

Lecture 19 – Phase transformations

PREVIOUSLY: In Lect. 11 we discussed the Gibbs free energy, $G(T, p) \equiv U + pV - TS = H - TS$, which is useful for situations maintained at constant T and p (e.g. chemical reactions).

We also found a relationship between G and the chemical potential μ :

$$G = \sum_{i=1}^n N_i \mu_i(T, p) \quad \text{and} \quad dG = -SdT + Vdp + \sum_{i=1}^n \mu_i dN_i$$

TODAY: Phase transformations

Phase – a macroscopic region of a system in which physical properties are homogeneous

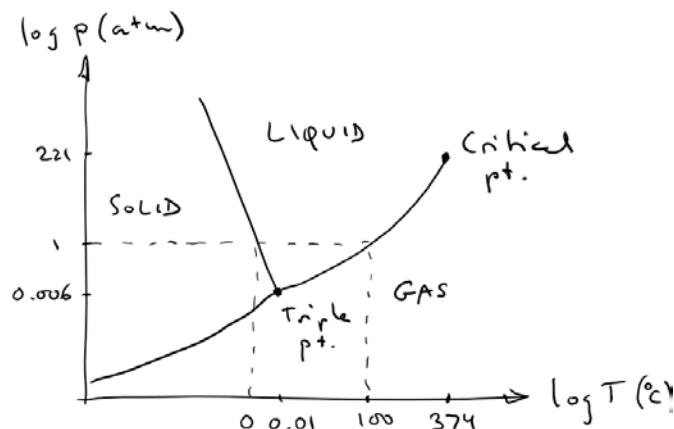
Ex: phases of matter: gas vs. liquid vs. solid
 superfluid/superconducting vs. normal phase
 ferromagnetic vs. paramagnetic phase
 crystallographic phases in solids (e.g. ice I, II, ...)
 alloy phases (e.g. Fe + C, steel)
 ...

Different phases will be favored depending on certain external parameters

(e.g. for gas/liquid/solid – T and p ; for ferromagnet/paramagnet – B field and T ; for two-component alloy – T and % of component of alloy)

KEY CONCEPT: Phase diagram – plot of phases of system vs. parameters they depend on

Ex: phase diagram of H_2O and terminology



Coexistence curves – boundaries where 2 phases coexist, i.e. at equilibrium

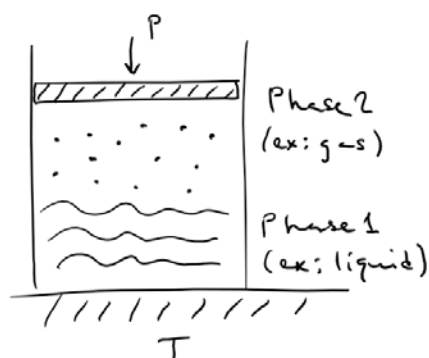
Triple point – condition where all 3 phases coexist, i.e. at equilibrium

Critical point – condition beyond which gas and liquid phases are indistinguishable (i.e. density of gas and liquid are the same)

KEY CONCEPT: Phase coexistence curve and the Clausius-Clapeyron equation

Let's look at behavior along a phase boundary, where two phases 1 & 2 are in equilibrium. For gas/liquid/solid phases, p and T are the parameters so $G = G(T, p)$ is the appropriate thermodynamic potential and G is minimized.

Phase boundary is equivalent to:

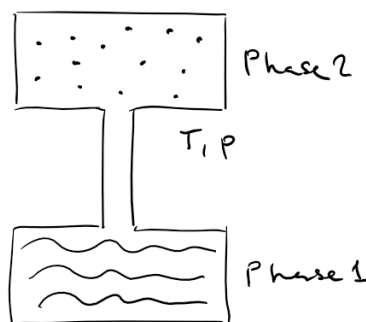


$$G = \sum_{i=1}^2 N_i \mu_i = \underbrace{N_1 \mu_1}_{G_1} + \underbrace{N_2 \mu_2}_{G_2} \quad \text{with } N_1 + N_2 = N_{\text{tot}} \text{ fixed}$$

At constant p and T equilibrium is given by:

$$\begin{aligned} dG = 0 &= -S dT + V dp + \sum_{i=1}^n \mu_i dN_i \\ &= \mu_1 dN_1 + \underbrace{\mu_2 dN_2}_{-dN_1} = (\mu_1 - \mu_2) dN_1 \end{aligned}$$

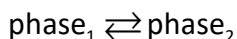
Therefore, $\mu_1(T, p) = \mu_2(T, p)$ along the coexistence curve.



Makes sense. Along phase boundary, phase 1 and 2 are in:
thermal equilibrium $T_1 = T_2$
mechanical equilibrium $p_1 = p_2$
diffusive equilibrium $\mu_1 = \mu_2$

i.e. gas molecules can join liquid phase and vice versa

Note: we can also think about this using chemical equilibrium. A phase transformation is similar to a chemical reaction between two species:



or, written as an equation

$$-1 \cdot \text{phase}_1 + 1 \cdot \text{phase}_2 = 0$$

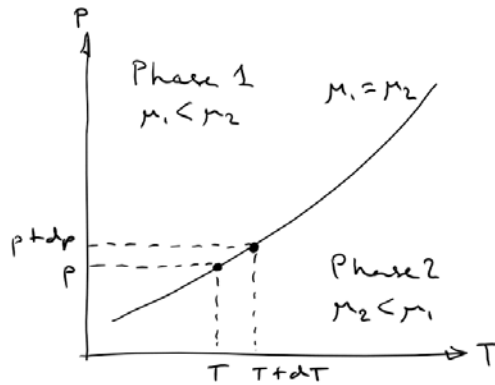
which gives the same equilibrium condition:

$$-\mu_1 + \mu_2 = 0$$

Note that on the coexistence curve

$$G = G_1 + G_2 = N_1 \mu_1 + N_2 \mu_2 = (N_1 + N_2) \mu_1 = N_{\text{tot}} \mu_1$$

G is independent of N_1 or N_2 , so any amount of phase 1 or 2 can coexist, so long as the total number N_{tot} of particles is fixed.



In phase 1: $\mu_1(T, p) < \mu_2(T, p)$
(favors increasing N_1 over N_2)

In phase 2: $\mu_1(T, p) > \mu_2(T, p)$
(favors increasing N_1 over N_2)

Can we relate the coexistence curve to the properties of the phases on either side?

At some p and T on the phase boundary $\mu_1(T, p) = \mu_2(T, p)$. Let's make a small change dT and find dp so that we stay on the coexistence curve:

$$\mu_1(T + dT, p + dp) \approx \mu_1(T, p) + \underbrace{\left(\frac{\partial \mu_1}{\partial T} \right)_p dT + \left(\frac{\partial \mu_1}{\partial p} \right)_T dp}_{d\mu_1}$$

and the same for phase 2.

If we stay on the coexistence curve $\mu_1(T + dT, p + dp) = \mu_2(T + dT, p + dp)$ and $d\mu_1 = d\mu_2$

Question 1: Relate the partial derivatives of μ_i to thermodynamic properties of its phase i

We found previously that $dG = -SdT + Vdp + \sum_{i=1}^n \mu_i dN_i$ so

$$-S = \left(\frac{\partial G}{\partial T} \right)_{p, N} \text{ and } V = \left(\frac{\partial G}{\partial p} \right)_{T, N}$$

Since the free energy of phase 1 is $G_1 = N_1 \mu_1$ this means that

$$\begin{aligned} \left(\frac{\partial \mu_1}{\partial T} \right)_p &= \frac{1}{N_1} \left(\frac{\partial G_1}{\partial T} \right)_{p, N_1} = -\frac{S_1}{N_1} \equiv -s_1 \\ \left(\frac{\partial \mu_1}{\partial p} \right)_T &= \frac{1}{N_1} \left(\frac{\partial G_1}{\partial p} \right)_{T, N_1} = \frac{V_1}{N_1} \equiv v_1 \end{aligned}$$

and similarly for phase 2. Here s_1 is the "entropy per particle", and v_1 is the "volume per particle" (or the inverse of the number density) for phase 1.

So, $d\mu_1 = -s_1 dT + v_1 dp = -s_2 dT + v_2 dp = d\mu_2$ and

$$\left. \frac{dp}{dT} \right|_{\text{coex. line}} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\Delta s}{\Delta v}$$

which is called the Clausius-Clapeyron equation

This equation tells us that the slope of the coexistence curve at some point p, T is related to the change in entropy Δs of the system when one molecule is transferred from phase 1 to 2 (or vice versa) and the change in its volume Δv when one molecule is transferred from phase 1 to 2 (or vice versa).

Ex 1: H₂O phase diagram

At the liquid-gas boundary:

$$\left. \frac{dp}{dT} \right|_{\ell \leftrightarrow g} = \frac{s_g - s_\ell}{v_g - v_\ell} > 0$$

Makes sense: $v_g \gg v_\ell$ (the density of a gas is much less than that of a liquid), and $s_g > s_\ell$ (a gas molecule has many more accessible states than a liquid molecule).

Question 2: What does the coexistence curve for solid and liquid H₂O say about their entropies and volumes per molecule?

The solid-liquid phase boundary for H₂O has a negative slope:

$$\left. \frac{dp}{dT} \right|_{s \leftrightarrow \ell} = \frac{s_\ell - s_s}{v_\ell - v_s} < 0$$

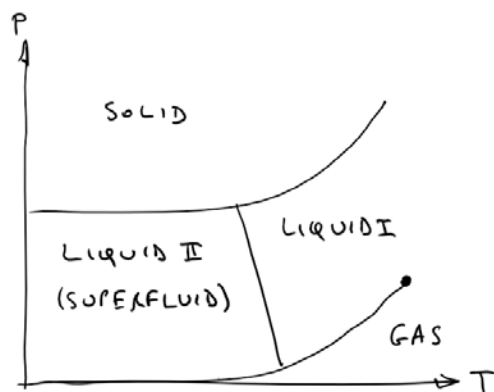
$s_\ell > s_s$ (ice is more ordered than liquid water, so its entropy must be less), but $v_\ell < v_s$ (ice is actually less dense than liquid water! Remember that ice floats)

(Note: water is unusual in that it expands upon freezing. For most materials $v_\ell > v_s$ and

$$\left. \frac{dp}{dT} \right|_{s \leftrightarrow \ell} > 0)$$

At the critical point the phases are indistinguishable so $\Delta s = 0$ and $\Delta v = 0$

$\left. \frac{dp}{dT} \right|_{\text{crit. pt.}}$ is singular and coexistence line ends



Ex 2: superfluid ^4He

The phase boundary between solid and superfluid ^4He is almost horizontal, so $s_{\text{LI}} \approx s_s$

In most materials, the solid is more ordered so $s_s > s_l$, but the superfluid phase is a Bose-Einstein condensate (roughly) which is a low entropy state.

KEY CONCEPT: First and second order phase transitions

For some phase transitions, $\Delta s = 0$ identically. There are two classes of phase transitions:

First order*	Second order (now called "continuous")
$S(V)$ change discontinuously across transition	$S(V)$ change continuously across transition
Ex: gas/liquid/solid transitions except at critical point	Ex: ferromagnet/paramagnet transitions, transitions at critical point

(* "First order" because S, V are first derivatives of G)

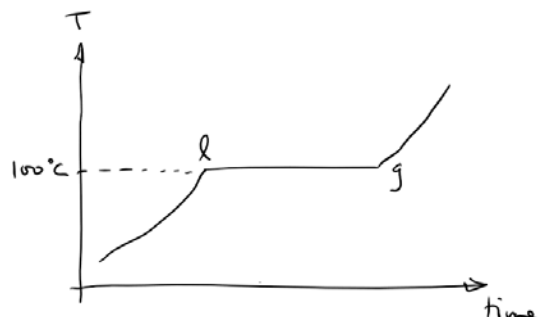
KEY CONCEPT: Latent heat

For a first order phase transition, crossing phase boundary requires a change in the entropy Δs . At constant T , this corresponds to a latent heat $L \equiv Q = T\Delta s$. (There is no latent heat for a second order phase transition because $\Delta s = 0$).

Ex: for liquid-to-gas transition, L is the heat that must be added to transfer one molecule reversibly from liquid to gas phase.

When you bring water to a boil, just below 100°C heat is put into H_2O not to change T , but solely to change its phase

Conversely, for gas-to-liquid transition L is released.



On the coexistence line $\mu_1 = \mu_2$ so

$$\frac{G_1}{N_1} = \frac{H_1 - TS_1}{N_1} = h_1 - Ts_1 = h_2 - Ts_2 = \frac{H_2 - TS_2}{N_2} = \frac{G_2}{N_2}$$

(where lowercase letters mean “per molecule”)

$$h_2 - h_1 = T(s_2 - s_1) = T\Delta s = L$$

So the latent heat is equal to the enthalpy difference per molecule between phases.

Usually we can get this from heat capacity at constant pressure (recall Lect. 9):

$$C_p = \left(\frac{dQ}{dT} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p = \left(\frac{\partial}{\partial T} (U + pV) \right)_p = \left(\frac{\partial H}{\partial T} \right)_p$$

$$\text{So, } H = \int C_p(T) dT \text{ and } \Delta H = \int (C_{p2} - C_{p1}) dT$$

We can rewrite the Clausius-Clapeyron equation in terms of the latent heat

$$\left. \frac{dp}{dT} \right|_{\text{coex. line}} = \frac{L}{T\Delta v}$$

KEY CONCEPT: Vapor-pressure equation

Consider the liquid/gas transition: $v_g \gg v_l$, so $\Delta v \approx v_g$

Let's also assume that the gas is ideal and that L is constant, independent of T .

Question 3: Using the ideal gas law and Clausius-Clapeyron equation, derive an expression for the liquid-gas coexistence line $p(T)$

From the ideal gas law $v_g = \frac{V}{N} = \frac{1}{n} = \frac{k_B T}{p}$, therefore

$$\left. \frac{dp}{dT} \right|_{l \leftrightarrow g} = \frac{L}{T v_g} = \frac{L}{k_B T^2} p$$

Integrating both sides:

$$\int \frac{dp}{p} = \int dT \frac{L}{k_B T^2}$$

which has solution $\ln p = -\frac{L}{k_B T} + \text{const.}$ or:

$$p(T) = p_0 e^{-L/k_B T}$$

This is called the vapor pressure equation

For water, this simple model works well for >8 orders of magnitude!

