Phase Diagrams:
How Substances Change from Solids to Liquids to Gasses

We will consider only a single substance and show how it can have many different phases depending upon P, V, and T. We will learn to read Phase Diagrams that tell which form of the substance is stable at any given P, V and T.

\[ G = H - TS \]

\[ G_m = \frac{G}{n} = \left( \frac{\partial G}{\partial n} \right) = \mu \]

\[ dG_m = dH_m - d \left( TS_m \right) \]

From the combined first and second laws and the definition of G or mu:

\[ d \mu = -S_m dT + V_m dP \]

\[ \left( \frac{\partial \mu}{\partial T} \right)_P = -S_m \text{ and } \left( \frac{\partial \mu}{\partial P} \right)_T = V_m \]

This chapter has one major idea: Relate changes of phase to the molar Gibbs Free Energy, or equivalently, the chemical potential. This provides a unifying principle for the change of phase of all substances. This builds a foundation to understand mixtures, which follows.
The most stable phase at T,P is that which has the lowest

\[ \mu = G_m(T, P) \]

WHY? For reactions at constant T and P (and we need no non-PdV-work, \( \text{d}G<0 \) is the criterion equivalent to \( \text{d}S(\text{Total})>0 \) that defines spontaneity

How the molar entropy changes with phase:

\[
\begin{align*}
S^\text{gas}_m &> S^\text{liquid}_m > S^\text{solid}_m
\end{align*}
\]

The slope of the dT dependence

How the molar volume changes with phase:

\[
\begin{align*}
V^\text{gas}_m &>> V^\text{liquid}_m \sim V^\text{solid}_m
\end{align*}
\]

The slope of the dP dependence
Need the Chemical Potential as a function of T and P

\[ d\mu_{\alpha} = V_{m,\alpha} dP - S_{m,\alpha} dT \]

\[ \Delta \mu_{\alpha} = \int_{T_o}^{T} \left( \frac{\partial \mu}{\partial T} \right)_P dT + \int_{P_o}^{P} \left( \frac{\partial \mu}{\partial P} \right)_T dP \]

\[ \Delta \mu_{\alpha} = -\int_{T_o}^{T} S_{m,\alpha} dT + \int_{P_o}^{P} V_{m,\alpha} dP \]

Assume that for any phase the S and V are constant

\[ \mu_{m,\alpha} = \mu_{m,\alpha}^{ref} - S_{m,\alpha} T + V_{m,\alpha} P \]

Each phase has its own molar entropy and molar volume. Phases are in equilibrium when the chemical potentials of each phase are the same. The phase with the lower chemical potential is the stable phase.
What determines relative slope of the lines?

Why are all the sloped negative?
Pressure dependence of $\mu$ leads to freezing point elevation or depression and boiling point elevation

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V_m$$
Diagram a shows the phase transitions at temperature $T_s$ with solid, liquid, and gas phases. Diagram b illustrates the phase transitions at temperature $T_t$ with similar phases.
The P-T phase diagram

Most important features are single phase regions, 2 phase coexistence curves, triple point, and critical point

\[ \Delta H_{\text{sublimation}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vaporization}} \]
Temperature vs heat input curves

![Diagram showing temperature vs heat input curves with phases: solid, liquid + solid, liquid, liquid + gas, gas, and associated heat changes: ΔH_{fus} for fusion and ΔH_{vap} for vaporization.]

- Temperature: T_b, T_m
- Heat Input: q_p
Hexagonal ice

Ice VI
Why Ice III must be in the phase diagram

• The Gibbs Phase rule: $F = c - p + 2$

If we have one component, e.g. water, and it exists in one phase, we can vary $T$ and $P$ pretty much at will and we still have water.

However, if we have ice and water in equilibrium, two phases, but still one component, we cannot vary both $T$ and $P$ at will and still have 2 phases. $P$ now moves as a function of $T$.

$F = \text{the degrees of freedom, } T \text{ and } P$.

c = \text{the number of components (one in this case)}
p = \text{the number of coexisting phases}$.
Sulfur

CO$_2$
The P-V phase diagram

- solid
- liquid
- solid + liquid
- solid + vapor
- liquid + vapor
- vapor
- triple line
- critical point

Axes:
- P (pressure)
- V (volume)
The P-V-T Phase Diagram
a in fig 8.4 =
\[ a \rightarrow b \rightarrow c \rightarrow d \rightarrow e \rightarrow f \]
c in fig 8.4 =
\[ q \rightarrow p \rightarrow o \rightarrow n \]
A theoretical basis for the Phase diagram

The chemical potential of two phases must be the same to be in equilibrium.

Root Relation \[ d\mu = -SdT + VdP \]

Two Components:

\[ \Delta \mu \equiv \mu_\beta - \mu_\alpha \]
\[ \Delta S_m = S_{m,\beta} - S_{m,\alpha} \quad \text{and} \quad \Delta V_m = V_{m,\beta} - V_{m,\alpha} \]

\[ \Delta d\mu = d\Delta \mu = 0 \quad \text{At Equilibrium} \]

\[ 0 = -\Delta S_m dT + \Delta V_m dP \]

Clapeyron equation

\[ \Delta S_m dT = \Delta V_m dP \]

or

\[ \frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m} \]

The above is valid when you move along a coexistence line where the chemical potential in the two phases remains constant. Consider two T,P places where the two phase coexist: T,P and T’,P’. They are related as follows, assuming the change in S and V is small over the small T,P change:
Clapeyron Equation

- At a phase transition the Gibbs phase energy is minimized and the difference in the chemical potentials is zero. Just like a chemical reaction at equilibrium. A substance going from one phase to another is very similar to a chemical reaction.
- Compare Clapeyron equation with Maxwell relation. Quite similar. The cyclic relation shows that we must vary P and T holding the chemical potential of the two phases to be the same. This means we move P and T along a coexistence line for the two phases.

Root Relation
\[ d\Delta \mu = -\Delta S_m \, dT + \Delta V_m \, dP \]

\[ \left( \frac{\partial \Delta \mu}{\partial T} \right)_P = -\Delta S_m \quad \left( \frac{\partial \Delta \mu}{\partial P} \right)_T = \Delta V_m \]

Use the Cyclic Relation:
\[ \left( \frac{\partial P}{\partial T} \right)_{\Delta \mu} = -\left( \frac{\partial \Delta \mu}{\partial T} \right)_P = \frac{\Delta S_m}{\Delta V_m} \]

This relation tells us that T and P can be traded off to keep the two phases in coexistence, and it is driven by the tradeoff of the entropy change and volume change in going from the phase stable at low temperature to the one at higher temperature.
At the equilibrium transition temperature

\[ \Delta G_m = \Delta H_m - T \Delta S_m \quad \Delta H_{m,\alpha \rightarrow \beta} = \Delta H_{m,\beta} - \Delta H_{m,\alpha} \]

\[ \Delta \mu = \Delta G_m = 0 \quad \Rightarrow \quad \Delta H_{m,\alpha \rightarrow \beta} = T_{\alpha \rightarrow \beta} \Delta S_{m,\alpha \rightarrow \beta} \]

Combine this with the Clapeyron Equation:

\[ \frac{dP}{dT} = \frac{\Delta S_{m,\alpha \rightarrow \beta}}{\Delta V_{m,\alpha \rightarrow \beta}} = \frac{\Delta H_{m,\alpha \rightarrow \beta}}{T_{\alpha \rightarrow \beta} \Delta V_{m,\alpha \rightarrow \beta}} \]

In going from \( s \rightarrow l \), (fusion) or \( s \rightarrow g \), (sublimation) or \( l \rightarrow g \) (vaporization) \( \Delta H \) is positive because bonds are broken, and therefore more choices are available to the constitutive molecules so \( \Delta S \) is positive also. The volume usually increases (but not always, eg water).
Comparing dP/dT for fusion and vaporization

Slope of solid-liquid curve much greater than for liquid-gas curve, primarily because of the great volume expansion in generating the gas.

\[
\left(\frac{dP}{dT}\right)_{\text{fusion}} = \frac{\Delta S_m^{\text{fusion}}}{\Delta V_m^{\text{fusion}}} \approx \frac{24 J \text{ mol}^{-1} K^{-1}}{\pm 4 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}} = \pm 6 \times 10^6 \text{ Pa K}^{-1}
\]

\[
\left(\frac{dP}{dT}\right)_{\text{fusion}} = \pm 60 \text{ bar} / \text{K}
\]

\[
\left(\frac{dP}{dT}\right)_{\text{vaporization}} = \frac{\Delta S_m^{\text{vaporization}}}{\Delta V_m^{\text{vaporization}}} \approx \frac{95 J \text{ mol}^{-1} K^{-1}}{2 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}} \approx 5 \times 10^3 \text{ Pa} K^{-1}
\]

\[
\left(\frac{dP}{dT}\right)_{\text{vaporization}} = 0.05 \text{ bar} / \text{K}
\]
The coexistence lines between condensed forms

Because the slopes are so large between condensed phases (such as solid to liquid) that the best description of the coexistence line is just the Clapeyron Equation:

\[
\Delta P = \int \left(\frac{dP}{dT}\right) dT = \int \frac{\Delta S^m}{\Delta V_m} dT \approx \frac{\Delta S^m}{\Delta V_m} \Delta T
\]

\[
P \approx T \frac{\Delta S^m}{\Delta V_m} + \left( P_{\text{ref}} - T_{\text{ref}} \frac{\Delta S^m}{\Delta V_m} \right)
\]

The coexistence pressure line is just linearly related to the temperature, so it is just a straight line on the P vs T plot. There must be a reference point that we do not know from any absolute principle, we just measure one point to get an intercept point, but the slope is given by the Clapeyron Equation.
The coexistence lines between condensed forms

• In the previous slide we assume DS was independent of temperature. Suppose we assume DH is independent of temperature. How does this change the answer:

\[ \Delta P = \int \left( \frac{dP}{dT} \right) dT = \int \frac{\Delta H_m}{T \Delta V_m} dT \]

\[ \Delta P \approx \frac{\Delta H_m}{\Delta V_m} \ln \frac{T}{T_{ref}} \]

\[ P = \frac{\Delta H_m}{\Delta V_m} \ln \frac{T_{ref}}{T_{ref}} + \frac{\Delta H_m}{T_{ref} \Delta V_m} (T - T_{ref}) + P_{ref} \]

\[ = T \frac{\Delta S_m}{\Delta V_m} + \left( P_{ref} - T_{ref} \frac{\Delta S_m}{\Delta V_m} \right) \]

For temperatures close to the reference phase transition temperature there is no difference in the consequences of either assumption.
The coexistence line between the condensed forms and the gas

- This coexistence line, as how the coexistence pressure depends on the temperature is slightly modified because the gas volume is so much larger than the condensed form volume and the gas volume depends strongly on the temperature.

\[ \Delta V_m \approx V_{m,\text{gas}} = \frac{RT}{P} \]

\[ \int \left( \frac{dP}{P} \right) = \int \frac{\Delta S^m}{RT} \, dT \]

\[ \ln \frac{P}{P_{\text{ref}}} \approx \frac{\Delta S^m}{R} \ln \frac{T}{T_{\text{ref}}} \]

Assume DS is independent of T;
Assume DH is independent of T

\[ \Delta V_m \approx V_{m,\text{gas}} = \frac{RT}{P} \]

\[ \int \left( \frac{dP}{P} \right) = \int \frac{\Delta H^m}{RT^2} \, dT \]

\[ \ln \frac{P}{P_{\text{ref}}} \approx -\frac{\Delta H^m}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \]

The Clausius-Clapeyron Equation
Which assumption is better?

Let’s think about this as a chemical reaction; The condensed phase has unit activity so the Equilibrium constant is:

\[ \Phi_\alpha \leftrightarrow \Phi_\beta \]

\[ K_P = P_\beta \]

\[ dG = dX \{\Delta \mu\} \]

\[ \Delta \mu = \Delta G_{rxn} = \Delta H_{rxn} - T \Delta S_{rxn} \]

\[ \ln \frac{K_P(T)}{K_P(T_{ref})} = \ln \frac{P}{P_{ref}} = - \frac{\Delta H_{rxn}}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \]

The van’t Hoff form of the reaction equilibrium is identical to the Clausius-Clapeyron Equation. So that is the one we will prefer. The two possible forms of the Clausius-Clapeyron Equation must be rather similar as in chemical reactions we assume both DH and DS are nearly independent of temperature.
The coexistence line between condensed forms and gas

The slope of the coexistence line is:

\[
\frac{dP}{dT} = \frac{\Delta H_{m,rxn}}{RT} \left( \frac{P}{T} \right) \approx \Delta S_{m,rxn} \left( \frac{P}{RT} \right)
\]

From the triple point enthalpies:

\[
\Delta S_{m,\text{sublimation}} = \Delta S_{m,\text{fusion}} + \Delta S_{m,\text{vaporization}} > \Delta S_{m,\text{vaporization}}
\]

\[
\Delta V_{m,\text{sublimation}} \approx \Delta V_{m,\text{vaporization}}
\]

therefore

\[
\left( \frac{dP}{dT} \right)_{\text{sublimation}} > \left( \frac{dP}{dT} \right)_{\text{vaporization}}
\]

The slope of the sublimation coexistence line must be a bit larger than that of the vaporization coexistence line in the vicinity of the triple point.
Summary of Coexistence Curves

\[ \Delta H_{\text{sublimation}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vaporization}} \]

\[ P = P_{\text{triple}} + \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} (T - T_{\text{triple}}) \]

\[ \ln \left( \frac{P}{P_{\text{triple}}} \right) \approx - \frac{\Delta H_{\text{vaporization}}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{triple}}} \right) \]
Vapor Pressure

- If you have a liquid or a solid and P and T are such that you are not on a coexistence line how can there be vapor?
- If the cylinder (with a movable piston has ONLY the one substance) then there cannot be a vapor.
- If you add an inert gas now you have two components, and, by the Gibbs phase rule, you can have two phases: The condensed phase and the vapor phase. Given P and T the vapor will have the partial pressure given at the coexistence curve at the specified temperature.
- The vapor pressure is a very weak function of the pressure on the system, and actually increases as the pressure increases (counter intuitive, see text for details).
Example Problem 8.2
The normal boiling temperature of benzene is 80.09°C, and the vapor pressure of liquid benzene is 104 Pa at 20.0°C. The enthalpy of fusion is 9.87 kJ/mol, and the vapor pressure of solid benzene is 88.0 Pa at –44.3°C. Calculate
a) \( \Delta H_{\text{vaporization}}^m \)  
b) \( \Delta S_{\text{vaporization}}^m \)  
c) the triple point temperature and pressure.
Solution

• Examine the Coexistence Curves, we have two data points on the vaporization line, so we can get the equation for that line
• B) We can calculate $\Delta H_{vaporization}^m$ using the Clausius-Clapyeron equation because we know the vapor pressure (of the gas) at two different temperatures
• B) The vaporization enthalpy is known from a) and the fusion enthalpy is given, so you can get the sublimation enthalpy.
• C) The entropy of vaporization is taken at the normal boiling point. Therefore the entropy of fusion and sublimation may also be found.
• D) The triple point is the intersection of all three lines. As you were not given any molar volumes you must look for the intersection of the sublimation and the vaporization lines. This will involve 2 equations and 2 unknowns.
A) \[ \ln \frac{P_b}{P_i} = -\frac{\Delta H_{m}^{\text{vaporization}}}{R} \left( \frac{1}{T_b} - \frac{1}{T_i} \right) \]

\[ \Delta H_{m}^{\text{vaporization}} = R \ln \frac{P_b}{P_i} = \frac{8.3 \text{ J mol}^{-1} \text{K}^{-1}}{\text{ln} \frac{1.01 \cdot 10^5 \text{ Pa}}{1 \cdot 10^4 \text{ Pa}}} \]

\[ \left( \frac{1}{273.15 + 80.09 \text{K}} - \frac{1}{273.15 + 20.0 \text{K}} \right)^{-1} \]

\[ \Delta H_{m}^{\text{vaporization}} = 33.2 \text{ kJ mol}^{-1} \]

\[ \Delta H_{m}^{\text{fusion}} + \Delta H_{m}^{\text{vaporization}} \]

\[ \Delta H_{m}^{\text{sublimation}} = 9.87 + 33.2 = 43 \text{ kJ / mole} \]

B) \[ \Delta S_{m}^{\text{vaporization}} = \frac{\Delta H_{m}^{\text{vaporization}}}{T_b} = \frac{33.2 \times 10^3 \text{ J mol}^{-1}}{273.15 + 80.09 \text{K}} = 93.9 \text{ J mol}^{-1} \text{K}^{-1} \]
c) At the triple point, the vapor pressures of the solid and liquid are equal.

\[
\ln \frac{P_{tr}}{P_{ref-Liq}} = - \frac{\Delta H_{m}^{\text{vaporization}}}{R} \left( \frac{1}{T_{tr}} - \frac{1}{T_{ref-Liq}} \right) \quad (\text{for } L \Rightarrow Vap)
\]

\[
\ln \frac{P_{tr}}{P_{ref-Sol}} = - \frac{\Delta H_{m}^{\text{subli}}}{R} \left( \frac{1}{T_{tr}} - \frac{1}{T_{ref-Sol}} \right) \quad (\text{for } S \Rightarrow Vap)
\]

We know the reference pressures for both the liquid and solid phases, and the heats of vaporization and sublimation. Subtracting the above two equations will cancel the triple pressure, and leave you with a single equation and a single unknown, the Triple Temperature.

\[
\ln \frac{P_{ref-Sol}}{P_{ref-Liq}} = - \left( \frac{\Delta H_{m}^{\text{vaporization}}}{R T_{tr}} - \frac{\Delta H_{m}^{\text{subli}}}{R T_{tr}} \right) + \left( \frac{\Delta H_{m}^{\text{vaporization}}}{R T_{ref-Liq}} - \frac{\Delta H_{m}^{\text{subli}}}{R T_{ref-Sol}} \right)
\]

\[
\frac{\Delta H_{m}^{\text{fusion}}}{R T_{tr}} = \ln \frac{P_{ref-Sol}}{P_{ref-Liq}} - \left( \frac{\Delta H_{m}^{\text{vaporization}}}{R T_{ref-Liq}} - \frac{\Delta H_{m}^{\text{subli}}}{R T_{ref-Sol}} \right)
\]
\[
\frac{\Delta H_{\text{fusion}}^{\text{m}}}{RT_{tr}} = \ln \frac{P_{\text{ref-Sol}}}{P_{\text{ref-Liq}}} - \left( \frac{\Delta H_{\text{vaporization}}^{\text{m}}}{RT_{\text{ref-Liq}}} - \frac{\Delta H_{\text{subli}}^{\text{m}}}{RT_{\text{ref-Sol}}} \right)
\]

\[
\ln \frac{P_{\text{ref-Sol}}}{P_{\text{ref-Liq}}} = \ln \left( \frac{88}{10^4} \right) = -4.7
\]

\[
\left( \frac{\Delta H_{\text{vaporization}}^{\text{m}}}{RT_{\text{ref-Liq}}} - \frac{\Delta H_{\text{subli}}^{\text{m}}}{RT_{\text{ref-Sol}}} \right) = \left( \frac{33}{R \cdot 293} - \frac{43}{R \cdot 229} \right) \cdot 10^3 = \frac{33}{2.4} - \frac{43}{1.9} = -9
\]

\[
\frac{\Delta H_{\text{fusion}}^{\text{m}}}{RT_{tr}} = -4.7 + 9 = 4.3
\]

\[
T_{tr} = \frac{\Delta H_{\text{fusion}}^{\text{m}}}{R4.3} = \frac{9.95 \cdot 10^3}{8.3 \cdot 4.3} = 280K
\]

As a check, the triple point temperature must be between the two temperatures used to reference the solid and the vapor, which were 230 and 293. And yes it is between them.
We calculate the triple point pressure using the Clausius Calpyeron equation from either the sublimation or vaporization lines

\[
\ln \frac{P_f}{P_i} = - \frac{\Delta H_{m}^{\text{vaporization}}}{R} \left( \frac{1}{T_f} - \frac{1}{T_i} \right)
\]

\[
\ln \frac{P_{tp}}{1 \cdot 10^5} = - \frac{33.2 \times 10^3}{8.3} \left( \frac{1}{280} - \frac{1}{273.8 + 80K_i} \right)
\]

\[
\ln \frac{P_{tp}}{P^o} = 8.4
\]

\[
P_{tp} = 4.7 \cdot 10^3 \text{ Pa} = 0.05 \text{ Atm}
\]
Surface Tension

\[ dA = \gamma d\sigma \]

where \( A \) is the Helmholtz energy, \( \gamma \) is the surface tension, and \( s \) is the unit element of area. The surface tension has the units of energy/area or \( J m^{-2} \) which is equivalent to \( N m^{-1} \) (Newtons per meter). Because \( dA < 0 \) for a spontaneous process at constant \( V \) and \( T \), equation 8.23 predicts that a liquid, or a bubble, or a liquid film suspended in a wire frame will tend to minimize its surface area.
Capillary rise and capillary depression

\[ p_{\text{inner}} = p_{\text{outer}} + \frac{2\gamma}{r \cos \theta} \]

and

\[ h = \frac{2\gamma}{\rho gr \cos \theta} \]

\[ h = \frac{2\gamma}{\rho gr} \]
Example Problem 8.4
Water is transported upwards in trees through channels in the trunk called xylem. Although the diameter of xylem channels varies from species to species, a typical value is $2.0 \times 10^{-5}$ m. Is capillary rise sufficient to transport water to the top of a redwood tree of 100 m height?

Solution
From equation 8.28,

$$h = \frac{2\gamma}{\rho gr \cos \theta} = \frac{2 \times 71.99 \times 10^{-3} Nm^{-1}}{997 \text{kg m}^{-3} \times 9.81 \text{ms}^{-2} \times 2.0 \times 10^{-5} \text{m}} = 0.74 \text{m}$$

No, capillary rise is not sufficient to account for water supply to the top of a redwood tree.
Liquid Crystals

5CB

PAA

36