
Phase Equilibria: One component systems

Phase diagrams

Clapeyron Equation

Phase Rule

• Phase Equilibria in a One Component System

Goal: Understand the general phenomenology of phase transitions and phase coexistence conditions for a single component system.

The **Chemical Potential** μ controls phase transitions and phase equilibria, as well as equilibrium in chemical reactions.

Know that at equilibrium, μ of each component is the same everywhere in the system

If have multiple phases μ_i , must have same value in every phase. Here we'll deal with **one component** systems only.

Remember our definition of μ :

$$\mu = \frac{G}{n}$$

Fundamental equation:

$$dG = -SdT + Vdp$$

divide by n

$$d\mu = -\bar{S}dT + \bar{V}dp$$

$\mu(T,P)$

$$d\mu = \left(\frac{\partial\mu}{\partial T}\right)_P dT + \left(\frac{\partial\mu}{\partial p}\right)_T dp$$

This allows us to say that

$$\left(\frac{\partial\mu}{\partial T}\right)_P = -\bar{S} \quad \text{and} \quad \left(\frac{\partial\mu}{\partial p}\right)_T = \bar{V}$$

Why are we interested in μ ?

Phase with the lowest value of μ is the most stable phase

For example, consider two phases (liquid and solid) of water at a fixed (T, p).

- If $\mu_s(T, p) = \mu_l(T, p)$ then... liquid water and ice coexist
- If $\mu_s(T, p) > \mu_l(T, p)$ then... the water is in the liquid phase
- If $\mu_s(T, p) < \mu_l(T, p)$ then... the water is in the solid phase

How does $\mu(T)$? **Slope of line is entropy**

$$\left(\frac{\partial \mu_s}{\partial T}\right)_p = -\bar{S}_s$$

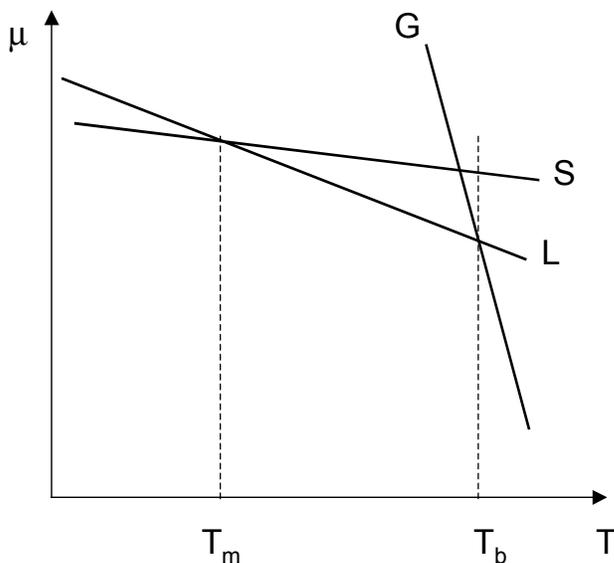
steepest negative

$$\left(\frac{\partial \mu_l}{\partial T}\right)_p = -\bar{S}_l$$

$$\left(\frac{\partial \mu_g}{\partial T}\right)_p = -\bar{S}_g$$

shallowest negative

$$S_{\text{gas}} \gg S_{\text{liq}} > S_{\text{solid}}$$



at a given T, pick the lowest value

Note also: @ $T=T_m$, solid and liquid phases coexist

$$\mu_s(T, p) = \mu_l(T, p)$$

Now, want to describe phase properties as a function of state variables, (p, T).

What happens if we change p? Our diagram hasn't accounted for that yet.

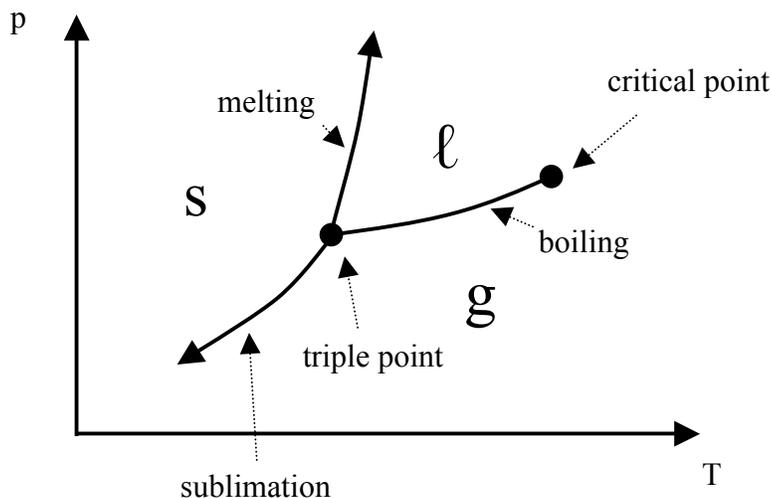
$$\left(\frac{\partial \mu}{\partial p}\right)_T = \bar{V} \quad d\mu = \bar{V} dp$$

If decrease p, $dp < 0$, $d\mu < 0$ so lines get **shifted down**.

Let's make a better diagram that has (p, T) as the variables

• Phase diagrams

Describe the phase properties as a function of state variables, for example in terms of (T, p).



phase diagram or an equilibrium diagram

Every point on the diagram represents a state of the system

Important parts of the phase diagram:

1) planar regions (areas in between lines)

For example: @ (p_1, T_1) : solid is the equilibrium phase. T and p can be changed independently in this region without changing the phase

In the single phase (planar) regions of the diagram, one of the chemical potentials is lower than the other two. T and p can be changed independently without changing phases.

2) Lines

Indicate coexistence of two phase

For the melting line, for example, solid and liquid coexist

on this line:

$$\mu_s(T, p) = \mu_l(T, p)$$

One equation $[\mu_s(T, p) = \mu_l(T, p)]$, two variables (T, p). This means that coexistence of two phases is described by $T=f(p)$ or $p=g(T)$. e.g. a line in the (T, p) phase diagram.

3) Triple point

At the triple point, the chemical potential of all three phases are the same... solid, liquid and gas coexist.

$$\mu_s(T, p) = \mu_l(T, p) = \mu_g(T, p)$$

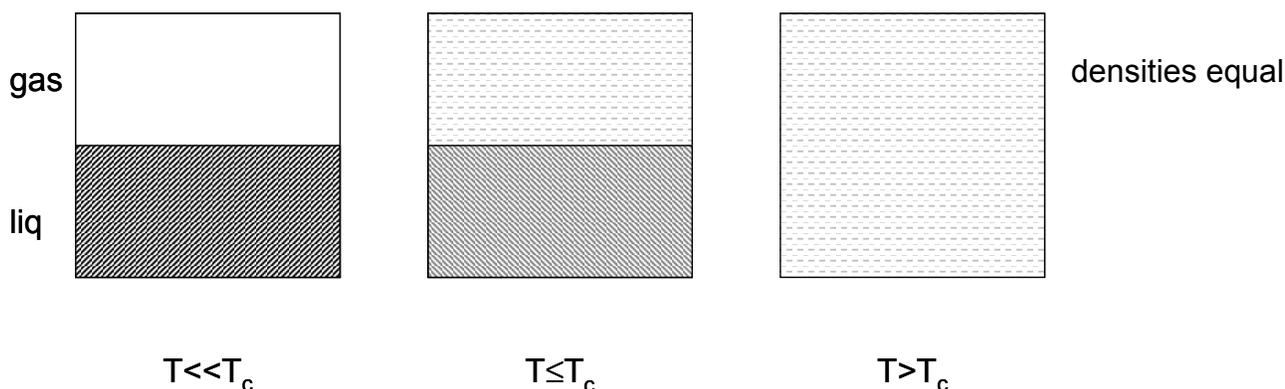
Two equations, two variables. This defines a unique point (T_t , p_t) in the (T , p) phase diagram.

For H_2O , $T_t = 273.16$ K and $p_t = 0.006$ bar

(Recall the definition of the temperature scale in Lecture # 2)

4) Critical point

line does not go on forever! It has a distinct end. it stops at critical point (T_c , P_c).



Above (T_c , P_c), l and g become indistinguishable: single fluid phase for all $T > T_c$, $P > P_c$.

Supercritical fluids are finding remarkably practical applications.

Supercritical water ($T_c = 375$ °C, $P_c = 221$ bar):

organic molecules readily soluble

inorganic salts nearly insoluble

organic compounds oxidized to CO_2 , N_2 , mineral salts

Supercritical carbon dioxide ($T_c = 31$ °C, $P_c = 75$ bar):

reaction solvent, replaces chlorinated and volatile organic compounds

dry cleaning solvent, replaces perchloroethylene

• **Where are the phase boundaries located?**

Can we understand the shape (i.e. slope) of the coexistence lines? For example, can we get an equation for $(dP/dT)_{\text{coexistence}}$?

Goal: to be able to predict, using state functions, phase transitions and equilibria.

Let α and β be two phases (e.g. α, β are l, s, or g).

On a coexistence curve, $\mu_\alpha(T, p) = \mu_\beta(T, p)$

Now take $T \rightarrow T + dT$ and $p \rightarrow p + dp$, staying on the coexistence line.

So then $\mu_\alpha \rightarrow \mu_\alpha + d\mu_\alpha$ and $\mu_\beta \rightarrow \mu_\beta + d\mu_\beta$

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

But since $d\mu = d\bar{G} = -\bar{S}dT + \bar{V}dp$, having $d\mu_\alpha = d\mu_\beta$

implies that $-\bar{S}_\alpha dT + \bar{V}_\alpha dp = -\bar{S}_\beta dT + \bar{V}_\beta dp$ on the coexistence line.

$$\left(\frac{dp}{dT} \right)_{\text{coexist}} = \left[\frac{\bar{S}_\beta - \bar{S}_\alpha}{\bar{V}_\beta - \bar{V}_\alpha} \right] = \left(\frac{\Delta\bar{S}}{\Delta\bar{V}} \right)_{\alpha \rightarrow \beta}$$

$\Delta\bar{S}$ = entropy change when changing from $\alpha \rightarrow \beta$

$\Delta\bar{V}$ = volume change when changing from $\alpha \rightarrow \beta$

Another way to write this is using $\mu = \bar{G} = \bar{H} - T\bar{S}$ so that

$\mu_\alpha = \mu_\beta$ on the coexistence line implies $\bar{H}_\alpha - T\bar{S}_\alpha = \bar{H}_\beta - T\bar{S}_\beta$

or $\Delta\bar{H}_{\alpha \rightarrow \beta} = T\Delta\bar{S}_{\alpha \rightarrow \beta}$. Using this then we obtain the two forms of the **Clapeyron Equation**
 (These are always valid)

$$\left(\frac{dp}{dT} \right)_{\text{coexist}} = \left(\frac{\Delta\bar{S}}{\Delta\bar{V}} \right)_{\alpha \rightarrow \beta} \text{ or } \left(\frac{dp}{dT} \right)_{\text{coexist}} = \left(\frac{\Delta\bar{H}}{T\Delta\bar{V}} \right)_{\alpha \rightarrow \beta}$$

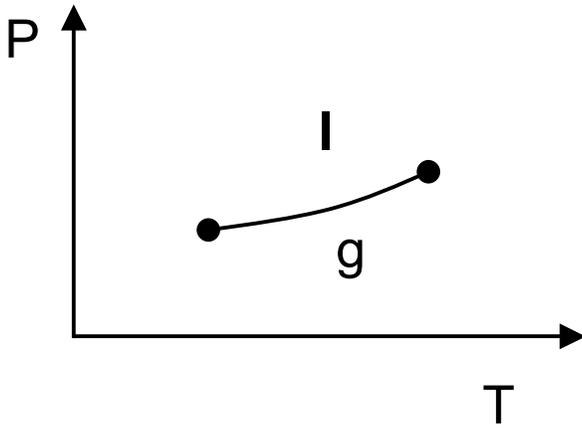
General: can be applied to any phase transition of a pure substance.

Have a good qualitative feel for $\Delta\bar{S}$, $\Delta\bar{V}$ when going from liquid \rightarrow gas, gas \rightarrow solid, etc., so we can use the Clapeyron equation to qualitatively understand the phase diagram.

Lecture 17

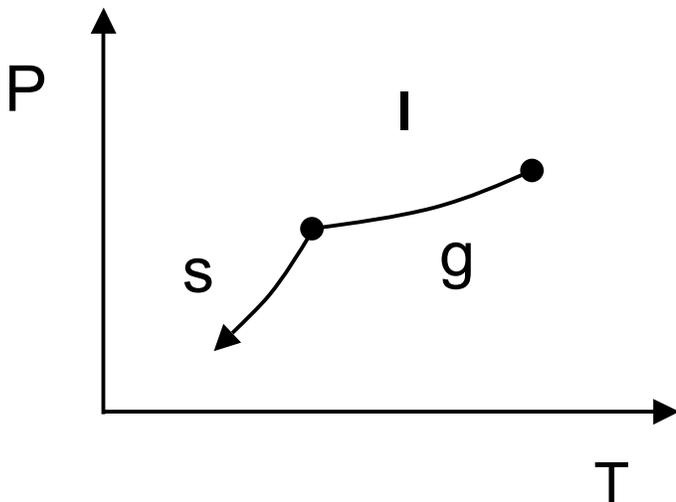
a) $l \rightarrow g$

$$\Delta \bar{S} > 0, \quad \Delta \bar{V} \gg 0 \quad \Rightarrow \quad \left(\frac{dp}{dT} \right)_{\text{coexist}} = \left(\frac{\Delta \bar{S}}{\Delta \bar{V}} \right)_{l \rightarrow g} > 0, \text{ but small (not steep)}$$



b) $s \rightarrow g$

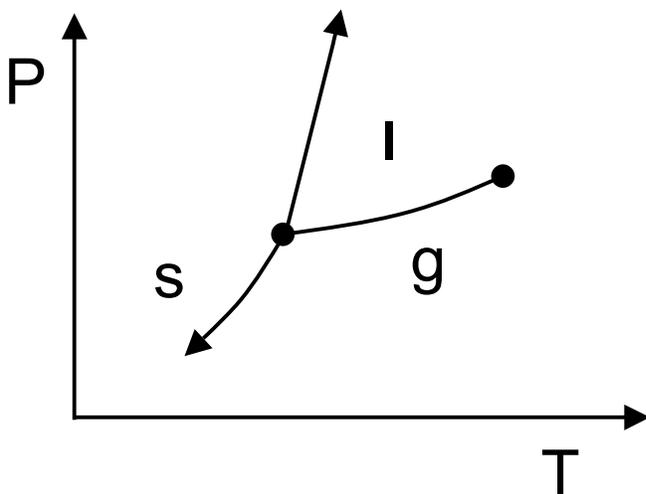
$$\Delta \bar{S} \gg 0, \quad \Delta \bar{V} \gg 0 \quad \Rightarrow \quad \left(\frac{dp}{dT} \right)_{\text{coexist}} = \left(\frac{\Delta \bar{S}}{\Delta \bar{V}} \right)_{s \rightarrow g} > 0, \text{ and steeper than for } l \rightarrow g$$



c) s → l

For most substances $V_l \geq V_s$ (almost equal) and $\bar{S}_l > \bar{S}_s$

$$\Rightarrow \left(\frac{dp}{dT} \right)_{\text{coexist}} = \left(\frac{\Delta \bar{S}}{\Delta \bar{V}} \right)_{s \rightarrow l} > 0, \text{ and very steep}$$



For most substances, raising the pressure above a liquid near the *liq* to solid coexistence line can cause it to freeze

Except for one of the most important substances on earth: H₂O. In this case $\bar{V}_l < \bar{V}_s$, so that

$$\left(\frac{dp}{dT} \right)_{\text{coexist}} < 0 .$$

Thus increasing the pressure above ice can cause it to melt, and the bottom of the ocean is not ice, but liquid water at 4°C.

Interestingly enough, silicon shows similar behavior (at much higher temperatures).

• **The Phase Rule**

How many intensive variables are needed to describe state of a system?

- If have two phases:
 - ∴ only **one** intensive variable (T or p) is needed to describe state of the system
 - system has one degree of freedom

- If one phase is present, **two** variables needed to describe state (T and p)
system has two degrees of freedom

- If have three phases(α, β, γ):

$$\mu_{\alpha}(T, p) = \mu_{\beta}(T, p) \quad \text{and also} \quad \mu_{\alpha}(T, p) = \mu_{\gamma}(T, p)$$

two equations, two unknowns: T and p are completely determined.

# phases present	1	2	3
degrees of freedom	2	1	0

Can construct a simple rule for a one component system:

$$F = 3 - P$$

F = degrees of freedom

P = number of phases present