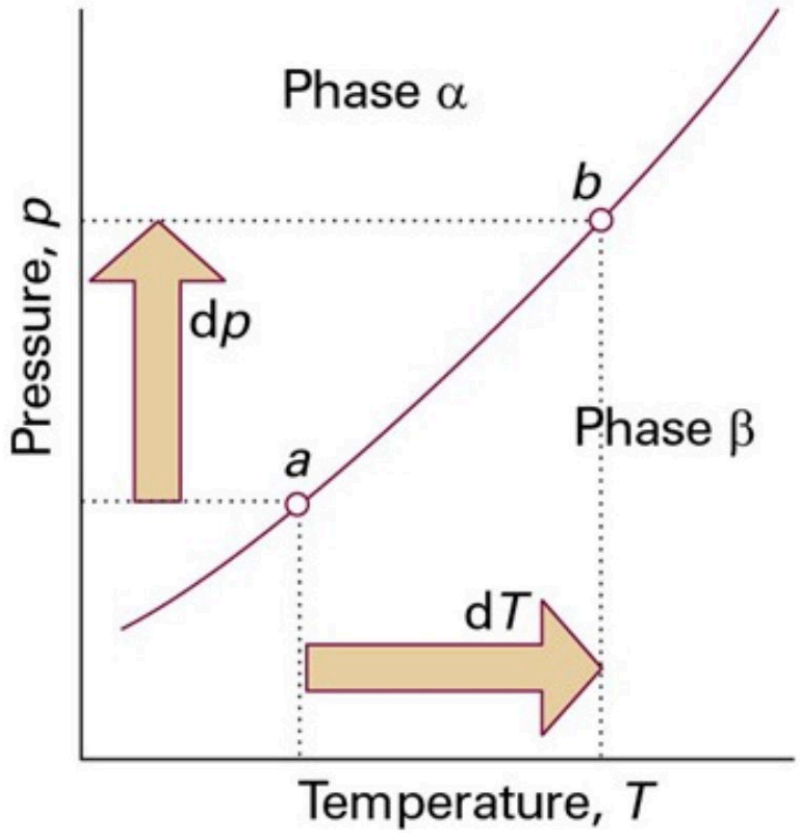
$$d\mu_\alpha = d\mu_\beta$$

$$-S_{m,\alpha}\,dT + V_{m,\alpha}\,dp = -S_{m,\beta}dT + V_{m,\beta}dp$$

$$\left(V_{m,\beta} - V_{m,\alpha}\right)dp = \left(S_{m,\beta} - S_{m,\alpha}\right)dT$$

$$\frac{dp}{dT} = \frac{\Delta S_{m,tr}}{\Delta V_{m,tr}}$$

This is the *Clausius-Clapeyron equation*

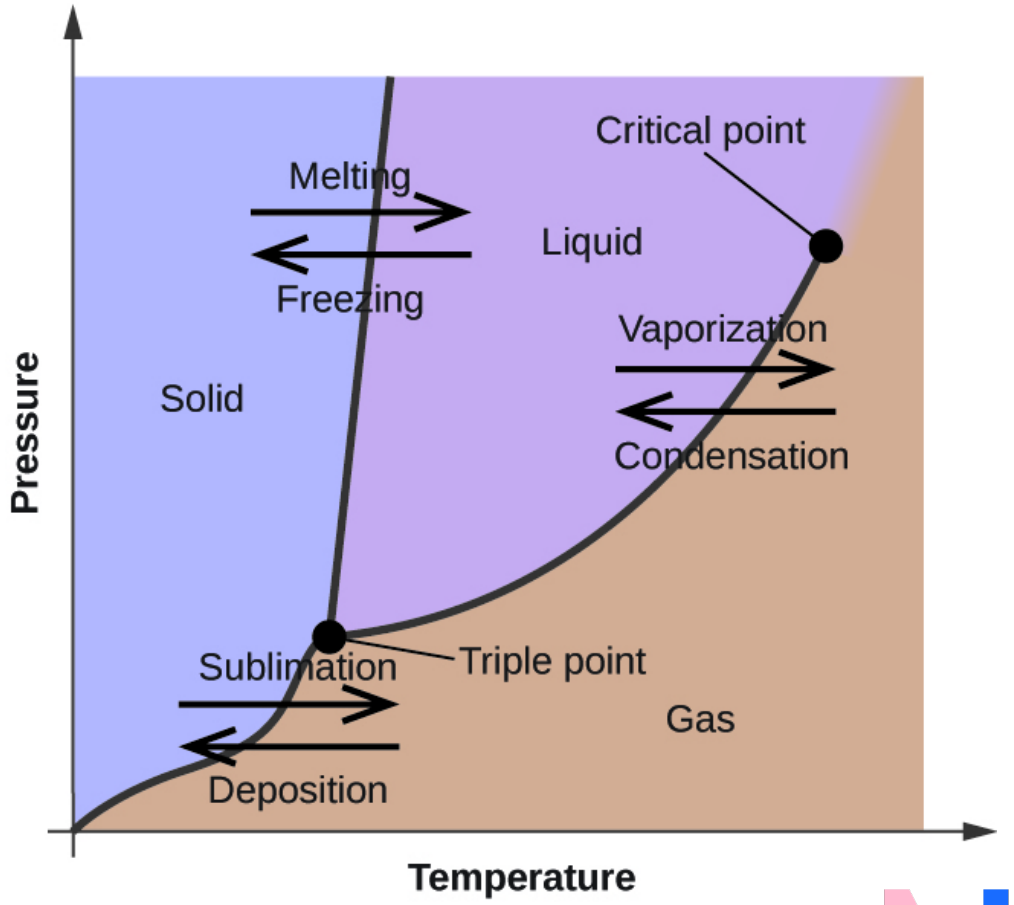


Location of phase boundaries

$$\frac{dp}{dT} = \frac{\Delta S_{m,tr}}{\Delta V_{m,tr}}$$

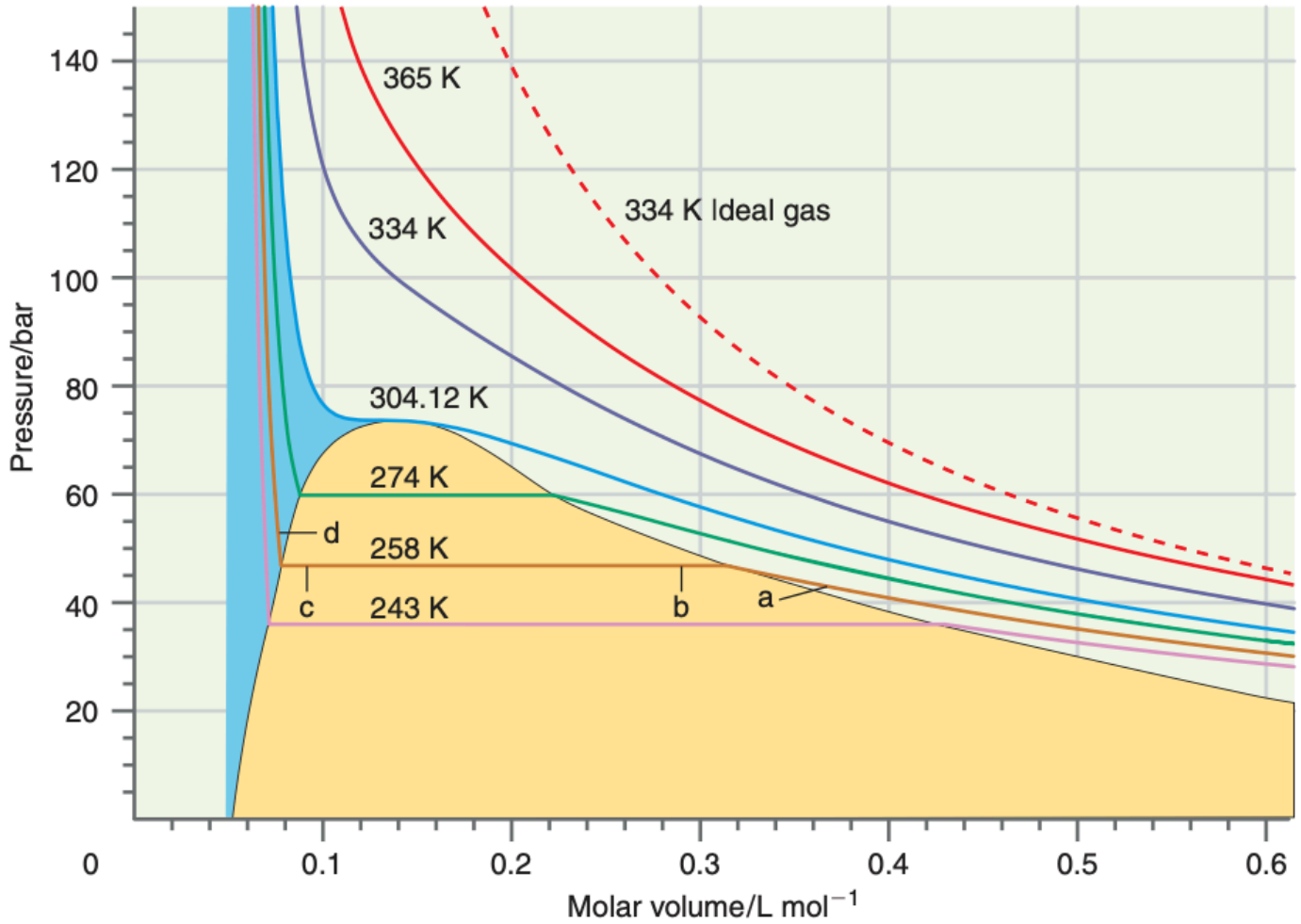
The solid-liquid coexistence curve is usually steep because $\Delta V_{m,melt}$ is small

The liquid-gas transition has a larger $\Delta V_{m,vap}$ and is usually more sensitive to pressure (i.e., more curved)

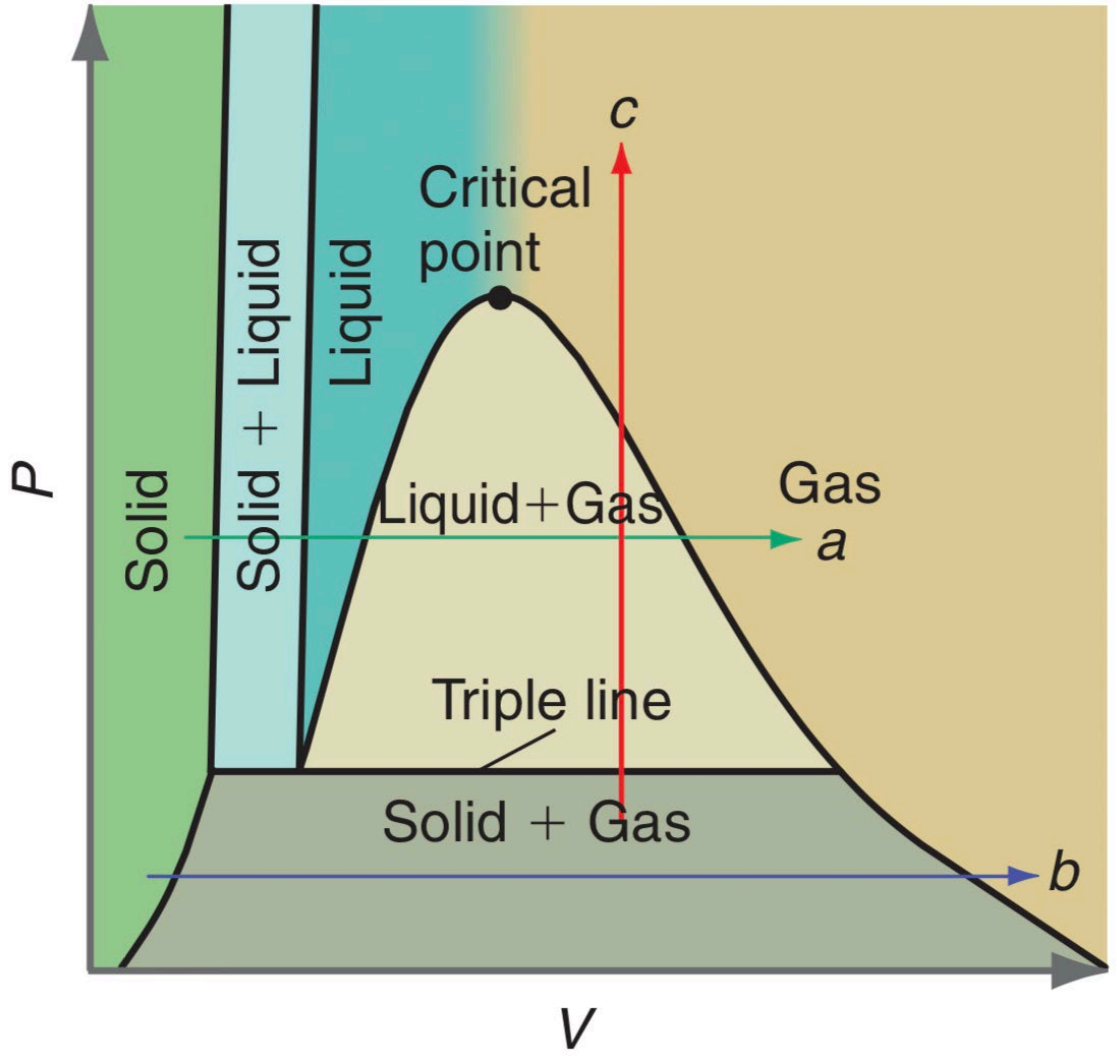


Mentimeter

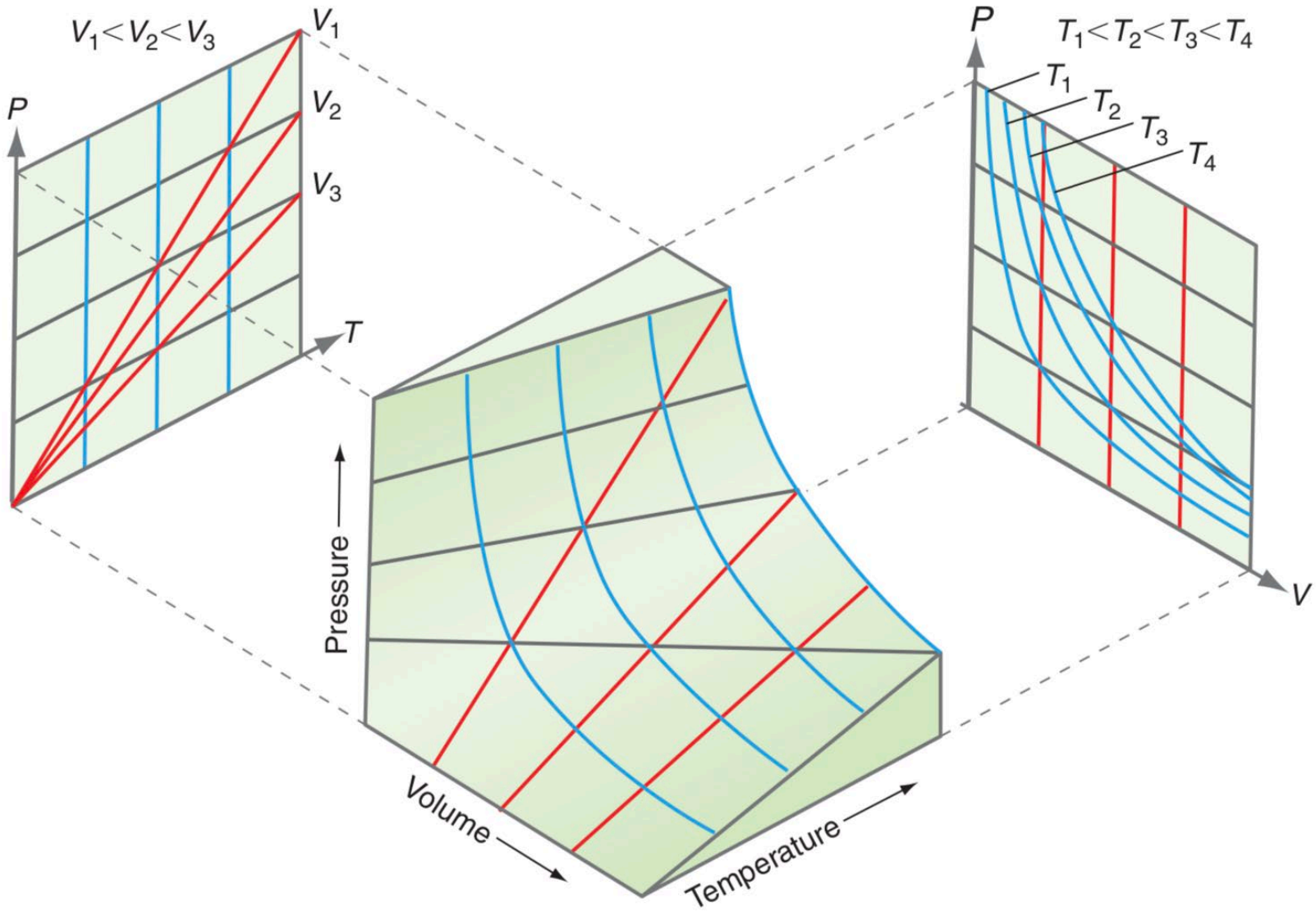
pV phase diagram of vdW fluid



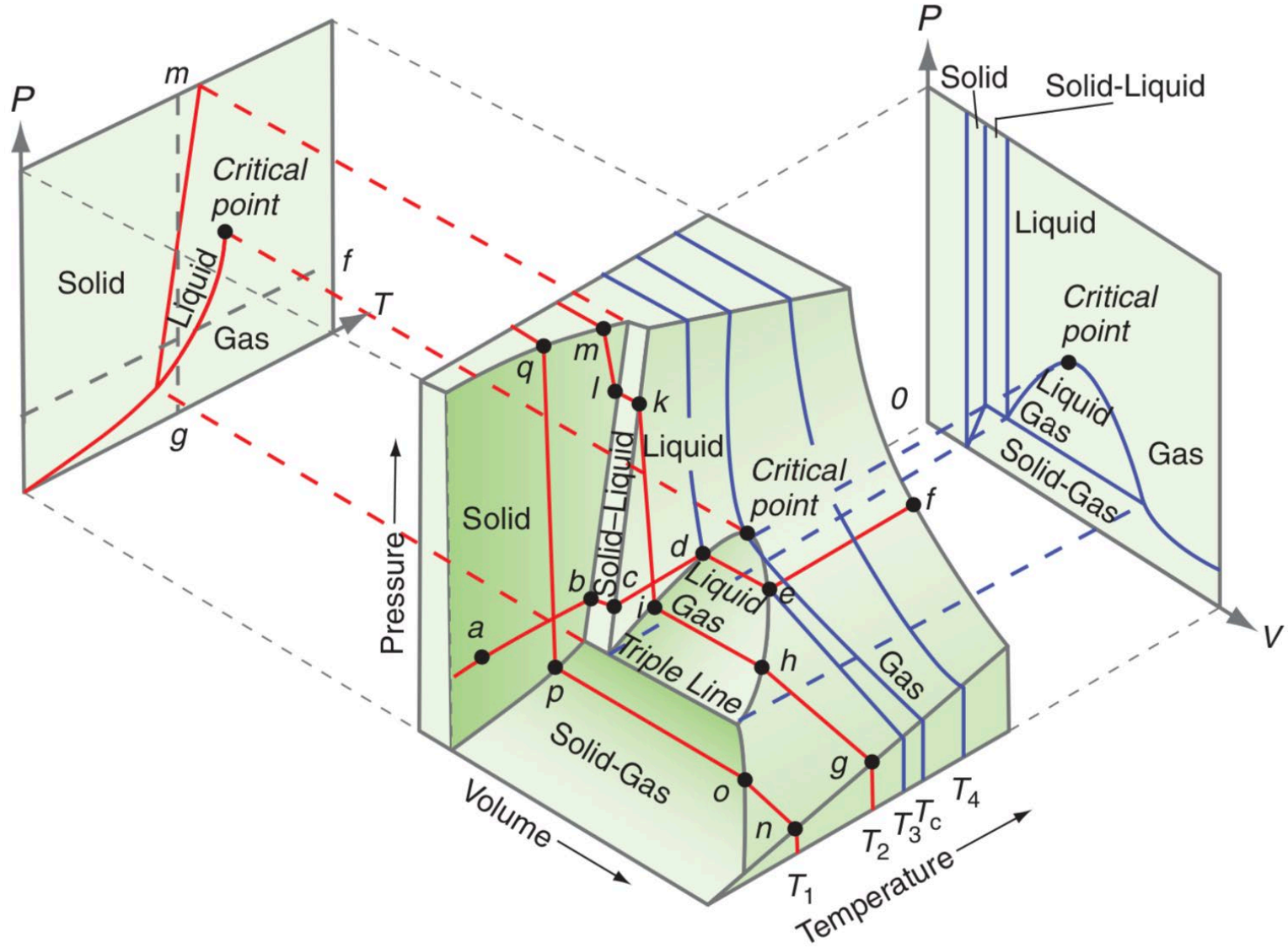
More general *pV* phase diagram



Extra material: *pVT* diagram for ideal gas



Extra material: More complicated *pVT* diagram



Summary

Key points:

- The chemical potential is the Gibbs free energy per particle
  - It determines which phase is more stable
- Phase diagrams contain a wealth of information about phase equilibrium in a substance and its phase transitions

Next time

Next time, we will look at experimental techniques for monitoring phase transitions, especially calorimetry.

Reading:

E&R (either book) 4.5–4.6