CHEMICAL POTENTIAL – Systems with Many Chemical Components

By and large, we have discussed systems that have only a fixed number of molecules, n_{total}, and only one type of chemical component. In this limited case, the Gibbs Free Energy is $dG = -SdT + VdP$. That means G is a function of T and P, or that G(T,P).

What if some number of moles of one molecule or phase turn into a few moles of another molecule or phase? It makes sense that the energy will change, but so far we haven't discussed how to keep track of that. We can account for the number of moles of each component by adding new terms to the Gibbs Free Energy.

> Using that Gibbs Free Energy is a state function and that it depends on T, P, as well as the number of each kind of molecule or phase (n_1, n_2, n_3…):

$$
\begin{aligned}
dG &= \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_{i\neq 1}} dn_1 + \ \dots \ + \left(\frac{\partial G}{\partial n_N}\right)_{T,P,n_{i\neq N}} dn_N \\
&= -SdT + VdP + \mu_1 dn_1 + \dots + \mu_N dn_N \\
&= -SdT + VdP + \sum_{i=1}^{N} \mu_i dn_i
\end{aligned}
$$

Where the chemical potential of species *i* is defined as $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{i\neq j}}$

We can think of μ as the free energy gained or lost when extra molecules of different components are added. Notice that we are still assuming that all steps are reversible, and that the only kind of work in the system is PV work.

To me, it is easiest to remember chemical potential as the partial molar free energy. It looks a lot like the molar free energy, $\Delta\overline{G}$, but instead of dividing by the total number of moles, we divide by the number of moles of only one of the components.

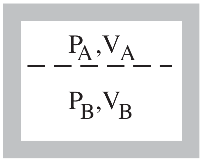
$\overline{G_i} = \mu_i = (\partial G/\partial n_i)_{T,P,n_{i\neq j}}$ and $G = \sum_i \mu_i n_i$ at constant T, P

We know that if P and T are constant, then at equilibrium, $G_{reactants} = G_{products}$, or $\Delta G = 0$. In a direct analogy, we also know that if P and T are constant, then at equilibrium, two different kinds of molecules A and B, or two different kinds of phases A and B have $\mu_A = \mu_B$.

In order to gain some intuition about chemical potential, we will review different systems.

Review of Equilibrium under Different Experimental Conditions

Example: Two gases (A and B) in mechanical equilibrium can freely exchange volume at constant total volume, constant T, and constant number of particles of A and B.



V_{total} = constant = $V_A + V_B$
T = constant
n_A = constant
n_B = constant

For constant V_{total} and T, the state function to choose is A (Helmholtz Free Energy). At equilibrium under constant T and V, $dA_{total} = 0$, and $dT = 0$, where $dA = -SdT - PdV$.

$$dA_{total} = dA_A + dA_B = -S_A dT_A - P_A dV_A - S_B dT_B - P_B dV_B$$

$$0 = 0 - (P_A dV_A + P_B dV_B)$$

We also know that

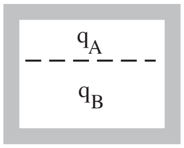
$$dV_{total} = dV_A + dV_B$$

Since V_{total} = constant, $dV_{total} = 0$, and $dV_A = -dV_B$

Therefore, at the equilibrium conditions above,

$\mathbf{P_A = P_B}$ (Now for an intuition check… this makes sense!)

Example: Two systems (A and B) are in equilibrium, can freely exchange heat at constant E and V, and are isolated from the surroundings. The number of particles of A and B are constant.



V_{total} = constant
E = constant
n_A = constant
n_B = constant

At equilibrium and constant E and V, the Second Law gives

$$dS_{total} = 0 = dS_A + dS_B$$

$$= dq_A/T_A + dq_B/T_B$$

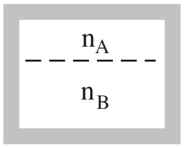
Free heat exchange in an insulated system implies

$$dq_A = -dq_B$$

Therefore, at the equilibrium conditions above,

$\mathbf{T_A = T_B}$ (Now do an intuition check… this makes sense!

Example: Two phases (A and B) of a single component are in equilibrium, can freely exchange number of particles (mass transfer) at constant T, P, and are insulated from an exchange of particles with the surroundings (n_{total} = constant).



P = constant
T = constant
n_{total} = constant = $n_A + n_B$

At equilibrium and constant T, P:

$$dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B$$
$$0 = 0 + 0 + \mu_A dn_A + \mu_B dn_B$$

Since the total number of moles is constant, $dn_A = -dn_B$.

Therefore, at the equilibrium conditions above, coexisting phases have

$$\boldsymbol{\mu_A = \mu_B}$$

As a segue to the next section, notice that the example above had:

1 component
2 phases (A and B)
1 equation to describe equilibrium ($\mu_A = \mu_B$)

Gibbs Phase Rule

The Gibbs Phase Rule relates the number of phases, P, which may coexist in a sample at equilibrium to the number of components, C, and the degrees of freedom, F. The number of degrees of freedom is the number of *intensive* variables that can be varied independently (e.g. T, P, and x_i). The number of phases does not depend on how many components are in that phase.

$$\mathbf{F = C - P + 2} \qquad \textbf{(Gibbs Phase Rule)}$$

(Note: If, in addition to knowing the number of phases, we also want to know the mass of each phase, then we need to know one extensive variable per phase.)

To understand where the Gibbs Phase Rule comes from, let's think about a linear algebra example. Imagine you have three unknowns, *a, b*, and *c*. If there are three equations that use *a, b,* and *c*, then you can solve exactly for *a, b*, and *c*. What if there are only two equations? In this example,

(# of independent variables) = (# of unknowns) - (# of equations or constraints)

Then if you choose some number for *a*, then you could solve for *b* and *c*. In other words, *a* is a variable that you varied independently, or a degree of freedom.

As an analogy, you could think of how many legs a table needs in order to be stable.

2 legs: This is an unstable system. It is underdetermined.
3 legs: There are just enough legs to give a stable solution.
4 legs: The system is overdetemined. To get it to work, you have to shim the 4th leg in order to yield the solution that you already found was good for only 3 legs.

Now let's think about molecules instead.

How many independent variables are there when we solve for Gibbs Free Energy?

1) At equilibrium, dG = 0.

   $$dG = -SdT + VdP + \sum_i \mu_i \, dn_i$$

   Just from looking at this equation, it would seem that to specify everything, we need to know the intensive variables T, P, and the dn_i for C components in each of the P phases.

   That means that at first glance there are 2 + (C)(P) unknown variables.

   However, if there are n components and we know the mole fractions of (n-1) of those components, then we know the mole fraction of the nth component too since $\sum x_i = 1$. So, we really only need to know C – 1 components rather than all C.

   That means there are really 2 + (C - 1)(P) unknown variables.

2) However, there are some constraints on the system which decrease the number of variables. At equilibrium, the chemical potentials of all C components must be equal in all P phases.

   This gives (C)(P – 1) independent constraints.

   To illustrate this, on the example on the last page there was 1 component in 2 phases in equilibrium. As a result we found 1 constraining equation (which was $\mu_A = \mu_B$). The number of constraints was (C)(P-1) = 1(2-1) = 1.

3) Thus, the total number of degrees of freedom (the number of intensive variables that can be varied independently) is the number of unknown variables minus the number of constraints:

   F = [# unknown variables] – [# constraints]

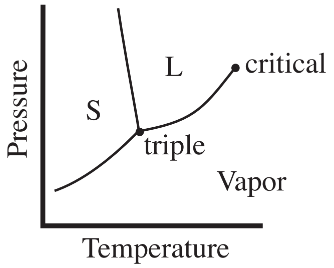
   F = [2 + (C - 1)(P)] – [(C)(P - 1)]

   F = C – P + 2

Phase Diagrams

Phase diagrams are convenient ways to represent the state of a system. For example, the phase diagram of water with respect to T and P is sketched below. This phase diagram has only 3 phases shown. Note that phase diagrams for other systems can have many more than 3 phases! An example of this is on the next page. Mapping phase diagrams is an area of current scientific research. In fact, it is what I do in my own laboratory.

Let's use our phase diagram of water to think about the Gibbs Phase Rule.



Triple Point
273.16K
0.006 atm

Example: How many independent variables are there for H_2O at its triple point?

There is only one component (H_2O), so C = 1. At the triple point, there are 3 coexisting phases and P = 3.

$$F = 1 - 3 + 2 = 0$$

There are no independent variables! By stating that water is at its triple point, we set the temperature and pressure to specific values. If we stray from these values by varying T or P then one or more of the coexisting phases will vanish. Because of this, triple points are often used to calibrate thermometers.

Example: How many variables can be independently varied for a system of H_2O (liquid) coexisting with H_2O (vapor)?

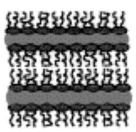
$$C = 1, \text{ and } P = 2 \quad \text{so} \quad F = 1 - 2 + 2 = 1$$

There is only one degree of freedom. Hence, if one of the variables (T) varies, the other variable (P) cannot be varied independently. Whatever T is sets the value of P in order for two phases to coexist in the system.

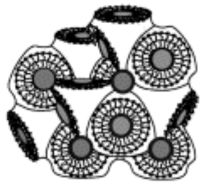
The text above mentions that many more than 3 phases exist in nature. Here is an example from lipids. When monoacylglycerol (1-monoolein) is added to water, a whole zoo of phases results. Drawings of how the lipids and water are arranged in the phases is at the left, along with the full names and shorthand of all SIX phases. The full, beautiful, complicated phase diagram is at the right. This work was done by Hong Qiu and Martin Caffrey ("The phase diagram of the monoolein/water system: metastability and equilibrium aspects" *Biomaterials* (2000) 21, 223-234).

lamellar crystal - L_C

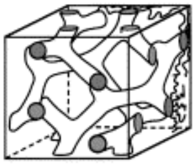
lamellar liquid crystal - L_α



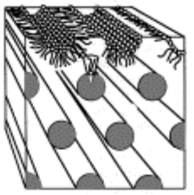
cubic - Pn3m



cubic - Ia3d

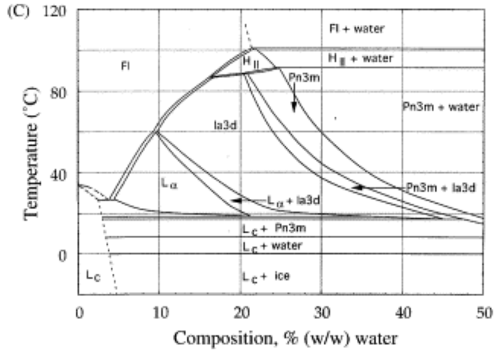


inverted hexagonal - H_{II}

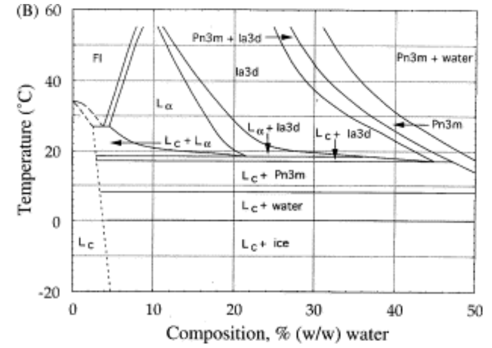


fluid isotropic - FI

Here's the full phase diagram:



Here is a blowup of the central region:



Clapeyron Equation

Previously we considered changes in Gibbs Free Energy by changing either pressure or temperature. It is not so hard to do both at the same time, using the Clapeyron equation. The Clapeyron equation is particularly helpful for in cases where there is equilibrium between two different phases, α and β, for a single component system.

As usual, assume that all steps are reversible and that the only work is P-V work.

$$\begin{tikzcd}
\alpha \text{ at } T_2, P_2 \arrow[r, "\Delta G"] \arrow[d, "\Delta G^{\alpha}"'] & \beta \text{ at } T_2, P_2 \\
\alpha \text{ at } T^0, P^0 \arrow[r, "\Delta G^0"'] & \beta \text{ at } T^0, P^0 \arrow[u, "\Delta G^{\beta}"']
\end{tikzcd}$$

$dG_{total} = dG^{\alpha} + dG^0 + dG^{\beta}$

where

$dG^{\alpha} = -S^{\alpha}\, dT^{\alpha} + V^{\alpha}\, dP^{\alpha}$

$dG^{\beta} = -S^{\beta}\, dT^{\beta} + V^{\beta}\, dP^{\beta}$

A perfect application of this is finding the temperature at which water boils at the top of a mountain (at a lower pressure). The water and vapor are in equilibrium at standard temperature and pressure, T^0 and P^0. They are also in equilibrium at the new temperature and pressure on top of the mountain, T_2 and P_2. That means…

$dG_{total} = 0$ (since in equilibrium T_2 and P_2)
$dG^0 = 0$ (since in equilibrium at T^0 and P^0)

Adding up all the paths, $dG_{total} = dG^{\alpha} + dG^0 + dG^{\beta}$

$$0 = (-S^{\alpha}\, dT^{\alpha} + V^{\alpha}\, dP^{\alpha}) + 0 + (-S^{\beta}\, dT^{\beta} + V^{\beta}\, dP^{\beta})$$

Since $dT^{\alpha} = -\, dT^{\beta}$ and $dP^{\alpha} = -\, dP^{\beta}$,

$$-S^{\alpha}\, dT^{\alpha} + V^{\alpha}\, dP^{\alpha} = -S^{\beta}\, dT^{\alpha} + V^{\beta}\, dP^{\alpha}$$

$$(V^{\alpha} - V^{\beta})dP^{\alpha} = (S^{\alpha} - S^{\beta})dT^{\alpha}$$

$$\left(\frac{dP^{\alpha}}{dT^{\alpha}}\right)_{eq} = \frac{S^{\alpha} - S^{\beta}}{V^{\alpha} - V^{\beta}}$$

Clapeyron Equation for coexisting phases.

$$\left(\frac{\Delta P}{\Delta T}\right)_{eq} = \frac{\Delta S}{\Delta V}$$

This is how it is usually written in books. Substituting Δ's on the left is O.K. when the difference in melting temperature from applying pressure is small. That works particularly well if neither phase is a gas. In a moment we'll discuss the Clausius-Clapeyron Equation, which considers a gas.

The Clapeyron Equation a very general equation. It describes any two coexisting phases in equilibrium at two different temperatures and pressures (the subscript "eq" means equilibrium). It is quite useful to know how pressure varies with temperature in two coexisting phases.

Even though the Clapeyron Equation as written above is useful, as we've seen several times previously, it isn't very convenient to calculate ΔS. Can we do anything to get rid of ΔS? To make the example more concrete, consider the melting of ice at a constant temperature $T_{transition}$. If the ice and water are in equilibrium at a constant temperature of the transition, then…

$$\Delta G_{melt} = \Delta H_{melt} - T_{transition}\Delta S_{melt} = 0$$

Then $$\Delta S_{melt} = \frac{\Delta H_{melt}}{T_{transition}}$$

Plugging into the equation above,

$$\boxed{\left(\frac{\Delta P}{\Delta T}\right)_{eq} = \frac{\Delta H_{transition}}{T_{eq}\Delta V}}$$ (Clapeyron Equation in another form)

Note that molar values can always be substituted as long as the units cancel.

$$\left(\frac{\Delta P}{\Delta T}\right)_{eq} = \frac{\Delta \overline{S}}{\Delta \overline{V}} = \frac{\Delta \overline{H}_{transition}}{T_{eq}\Delta \overline{V}}$$

Personally, I find it hard to remember which direction ΔV goes. If it helps, you can use Le Châtlier's Principle to assign the sign later, or you could rewrite the equation this way:

$$\left(\frac{\Delta P}{\Delta T}\right)_{eq} = \frac{\Delta \overline{S}}{\Delta \overline{V}} = \frac{\Delta \overline{H}_{transition}}{T_{eq}\left(\overline{V}^{\alpha} - \overline{V}^{\beta}\right)}$$

Example: (Smith p. 45)
If ice is put under 1001 atm pressure, at what temperature will it melt? In other words, at what temperature are ice and liquid water in equilibrium at 1001 atm?

For water at 0°C and 1 atm, $\Delta \overline{H}_{melting}$ = 6.0 kJ/mol, with $\Delta \overline{V}_{water} - \Delta \overline{V}_{ice}$ = -1.6 x 10^{-6} m^3/mol.

$$\left(\frac{\Delta P}{\Delta T}\right)_{eq} = \frac{\Delta \overline{H}_{transition}}{T_{eq}\Delta \overline{V}}$$

$$\Delta T = \frac{T_{eq}\,\Delta \overline{V}}{\Delta \overline{H}_{transition}}(\Delta P) \qquad where\ dP = 1001\ atm - 1\ atm = 10^{8}\ Pa$$

$$= \frac{(273K)\left(-1.6\cdot 10^{-6}\,\frac{m^3}{mol}\right)}{6\cdot 10^{3}\,\frac{J}{mol}}\left(10^{8}\,Pa\right)$$

$$= -7.3K$$

So, ice under 1001 atm pressure will melt at 273K - 7K = 266K.

(Note: You might have used Le Châtlier's Principle to predict ahead of time that the melting temperature of water would decrease when the system was put under pressure.)

Clausius-Clapeyron Equation for Vaporization (or Sublimation)

The Clapeyron Equation allowed us to relate the change in pressure to a change in temperature for a system with only one component in equilibrium between any two phases. If one of the phases is a vapor, the relation between pressure and temperature becomes even simpler!

There are three approximations:

(i) $V_g >> (V_{liq} \text{ or } V_{solid})$, so $\Delta V_{vaporization} = V_g - V_{liq} \approx V_g$

(ii) The vapor behaves as an ideal gas $V_g = nRT/P$

(iii) $\Delta H_{vaporization}$ (or $\Delta H_{sublimation}$) is practically independent of T

Then the Clapeyron Equation becomes

$$\left(\frac{dP}{dT}\right) = \frac{\Delta H_{vap}}{T_{transition}\Delta V_{vap}} = \frac{\Delta H_{vap}}{T\, V_{gas}} = \frac{\Delta H_{vap}}{T\left({}^{nRT}\!/_{P}\right)} = \frac{\Delta H_{vap}}{nRT^2}P$$

$$\int_{P_i}^{P_f} \frac{dP}{P} = \int_{T_i}^{T_f} \frac{\Delta H_{vap}}{nR}\frac{dT}{T^2}$$

$$\int_{P_i}^{P_f} \frac{dP}{P} = \frac{\Delta H_{vap}}{nR}\int_{T_i}^{T_f} \frac{dT}{T^2}$$

Separate Variables and Integrate

$$\ln\left(\frac{P_f}{P_i}\right) = -\frac{\Delta H_{vap}}{nR}\left(\frac{1}{T_f} - \frac{1}{T_i}\right)$$

Clausius-Clapeyron Equation

This equation is quite useful because it relates the enthalpy of vaporization (or sublimation) to variables that are easy to measure in the lab (T and P).

Note: In the derivation above, we decoupled ΔH from temperature, which allowed us to both let $T_{transition}$ *become plain old T, and to take ΔH outside the integral above. This is usually a pretty good assumption, although strictly enthalpy depends on temperature (ΔH(T)). To do it absolutely, positively correctly in all circumstances, you'd need to leave H inside the integral… but we will ignore that here.*

Now let's take a moment to review all the cool stuff we've learned:

Review of Equations Using Gibbs Free Energy

Start from dG = - SdT + VdP

$\Delta\overline{G}_{total} = \Delta\overline{G}^0 + \left(\overline{V}_{products} - \overline{V}_{react}\right)\Delta P_{products}$	No name.	Constant temperature, changing pressure. Assumes V is not very dependent on P (solid or liquid).
$\Delta G = G_f - G_i = nRT \ln(P_f/P_i)$	No name.	Constant temperature, changing pressure. Assumes ideal gas.
$\Delta\overline{G}_{total} = \Delta\overline{G}^0 - \left(\overline{S}_{products} - \overline{S}_{react}\right)\Delta T_{products}$	No name.	Constant pressure, changing temperature. Assumes S is not very dependent on T.
$\left(\dfrac{\Delta P^\alpha}{\Delta T^\alpha}\right)_{eq} = \dfrac{S^\alpha - S^\beta}{V^\alpha - V^\beta}$	Clapeyron Equation (I)	Good for two phases in equilibrium in which both pressure and temperature change, and you happen to know entropy. Not for gas.
$\left(\dfrac{\Delta P}{\Delta T}\right)_{eq} = \dfrac{\Delta H_{transition}}{T_{eq}\Delta V}$	Clapeyron Equation (II)	Good for two phases in equilibrium in which both pressure and temperature change, and you happen to know enthalpy. Not for gas.
$\ln\left(\dfrac{P_f}{P_i}\right) = -\dfrac{\Delta H_{vap}}{nR}\left(\dfrac{1}{T_f} - \dfrac{1}{T_i}\right)$	Clausius-Clapeyron Equation	Good for vaporization or sublimation in which both temperature and pressure change.

Review of State Functions

At this point, we have covered everything in our table of state variables.

State Function	is written as	is especially useful at	when reversible and only PV work	such that	Conditions for spontaneous processes
E (or U) = internal energy	E	constant volume	dE = TdS - PdV	E(V, S)	$(dE)_{V,S} \leq 0$
H = enthalpy	E + PV	constant pressure	dH = TdS + VdP	H(P, S)	$(dH)_{P,S} \leq 0$
A (or F) = Helmholtz Free Energy	E – TS	constant volume constant temperature	dA = -SdT - PdV	A(T, V)	$(dA)_{T,V} \leq 0$
G = Gibbs Free Energy	E + PV – TS	constant temperature constant pressure	dG = -SdT + VdP	G(T, P)	$(dG)_{T,P} \leq 0$
S = Entropy		constant volume constant int. energy	$dS = dq_{rev}/T$	S(V, E)	$(dS)_{V,E} \geq 0$